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Using transient breakthrough experiments for screening of adsorbents for separation of C2H4/CO2 mixtures

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ABSTRACT

The recovery of C2H4 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 N2/H2/CO/CO2/CH4/C2H6/C2H4 mixtures, typically containing less than 15% C2H4. For recovery of C2H4, 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 CO2, and C2H4 are significantly higher than that of other gaseous constituents; consequently, the C2H4/CO2 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 C2H4/CO2 ratios. On the basis of the breakthroughs, the adsorbents could be distinguished in three different categories: (i) 13X and 4A are selective to CO2, (ii) CaX, NaY, and 5A are virtually non-selective, and (iii) AC is selective to C2H4 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 (C2H4, 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 C2H4 have received increased attention in recent years; two such alternatives are discussed below.

The oxidative coupling of methane (OCM) process involves reaction of CH4 with oxygen under high temperatures (973–1173 K) to produce C2H4, followed by in-situ oxidation to C2H4 [1]. The partial or total combustion to CO or CO2 are the main side reactions. Typically, the conversion of methane < 40% and the selectivity to C2H4 and to C2H6 is less than 50% and the reactor effluent consists of H2/CO/CO2/CH4/C2H6/C2H4 mixtures typically containing < 10% C2H4. The conventional schemes for recovery of C2H4, involving amine absorption followed by cryogenic distillation at high pressure, are energy intensive [2,3]. Use of pressure swing adsorption (PSA) technology for C2H4 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 C2H4-selective sorbent in which the C2H4-free raffinate is recycled back to the reaction train [5]; see Fig. 1. CO2 is removed from the C2H4-rich extract stream and subsequently distilled to obtain C2H4 of the required purity. C2H4, 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 CO2, C2H6, along with the valuable C2H4 in concentrations up to 16% [7]. Recovery of C2H4 by selective adsorption could significantly contribute to the economic viability of syngas production from biomass.

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The primary objective of this article is examine whether any commercially available adsorbents could offer comparable C2H4/CO2 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 Mn2(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 CO2, and C2H4 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.

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

where \( x_i \) is the mole fraction in the adsorbed phase

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

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:

\[ \pi A = \int_0^T \frac{q_i^0(f)}{f} \, df = \int_0^T \frac{q_j^0(f)}{f} \, df = \int_0^T \frac{q_k^0(f)}{f} \, df = ... \]

where \( q_i^0(f) \) is the pure component adsorption isotherm, and \( f \) is the gas phase fugacity. The units of \( \frac{f}{T} \) 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 \( q_j \) is calculated from

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**Fig. 1.** OCM process flow scheme with C2H4-selective adsorbent in the PSA adsorber beds; this flow scheme is adapted from Radaelli et al. [5].
\[ q_i = q_i^0 + q_i^t + \cdots + q_i^n = \frac{1}{q_i^{x_1}} + \frac{1}{q_i^{x_1}} + \cdots + \frac{1}{q_i^{x_n}} \]  

(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 flowline.

In Fig. 2, the IAST calculations of the adsorbed phase mole fraction of C\(_2\)H\(_4\) for binary C\(_2\)H\(_4\)(1)/CO\(_2\)(2) mixtures, \( x_1 \), is plotted as a function of the mole fraction of C\(_2\)H\(_4\) in the bulk gas phase mixture, \( y_1 \). The larger the departure from the parity line, \( x_1 = y_1 \), 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 CO\(_2\). Zeolite SA, the material with the largest deviation from the parity line, has the highest selectivity to CO\(_2\), whereas the CO\(_2\)/C\(_2\)H\(_4\) selectivity of CaX and NaY are close to unity. For selective adsorption of C\(_2\)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 C\(_2\)H\(_4\).

In order to determine the reliability of IAST estimations for C\(_2\)H\(_4\)/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 Flowrence set-up, 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), SA (=CaA = LTA-SA, Acros), and Activated carbon (GCN 3070 Cabot corp.), that were crushed and sieved to obtain 150–250 \( \mu \)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 C\(_2\)H\(_4\)/CO\(_2\)/N\(_2\)/Ar mixtures using different C\(_2\)H\(_4\)/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% 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 C\(_2\)H\(_4\)/CO\(_2\) ratios in the feed mixture are chosen: Run 1 (C\(_2\)H\(_4\)/CO\(_2\) = 3), Run 2 (C\(_2\)H\(_4\)/CO\(_2\) = 1.5), Run 3 (C\(_2\)H\(_4\)/CO\(_2\) = 0.8), and Run 4 (C\(_2\)H\(_4\)/CO\(_2\) = 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 Run 4, respectively, for each sorbent. For 13X, CaX, NaY, and AC, the breakthrough characteristics are reasonably sharp, indicating that diffusional limitations are of negligible importance. It is worth noting that the breakthroughs of C\(_2\)H\(_4\) and 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, C\(_2\)H\(_4\) breaks through before CO\(_2\), whereas in Run 4, CO\(_2\) breaks through earlier than C\(_2\)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 \( m_{ads} \) 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 C\(_2\)H\(_4\), expressed as moles per kg of adsorbent in the packed tube, can be determined from a material balance

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

(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, \( t = \infty \), is the time required to reach steady-state. Analogously, the uptake of CO\(_2\) is

\[ q_i = \frac{c_i Q}{m_{ads}} \int_0^t (y_{2, feed} - y_{2, exit}) dt \]  

(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 C\(_2\)H\(_4\), \( x_i = q_i/(q_i + q_j) \), essentially invoking the assumption that the mixture can be considered to be a pseudo-binary due to the relatively poor adsorptivity of both Ar and 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 C\(_2\)H\(_4\), \( x_i \), is plotted as a function of the mole fraction of C\(_2\)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 CO\(_2\)-selective, and AC is C\(_2\)H\(_4\)-selective. The data for CaX, and NaY lie close to the \( y_i = x_i \) 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 C\(_2\)H\(_4\) and 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 Hoie [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 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, Equation 1 was applied in a modified differential form, namely

\[ \int_0^t \frac{dy}{dt} dt = \int_0^t \frac{dQ}{dt} dt \]

Fig. 2. IAST calculations for adsorption of binary C\(_2\)H\(_4\)(1)/CO\(_2\)(2) mixtures in different sorbents at 313 K and total pressure of 1 bar. The adsorbed phase mole fraction of C\(_2\)H\(_4\), \( x_i \), is plotted as a function of the mole fraction of C\(_2\)H\(_4\) in the bulk gas phase mixture, \( y_i \). See Supplementary Material for information on the unary isotherm fit parameters and details of IAST calculations.
zeolite, we need to introduce activity coefficients $\gamma_i$ into Eq. (1)

$$p_i = P^0_i x_i \gamma_i$$

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

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

Fig. 3. Experimental breakthroughs for Ar/C$_2$H$_4$/CO$_2$/N$_2$ mixtures in (a) 13X, (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$_2$H$_4$/CO$_2 \approx 3$). The continuous solid black lines are breakthrough simulations using the IAST for determination of mixture adsorption equilibrium. The % N$_2$ in the outlet gas can be determined by taking the sum of the mole % = 100.

The Wilson model for activity coefficients are given for binary mixtures by
\[
\ln(\gamma_i) = \left(1 - \ln(x_iA_{1i} + x_2A_{2i}) - \frac{x_iA_{1i}}{x_iA_{1i} + x_2A_{2i}}\right) \left(1 - \exp\left(-\frac{C_{\text{IAST}}}{RT}\right)\right)
\]
\[
\ln(\gamma_i) = \left(1 - \ln(x_iA_{1i} + x_2A_{2i}) - \frac{x_iA_{2i}}{x_iA_{1i} + x_2A_{2i}}\right) \left(1 - \exp\left(-\frac{C_{\text{IAST}}}{RT}\right)\right)
\]

In Eq. (9), \(A_{11} = 1\); \(A_{22} = 1\), and \(C\) is a constant with the units kg mol\(^{-1}\). The introduction of \(1 - \exp\left(-\frac{C_{\text{IAST}}}{RT}\right)\) imparts the correct limiting behaviors \(\gamma_i \to 1\); \(\frac{\delta \gamma_i}{\delta \Lambda_i} \to 0\) for the activity coefficients in the Henry regime, \(p_i \to 0\); \(\frac{\delta \gamma_i}{\delta \Lambda_i} \to 0\). As pore saturation conditions are approached, this correction factor tends to unity \(1 - \exp\left(-\frac{C_{\text{IAST}}}{RT}\right) \to 1\). The choice of \(A_{12} = A_{21} = 1\) in Eq. (9), yields unity values for the activity coefficients reduces to the IAST. The \(x_i vs. \gamma_i\)
data for 5A zeolite are well represented by the choice of the Wilson parameters $\Lambda_1 = 32; \Lambda_2 = 0.03; C = 1 \text{ mol kg}^{-1}$ as evidenced by the RAST calculations represented by the solid black line in Fig. 5b.

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]

$$
-D_{ii} \frac{\partial^2 c_i(r, z)}{\partial z^2} + \frac{\partial c_i(r, z)}{\partial t} + \frac{\partial (\nu(r, z) c_i(r, z))}{\partial r} + \frac{(1 - \varepsilon)}{\varepsilon} \rho \frac{\partial q_i(r, t)}{\partial t} = 0; \quad i = 1, 2, \ldots n
$$

(10)

In Eq. (10), $t$ is the time, $z$ is the distance along the adsorber, $\varepsilon$ is the bed voidage, $D_{ii}$ is the axial dispersion coefficient, $\nu$ is the interstitial gas velocity, and $\dot{q}_i(r, t)$ is the spatially averaged molar loading within the crystallites of radius $r_c$, monitored at position $z$, and at time $t$ [23]. Ruthven et al. [22] state "when mass transfer resistance is significantly greater than axial dispersion, one may neglect the axial dispersion term and assume plug flow". The assumption of plug flow is invoked in all the simulation results presented in this article.

The radial distribution of molar loadings, $q_i$, is obtained from a solution of a set of integral equations describing the transient uptake within a spherical crystallite of radius $r_c$.

$$
\rho \frac{\partial q_i(r, t)}{\partial t} = -\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 N_i)
$$

(11)

The intra-crystalline fluxes $N_i$ in turn, are related to the radial gradients in the molar loadings by

$$
N_i = -\rho D_i \frac{\partial q_i}{\partial r}; \quad i = 1, 2 \ldots n
$$

(12)

In Eq. (12), $D_i$ is the Maxwell-Stefan (M-S) diffusivity for interaction of species $i$ with the material framework. The use of Eq. (12) essentially implies that we are ignoring the influence of thermodynamic coupling effects [26].

At any time $t$, the component loadings at the surface of the particle $q_i(r_c, t) = q_i^*$ is in equilibrium with the bulk phase gas mixture; the loadings $q_i^*$ are determined by use of the IAST, or RAST.

The spatial-averaged component loading within the crystallites of radius $r_c$ is calculated using

$$
\bar{q}_i = \frac{3}{r_c^2} \int_0^{r_c} q_i(r, t) r^2 dr
$$

(13)

At time, $t = 0$, the inlet to the adsorber, $z = 0$, is subjected to a step input of the feed gas mixture, with inlet partial pressures $p_i0$, and this step input is maintained till the end of the adsorption cycle when steady-state conditions are reached.
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 $D_i/r_i^2 = 0.1 \text{ s}^{-1}$ for Ar, N$_2$, and CO$_2$; For C$_2$H$_4$, the inter-cage hopping is small.
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 diffusional 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 C\(_2\)H\(_4\)/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 C\(_2\)H\(_4\) and CO\(_2\). This indicates that the unary isotherms anticipate more 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 C\(_2\)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 C\(_2\)H\(_4\)/CO\(_2\) and 40/4/49/7 CH\(_4\)/C\(_2\)H\(_6\)/CO\(_2\)/C\(_2\)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 \( A_{ij} = 32; \quad A_{ji} = 0.03; \quad C = 1 \text{ mol kg}^{-1} \), determined from fitting the \( x_i \) vs \( y_j \) data for 5A zeolite in Fig. 5b.

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, C\(_2\)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 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 isotherms are not for the Cabot AC used in the experiments.

For 13X and 4A zeolites, the data in Fig. 7a, d show that purified 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 C\(_2\)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 C\(_2\)H\(_4\) is not strong enough to enable pure C\(_2\)H\(_4\) recovery as raffinate.

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

6. Conclusions

Transient breakthrough experiments with C\(_2\)H\(_4\)/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 C\(_2\)H\(_4\). The results indicate that AC is the most suitable adsorbent for this purpose. Though AC exhibits a lower C\(_2\)H\(_4\)/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 C\(_2\)H\(_4\) from CO\(_2\)-bearing mixtures has not been highlighted in the published literature [1,4,5]. Of the other sorbents 4A, and 13X are CO\(_2\)-selective, and suitable for CO\(_2\) capture of refinery off-gases containing C2 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 isotherms 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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