Variable desorbent strength: influence on SMB operating conditions and performance

Catherine Laroche · Damien Leinekugel-le-Cocq · Philibert Leflaive

Abstract The aim of this work was to evaluate the role of desorbent selectivity variation on the tuning and the performance of a SMB process. For this purpose a separation regions study in the case of a four-zones non-linear transfer limited SMB was carried out. The SMB unit was modelled considering the equivalent True Moving Bed (TMB). A set of 11 desorbents with different strength was considered: 3 desorbents with constant strength and 8 desorbents with variable strength. For each system, the optimal operating conditions are determined using the separation regions approach, with plots in both (Q_2, Q_F) and (Q_4, Q_D) planes. Depending on the separation considered, a variable selectivity desorbent can lead to an improvement or can be detrimental to process performances. A careful choice of desorbent selectivity (either constant or variable) is then crucial to achieve maximal process performance.

Keywords Simulated Moving Bed (SMB) · Desorbent strength · Robust operating conditions · Separation regions study

1 Introduction

Simulated Moving Bed technology is commonly used in the petrochemical industry for xylene isomers or linear paraffins separations. Those applications need very large scale industrial units to produce low value products. One of the major operating costs in such a process is due to downstream separations. Minimizing desorbent consumption is then a major requirement to minimize downstream distillation cost. For petrochemical applications, desorbent consumption is therefore a key performance criterion as important as purity, recovery or productivity.

In this paper, we will focus on the impact of desorbent strength on SMB operating conditions and performance, particularly in terms of productivity, desorbent consumption for a given purity and recovery. The robustness of the operation is also addressed (which is also a major issue in industrial operation). Several constant desorbent strengths are considered, as well as several variable desorbent strengths.

2 SMB principle and role of the desorbent

Simulated moving bed (SMB) is a continuous multi-column adsorption process which derives from the true moving bed (TMB), an adsorption-based separation process implying a fluid-solid counter-current. For TMB, the solid phase flows down counter-currently to the mobile phase stream. The feed mixture is introduced in the column and the most adsorbed component is carried by the solid to the bottom of the column (where it will be collected in the extract) whereas the less retained component is carried upward with the mobile phase and collected in the raffinate (Fig. 1-a).

As a constant solid flow is not readily feasible, SMB is preferred. It is composed of several interconnected fixed beds (usually 24 for paraxylene production) and the counter-current is simulated by a discrete switching of inlets and outlets. In the SMB unit, four different operating zones (zones 1 to 4) can be distinguished, according to the position of the inlet and outlet streams, as seen on the schematic on Fig. 1b.

Each of these operating zones performs a different function.

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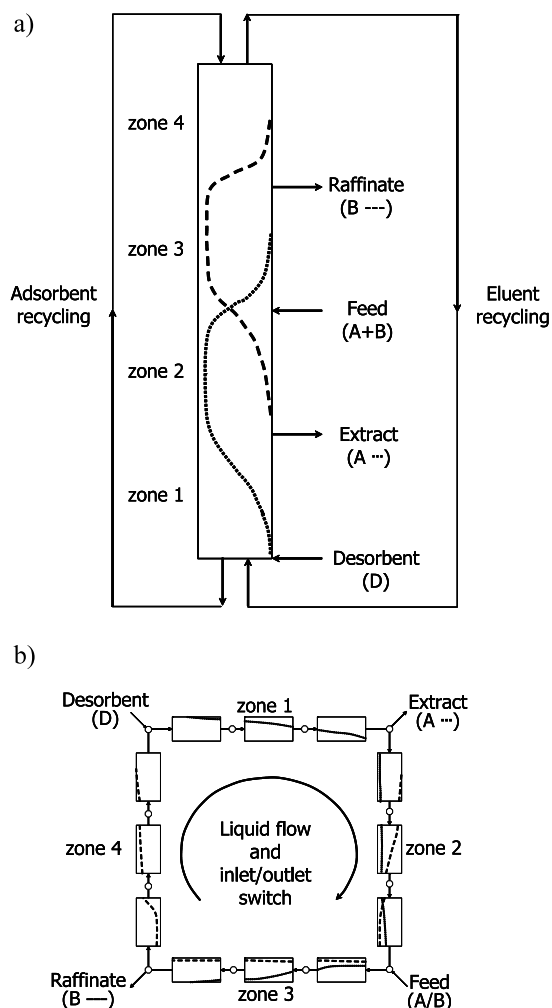
Fig. 1 Schematic of four-section true moving bed (**a**) and simulated moving bed (**b**)

- The function of zone 1 is the regeneration of the adsorbent. Desorbent is at high concentration and desorbs the most retained component from the adsorbent.
- The function of zone 2 is to prevent less adsorbed components (B&C) to reach the extract withdrawal point and to contaminate the extract.
- The function of zone 3 is to prevent the contamination of raffinate by the more adsorbed component (A).
- The function of zone 4 is the regeneration of the desorbent. Desorbent is at high concentration as almost pure desorbent is recycled in zone 1.

Desorbent is present at relatively high concentration in all zones of the SMB. The tuning and the overall performances of an SMB process are directly related to the thermodynamics of the system, which can be described by the relative selectivities of the different compounds of this system. Desorbent strength is therefore a key parameter for the flow streams tuning in the different zones and has a strong impact on process performance. Specifically, minimum des-

orbent requirement has received much attention from the literature (Rajendran et al. 2009; Lim 2004, 2007; Mazzotti et al. 1994, 1997, 2004; Morbidelli et al. 1985; Wu et al. 1999; Storti et al. 1995).

The requirement for good SMB performances is twofold:

- on the one hand, the process has to fulfill the level of purity of the desired component as it is generally imposed by product quality requirement (market specifications)
- on the other hand, the minimization of investment and operating costs implies to maximize the recovery and productivity in order to reduce the size of the SMB unit and to minimize the desorbent consumption in order to cut downstream separation operating costs.

Storti et al. have first reported in 1989 on the influence of desorbent strength on desorbent consumption and productivity. The performance of the separation process is determined by the strength of the desorbent with respect to that of the components to be separated. Different cases are defined:

1. weak desorbent, i.e. desorbent strength < less adsorbed component strength;
2. weak-intermediate desorbent, i.e. less adsorbed component strength < desorbent strength < strength of the most adsorbed component produced in the raffinate stream;
3. intermediate desorbent, i.e. strength of the most adsorbed component produced in the raffinate stream < desorbent strength < strength of the less adsorbed component produced in the extract stream;
4. strong-intermediate desorbent, i.e. strength of the less adsorbed component produced in the extract stream < desorbent strength < strength of the most adsorbed component produced in the extract stream;
5. strong desorbent, i.e. desorbent strength > strength of the most adsorbed component produced in the extract stream.

Using Equilibrium Theory with constant selectivities, the authors show that when a particular component of a binary mixture is desired, desorbent should have a strength as close as possible to that of such a component, since it produces maximum enrichment. Moreover, the best performances are obtained when this component is produced at the extract (i.e. is the most adsorbable component) and when the desorbent strength is strong-intermediate, since this leads to lower desorbent requirement. In 1995, Storti et al. (1995) focused on the impact of the desorbent strength on the tuning of zones 2 and 3 flow-rates. Their results show that an intermediate desorbent (as compared to strong or weak) is the most efficient when high purity and high yield are expected, as for paraxylene recovery from mixed xylenes where the targets are purity above 99.7% and recovery above 97%. The choice of an intermediate desorbent represents a good compromise between the following two tasks: to be adsorbed in zone 1

so as to facilitate the desorption of the most adsorbed component (for this aim strong desorbent is preferred) and to be desorbed in zone 4 so as to facilitate the adsorption of the less adsorbed components (for this purpose, a weak desorbent is recommended).

Now considering desorbent consumption, Storti et al. (1989) and Lim (2007) both showed that a strong desorbent allows a minimization of the desorbent requirement.

The conclusion to be drawn from those studies is that the best desorbent is a compromise between a desorbent with intermediate strength for a high purity product and a good robustness in the zones 2 and 3, and a strong desorbent for the minimization of the desorbent consumption.

The concept of applying solvent strength gradients in the SMB process has been used for improving the separation performance of enantiomers or fine chemicals (Jensen et al. 2000; Antos and Seidel-Morgenstern 2001; Abel et al. 2004). In such process, the feed stream contains solvent. The solvent gradient SMB operation is obtained by using a different and stronger solvent in the desorbent stream fed to zone 1 than the one present in the feed stream, leading to a mixture of solvents as mobile phase.

In large scale petrochemical applications however, this concept is no longer applicable as there is no solvent in the feed stream. But the solution might be the use of a desorbent with variable strength, i.e. strong in zone 1 and exhibiting an intermediate strength in zones 2 and 3 of the SMB process. In order to verify the feasibility of this concept, different desorbents have been tested, by performing liquid phase adsorption experiments in the presence of paraxylene on a commercial adsorbent used for xylenes isomers separation. The selectivity between paraxylene as the desired product and the desorbent was measured for various compositions of paraxylene (component A) and desorbent D in the mixture. The measurements obtained with two desorbents D_1 and D_2 (shown in Fig. 2) experimentally demonstrate that desorbent can exhibit either constant or variable strength. As can be seen from the plot on Fig. 2, the selectivity between paraxylene with respect to the desorbent remains more or less constant in the case of desorbent D_1, whereas an important increase is observed in the case of desorbent D_2.

To our knowledge, no paper provides insight about the influence of the variation of a non-constant desorbent selectivity on SMB tuning and performance.

The objective of this paper is to identify the optimal desorbent along with its associated operating conditions for a given separation.

This task will first be tackled with process modelling using a detailed TMB model accounting for finite mass transfer resistance and axial mixing. The methodology used is the following:
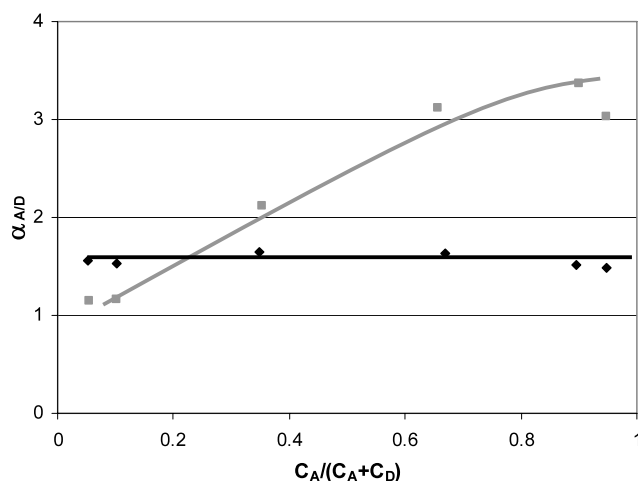
Fig. 2 Measured selectivities between paraxylene (component A) and two different desorbents D_1 (♦) and D_2 (■) on a commercial adsorbent: plot of $\alpha_{A/D}$ as a function of $\frac{c_A}{c_A + c_D}$

– a set of 11 desorbent strengths was considered:
  - 3 constant strengths,
  - 8 variable strengths (depending on the extract compound concentration): different cases have been investigated in order to study the strength variation, i.e. increasing or decreasing, extent of the variation and mean value;
– for each system, the optimal operating conditions, i.e. optimal flow-rates in the different zones, are determined using the separation regions approach.

3 Modelling Methodology

The modelling part of this study deals with the separation close to the one used to produce paraxylene from a mixture of paraxylene, metaxylene, orthoxylene and ethylbenzene. Since metaxylene and orthoxylene have the same strength (Minceva and Rodrigues 2005), it can be considered as a ternary mixture $(A + B + C)$ where A represents paraxylene, B represents ethylbenzene, and C represents both metaxylene and orthoxylene. Paraxylene, i.e. component A, is the most adsorbed component and is extracted with a purity over 99.7% and a recovery over 97%.

In this study, the separation regions graphical representation, first introduced by Storti et al. (1989) (see also Azevedo and Rodrigues 1999), is used to compare the various studied systems. The triangle shaped regions for zones 2 and 3, and the rectangle shaped regions for zones 1 and 4, define the range of operating conditions (flow-rates Q_2, Q_3 and Q_1, Q_4) which allow to achieve the separation with the required purity and recovery.

The adsorbent is a pelletized zeolite, containing two levels of porosity, wherein the kinetics of mass transfer are

non negligible. As the equilibrium theory, which is often used to determine the separation regions does not apply in these conditions, the separation regions were determined by process simulation.

In this paper, a separation regions analysis for different desorbent strength is carried out. In the case of finite mass transfer, it is no longer possible to use dimensionless flow-rate ratios m_j as proposed by Storti et al. (1989), but one has to use the net fluid flow-rates Q_j, the net solid flow-rate being fixed by the inlet-outlet switching time. The separation regions were therefore determined with the different desorbent strengths both in the (Q_2, Q_F) (triangle shaped separation region) and the (Q_4, Q_D) planes (rectangle shape separation region).

The advantage of this comparison method based on the separation regions in the (Q_2, Q_F) and the (Q_4, Q_D) planes is that it enables to evaluate both the performance of the separation (maximum feed flow-rate and minimum desorbent flow-rate) and the robustness of the operating conditions (characterized by the width of the regions near the operating point at maximum feed flow-rate). By robust operating conditions, we mean that small disturbances in the operating parameters do not modify the qualitative behavior of the SMB.

While constructing the separation regions in a given plane (Q_2, Q_F) or (Q_4, Q_D), we make sure that the flow-rates used in the other two zones are localized in the middle of their own separation region and not too close from their borderlines.

Separation regions in both (Q_2, Q_F) and (Q_4, Q_D) planes were plotted using a three steps procedure:

(1) simulations were carried out for a broad range of flow-rates values in a systematic way using a large grid;
(2) triangles or rectangle edges were plotted using a tighter grid;
(3) the higher triangle vertex in the (Q_2, Q_F) plane and the rectangle vertex in the (Q_4, Q_D) plane are obtained using a very fine mesh.

The triangle shaped Q_2–Q_F separation region can be either thin or wide near the triangle vertex, depending on selectivities of the different components. The triangle width at the vertex is a good way of estimating the robustness of the operating conditions. Storti et al. (1993) provide a criterion for robust design, so that a small perturbation in the operating conditions does not modify the qualitative behavior of the SMB unit. Robust operating conditions are needed when dealing with large size SMB units running for many years without stop, and possible disturbances of feed composition or flow-rates. In order to evaluate the maximum robust feed flow-rate, we find the point with the highest feed flow rate for which variations of 1% of feed and zone 2 flow-rates remains within the separation region. This approach is similar

Table 1 SMB parameters and adsorbent properties

Bed length	1.1 m
Bed internal radius	3.5 m
Interstitial porosity	0.32
Macro-porous porosity	0.41
LDF coefficient in the macro-porosity	0.5 s^{-1}
LDF coefficient in the micro-porosity	0.16 s^{-1}
Adsorption capacity, Γ_∞	0.12 kg/kg
B/A selectivity	$\alpha_{B/A} = 0.49$
C/A selectivity	$\alpha_{C/A} = 0.27$
Switching time	71 s

Table 2 Constant desorbent selectivities

Constant desorbent strength	
	$\alpha_{A/D}$
High	1.0
Medium	1.3
Low	1.9

to the robust design criteria proposed by Storti, although our flow-rate variation allowance is 1%, instead of 2% taken in Storti et al. (1993).

3.1 Model description

The model is based on the analogy with the True Moving Bed (TMB). The unit is a classical 4 zones SMB with 24 identical beds. Mass transfer through the pellet's macro-porosity and in the zeolite crystals is represented by a double Linear Driving Force (LDF) model. All the components have the same mass transfer resistance parameters. Considering the same saturation loading capacity for all components, and since the process is operated under liquid phase, i.e. the adsorbent is saturated, the following multi-component constant selectivity stœchiometric Langmuir isotherm is used:

$$\theta_i = \frac{\Gamma_i}{\Gamma_\infty} = \frac{\alpha_{i/A}.c_i}{\sum_j \alpha_{j/A}.c_j} \quad \text{with } \alpha_{i/A} = \frac{1}{\alpha_{A/i}}$$

The parameters of the system used for the simulation are given in Table 1.

As far as desorbent strength is concerned, 11 different cases were studied: 3 constant strengths, whose values can be seen in Table 2 and 8 variable selectivities as seen on Fig. 3.

The considered constant strengths are characteristics of intermediate desorbent. Notice that the high constant strength case with $\alpha_{A/D} = 1.0$ corresponds to the limiting value separating strong and intermediate desorbent.
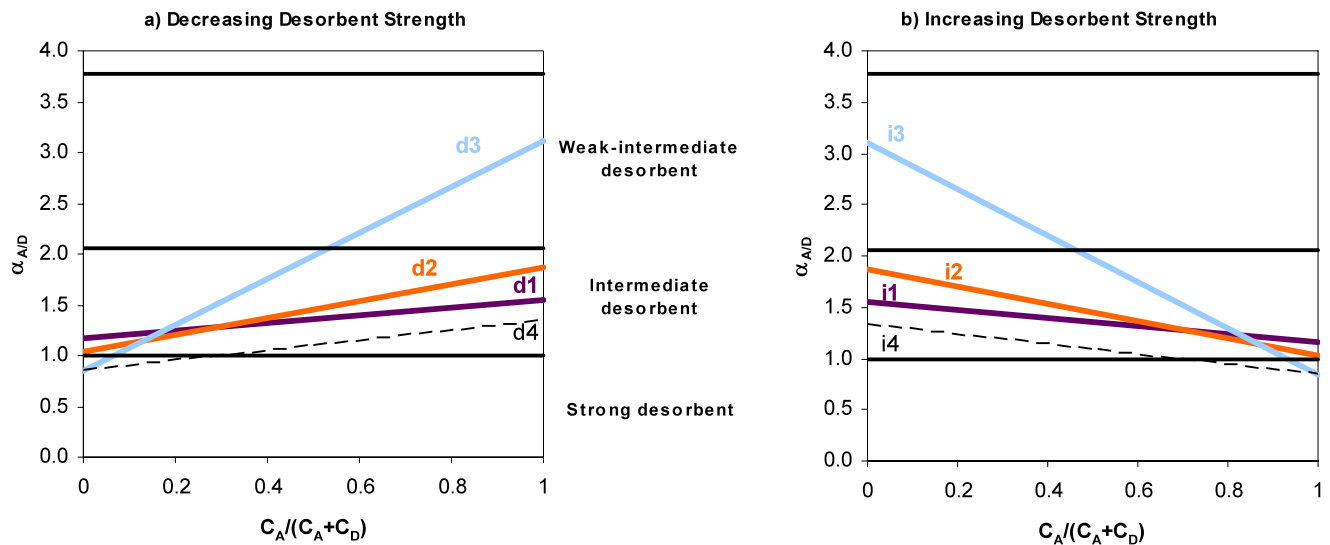
Fig. 3 Linear variation of selectivities $\alpha_{A/D}$ as a function of $\frac{c_A}{c_A+c_D}$. (**a**) Decreasing desorbent strength; d1: $\alpha_{A/D} = 1.2 \rightarrow 1.6$; d2: $\alpha_{A/D} = 1.0 \rightarrow 1.9$; d3: $\alpha_{A/D} = 0.8 \rightarrow 3.1$; d4: $\alpha_{A/D} = 0.8 \rightarrow 1.3$. (**b**) Increas-ing desorbent strength; i1: $\alpha_{A/D} = 1.6 \rightarrow 1.2$; i2: $\alpha_{A/D} = 1.9 \rightarrow 1.0$; i3: $\alpha_{A/D} = 3.1 \rightarrow 0.8$; i4: $\alpha_{A/D} = 1.3 \rightarrow 0.8$

In order to represent a variable desorbent strength, we consider a linear variation of the selectivity between component A and the desorbent with respect to the ratio between the A component concentration and the sum of desorbent D and A component concentration:

$$\alpha_{A/D} = \alpha_{A/D}^0 \frac{c_A}{c_A + c_D} + \alpha_{A/D}^1 \quad (1)$$

For the study of desorbent selectivity variation, the following characteristics have been investigated:

– increasing or decreasing strength,
– extent of the variation,
– mean value.

By increasing strength, we mean an increase of desorbent strength with $\frac{c_A}{c_A+c_D}$, i.e. a decrease of the selectivity $\alpha_{A/D}$ with $\frac{c_A}{c_A+c_D}$.

By decreasing strength, we mean a decrease of desorbent strength with $\frac{c_A}{c_A+c_D}$, i.e. an increase of the selectivity $\alpha_{A/D}$ with $\frac{c_A}{c_A+c_D}$.

3.2 Resolution method

The computing code of TMB has been developed in Fortran. A dynamic version of the model was used to ensure a good stability of the simulator. It was especially useful to avoid initialization problems for non-conventional tunings of the SMB. Moreover, each simulation was initialized with the converged profile of the previous simulation (i.e. previous grid point), enabling a faster convergence.

A first order finite volume method was used as the spatial discretization method, considering 40 volumes per adsorption bed. The resulting ordinary differential equations were solved using the DDASPK integration routine based on the Petzold-Gear BDF method. Since the TMB model is solved dynamically, one has to define convergence criterion to stop the simulation when the system reaches a periodic state. Two convergence tests were used:

- a global one:

$$\sum_{i=1}^{N_{eq}} |\mathbf{X}_{n-10}(i) - \mathbf{X}_n(i)| \leq 5 \times 10^{-6} \quad (2)$$

- a local one:

$$\max(|\mathbf{X}_{n-10}(i) - \mathbf{X}_n(i)|) \leq 5 \times 10^{-5} \quad (3)$$

4 Simulation results

4.1 (Q_2, Q_F) plane analysis

Simulation results can be seen on Fig. 4. Figure 4 shows the separation regions with the required purity and recovery on Q_F vs. Q_2 plots for the same ternary separation, but different desorbent strengths.

All separation regions with a constant selectivity desorbent (Fig. 4a) exhibit a triangle-shaped region with curved borderlines. In the case of $\alpha_{A/D} = 1.3$ both borderlines, i.e. the constant-purity line (on the left-hand side of the triangle) and the constant-recovery line (on the right-hand side of the triangle), exhibit a noticeable curvature.
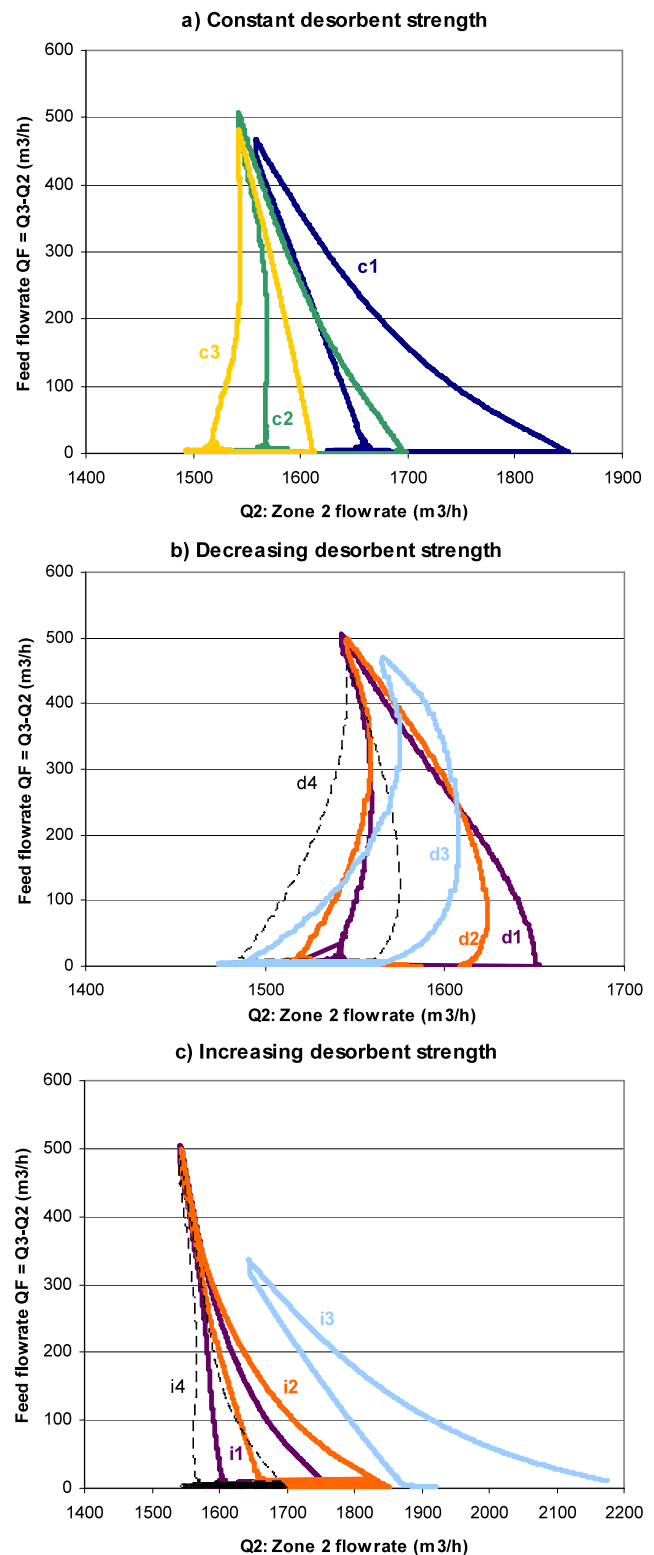
Fig. 4 Effect of desorbent selectivity on the Q_2–Q_F separation regions. (**a**) Constant desorbent strength; c1: $\alpha_{A/D} = 1.9$; c2: $\alpha_{A/D} = 1.3$; c3: $\alpha_{A/D} = 1.0$. (**b**) Decreasing desorbent strength; d1: $\alpha_{A/D} = 1.2 \rightarrow 1.6$; d2: $\alpha_{A/D} = 1.0 \rightarrow 1.9$; d3: $\alpha_{A/D} = 0.8 \rightarrow 3.1$; d4: $\alpha_{A/D} = 0.8 \rightarrow 1.3$. (**c**) Increasing desorbent strength; i1: $\alpha_{A/D} = 1.6 \rightarrow 1.2$; i2: $\alpha_{A/D} = 1.9 \rightarrow 1.0$; i3: $\alpha_{A/D} = 3.1 \rightarrow 0.8$; i4: $\alpha_{A/D} = 1.3 \rightarrow 0.8$

The case corresponding to the strongest constant desorbent strength with $\alpha_{A/D} = 1.0$ exhibits only one curved borderline, which corresponds to the constant-purity line and one straight line, which corresponds to the constant-recovery line. The weakest constant desorbent strength with $\alpha_{A/D} = 1.9$ exhibits an opposite behavior, with a curved constant-recovery line, and an almost straight constant-purity line.

Those observations are in accordance with the results of Mazzotti et al. (1994) using equilibrium theory, who noted that in the case of intermediate desorbent the triangle-shaped region shows two curved borderlines which are more or less stretched depending on the adsorption selectivities, and that in the other cases (strong or weak), only one curved borderline is present.

We can also see on Fig. 4 that the position of the separation region depends on the desorbent strength. Indeed, the stronger the desorbent, the more the separation region is shifted to the left in the (Q_2, Q_F) plane, i.e. the lower the value of Q_2 is required to achieve the separation with the desired purity and recovery, for the same feed flow-rate. This effect has previously been reported by Storti et al. (1995) using equilibrium theory. It can be explained by a greater difficulty for component A to adsorb in zones 2 and 3 when the desorbent is stronger: a lower Q_2 value is then needed to make component A to adsorb in zones 2 and 3 and to reach the extract withdrawal point at a sufficient concentration to get high purity and recovery.

The separation regions obtained with the variable selectivity desorbents significantly differ in their shape from that of the constant selectivity desorbents. For low feed rates, i.e. at the base of the triangle, the variable desorbent has the same behavior as a constant strength desorbent. In these conditions (with very low feed flow-rates), the system is essentially free of component A and the variable desorbent selectivity is equal to its higher value for increasing desorbent strength, and to its lower value for decreasing desorbent strength (see (1)). For higher feed flow-rates, the concentration in component A increases. The behavior of the systems with increasing desorbent strength logically tends to behavior of the systems with higher constant desorbent strength. The behavior of the systems with decreasing desorbent strength logically tends to behavior of the systems with lower constant desorbent strength.

Another conclusion that can be drawn from the effect of the desorbent strength on the Q_2–Q_F triangles is that whatever the desorbent used, the vertices of the triangle-shaped separation regions are close one to the others, except for the two desorbent strengths with large variation extent:

Fig. 5 Close-up of the effect of desorbent selectivity on the maximum feed flow-rate and determination of the maximum robust feed flow-rate (points with accuracy intervals). (**a**) Constant desorbent strength; c1: $\alpha_{A/D} = 1.9$; c2: $\alpha_{A/D} = 1.3$; c3: $\alpha_{A/D} = 1.0$. (**b**) Decreasing desorbent strength; d1: $\alpha_{A/D} = 1.2 \to 1.6$; d2: $\alpha_{A/D} = 1.0 \to 1.9$; d3: $\alpha_{A/D} = 0.8 \to 3.1$; d4: $\alpha_{A/D} = 0.8 \to 1.3$. (**c**) Increasing desorbent strength; i1: $\alpha_{A/D} = 1.6 \to 1.2$; i2: $\alpha_{A/D} = 1.9 \to 1.0$; i3: $\alpha_{A/D} = 3.1 \to 0.8$; i4: $\alpha_{A/D} = 1.3 \to 0.8$

a) Constant desorbent strength

b) Decreasing desorbent strength

c) Increasing desorbent strength

$\alpha_{A/D} = 0.8 \to 3.1$ and $\alpha_{A/D} = 3.1 \to 0.8$ (see on Fig. 5 a close-up around the vertices).

This effect can be attributed to the fact that for very high feed flow-rates, the desorbent concentration in zones 2 and 3 is minimized, leading to a reduced co-adsorption competition between feed components and desorbent. Therefore, the desorbent strength has less impact at this point.

For the variable desorbent strength $\alpha_{A/D} = 3.1 \to 0.8$, the maximum feed flow-rate is far from the other ones. Such a large variation of desorbent strength is completely different from the others intermediate desorbent strength cases. In fact, the desorbent is weak most of the time in the system. The maximum Q_F reached with this mostly weak desorbent is smaller than for the other intermediate desorbent strength cases. It explains why the triangle vertex is lower than the vertex of the others systems. It also explains why the triangle is shifted to high Q_2 values, since the proportion of desorbent with respect to feed components for this system is higher at the triangle vertex than for the other systems.
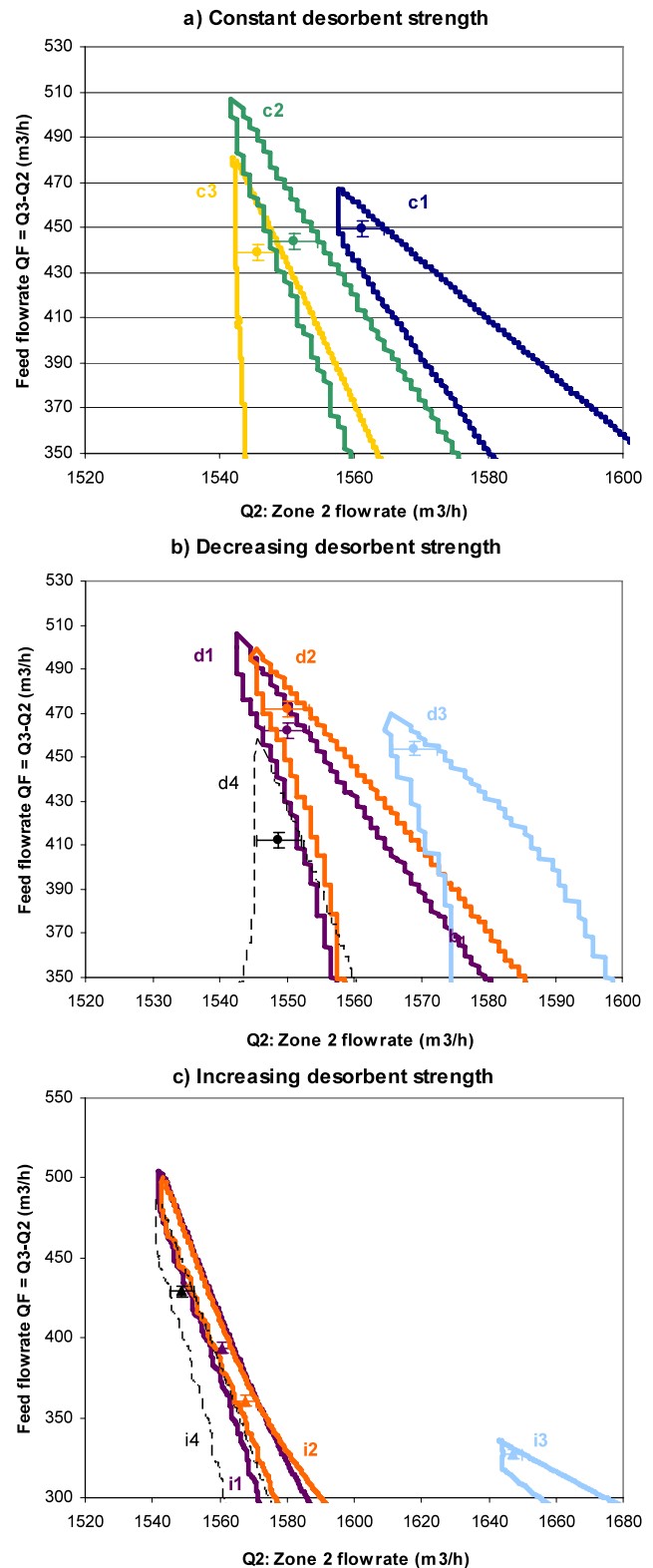
For the variable desorbent strength $\alpha_{A/D} = 0.8 \to 3.1$, the maximum feed flow-rate tends towards the other ones. It does not reach the other ones, since this large variation of desorbent strength gives a weak behavior of the desorbent in most of the system, contrarily to the others intermediate desorbent strength cases.

We can see on Fig. 5 that near the triangle vertex, the increasing desorbent strength give wider separation regions than the constant desorbent strength, and the constant desorbent strength give wider separation regions than the decreasing desorbent strength. The wider the separation region is, the more robust the operating conditions are.

To compare the 11 studied desorbent strengths, we compile in Table 3 both the maximum feed flow-rate at the vertex, and the maximum feed flow-rate to have robust operating conditions.

We observe that systems with decreasing desorbent strength can reach high maximum feed flow-rate values (the highest maximum Q_F among the 11 cases is reached in the case of $\alpha_{A/D} = 1.6 \to 1.2$). However, systems with decreasing desorbent strength show very thin triangles in the vertex neighborhood, and thus the robust feed flow rate are very low. It is noticed that the larger the extent of desorbent strength variation is, the thinner the triangle at the vertex is.

On the opposite, systems with increasing desorbent strength give wide triangle shape. The larger the extent of desorbent strength variation is, the more robust are the operating conditions at high feed flow-rate (see Fig. 5 and Table 3). The highest maximum robust feed flow-rate is obtained in the case of $\alpha_{A/D} = 1.0 \to 1.9$, even though its

Table 3 Maximum and robust feed flow-rates

$\alpha_{A/D}$	Feed flow-rate at vertex (m^3/h)	Robust feed flow-rate (m^3/h)
$\alpha_{A/D} = 1.9$	466.8	**449.6**
$\alpha_{A/D} = 1.3$	**507.0**	444
$\alpha_{A/D} = 1.0$	480.9	439.1
$\alpha_{A/D} = 1.2 \to 1.6$	**506.0**	462.0
$\alpha_{A/D} = 1.0 \to 1.9$	499.0	**472**
$\alpha_{A/D} = 0.8 \to 3.1$	470.0	454
$\alpha_{A/D} = 0.8 \to 1.3$	458.3	412.1
$\alpha_{A/D} = 1.6 \to 1.2$	**507.6**	393.8
$\alpha_{A/D} = 1.9 \to 1.0$	500.7	360.6
$\alpha_{A/D} = 3.1 \to 0.8$	335.5	327.6
$\alpha_{A/D} = 1.3 \to 0.8$	489.8	**429.3**

maximum feed flow-rate at the vertex is lower than the one obtained with $\alpha_{A/D} = 1.2 \to 1.6$.
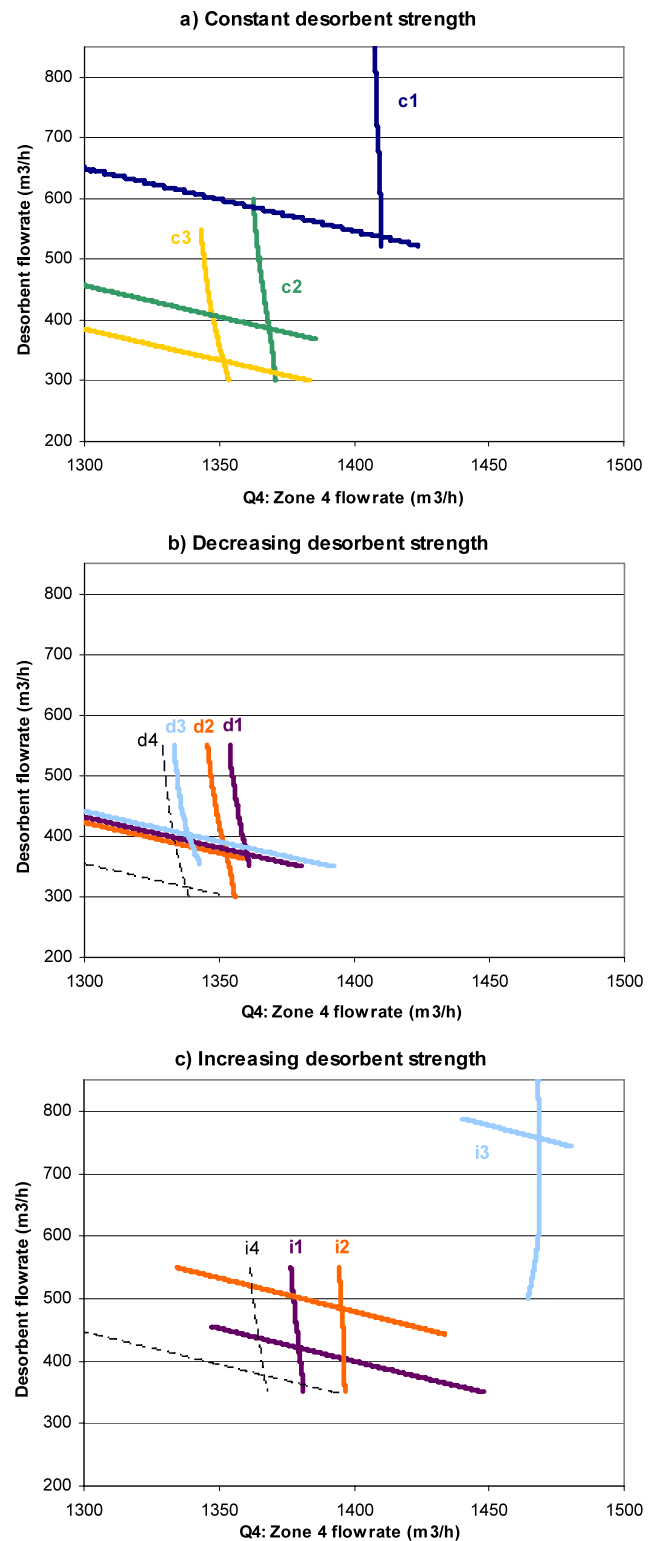
An increasing desorbent strength with large variation extent seems to be the best characteristics to maximize feed flow-rate, i.e. productivity, while using robust operating conditions. However, we see that extremely large variation extent such as $\alpha_{A/D} = 0.8 \to 3.1$ are not suitable. Although it gives a wide triangle shape, the obtained maximum feed flow-rate is too low compared to the others to reach a sufficiently high maximum robust feed flow-rate (see Fig. 5).

4.2 (Q_4, Q_D) plane analysis

Figure 6 shows the separation regions with the required purity and recovery for the same ternary separation, with different values of the desorbent strength. The separation zones in the (Q_4, Q_D) plane exhibit a rectangular shape.

As can be seen on Fig. 6a, desorbent strength has a strong impact on the Q_4–Q_D separation regions. First, the position of the separation region depends on the desorbent strength. Indeed, the stronger the desorbent, the more the separation region is shifted to the bottom and to the left in the (Q_4, Q_D) plane, i.e. the lower the values of Q_4 and Q_D are required to achieve the separation with the required purity and recovery. Indeed, for a weaker desorbent, a higher zone 4 maximum flow-rate can be used as the adsorption of components B and C become more favorable in zone 4. In the same way, the stronger the desorbent, the lower the minimum zone 1 flow-rate ($Q_1 = Q_4 - Q_D$) is needed, since component A is more easily desorbed in zone 1. When comparing the position of the different corners of the rectangles, we can bring to the fore that the use of a strong desorbent permits a lower minimum desorbent flow-rate.

As can be seen on Fig. 6b, the shape of Q_4–Q_D separation regions obtained for variable desorbent strengths are very similar to those obtained with constant desorbent strength. Contrarily to the Q_2–Q_F separation regions, no modification

Fig. 6 Effect of desorbent selectivity on the Q_4–Q_F separation regions. (**a**) Constant desorbent strength; c1: $\alpha_{A/D} = 1.9$; c2: $\alpha_{A/D} = 1.3$; c3: $\alpha_{A/D} = 1.0$. (**b**) Decreasing desorbent strength; d1: $\alpha_{A/D} = 1.2 \to 1.6$; d2: $\alpha_{A/D} = 1.0 \to 1.9$; d3: $\alpha_{A/D} = 0.8 \to 3.1$; d4: $\alpha_{A/D} = 0.8 \to 1.3$. (**c**) Increasing desorbent strength; i1: $\alpha_{A/D} = 1.6 \to 1.2$; i2: $\alpha_{A/D} = 1.9 \to 1.0$; i3: $\alpha_{A/D} = 3.1 \to 0.8$; i4: $\alpha_{A/D} = 1.3 \to 0.8$

Table 4 Feed and desorbent flow-rates

$\alpha_{A/D}$	Feed flow-rate at vertex (m³/h)	Robust Feed flow-rate (m³/h)	Desorbent minimum flow-rate (m³/h)	Minimum ratio Q_D/robust feed flow-rate
$\alpha_{A/D} = 1.9$	467	450	539	1.20
$\alpha_{A/D} = 1.3$	**507**	444	386	0.87
$\alpha_{A/D} = 1.0$	481	**439**	334	0.76
$\alpha_{A/D} = 1.2 \rightarrow 1.6$	**506**	462	374	0.81
$\alpha_{A/D} = 1.0 \rightarrow 1.9$	499	**472**	367	0.78
$\alpha_{A/D} = 0.8 \rightarrow 3.1$	470	454	404	0.89
$\alpha_{A/D} = 0.8 \rightarrow 1.3$	458	412	314	0.76
$\alpha_{A/D} = 1.6 \rightarrow 1.2$	**508**	394	425	1.08
$\alpha_{A/D} = 1.9 \rightarrow 1.0$	501	361	482	1.34
$\alpha_{A/D} = 3.1 \rightarrow 0.8$	336	328	755	2.30
$\alpha_{A/D} = 1.3 \rightarrow 0.8$	490	**429**	381	0.89

of the borderlines curvature due to desorbent strength variation is observed. Indeed, in zones 4 and 1, component A concentration is very low and the desorbent is concentrated, thus the desorbent selectivity presents only small variations.

When comparing the decreasing desorbent strengths $\alpha_{A/D} = 0.8 \rightarrow 3.1$ and $\alpha_{A/D} = 0.8 \rightarrow 1.3$, we observe that zone 4 maximum flow-rates for those two cases are very close one to the other. It is due to the fact that zone 4 is essentially free of component A, and thus the desorbent selectivity is very close to its lower value, i.e. $\alpha_{A/D} = 0.8$ for those 2 cases, in zone 4. The main difference between the two cases is the desorbent minimum flow-rate. This behavior is due to the presence of component A in zone 1, and of the strongest influence of component A on the desorbent selectivity in the case $\alpha_{A/D} = 0.8 \rightarrow 3.1$ than in the case $\alpha_{A/D} = 0.8 \rightarrow 1.3$. Therefore, the desorbent with $\alpha_{A/D} = 0.8 \rightarrow 3.1$ is weaker in zone 1, leading to a higher minimum desorbent flow-rate compared to desorbent with $\alpha_{A/D} = 0.8 \rightarrow 1.3$.

We can also see on Fig. 6b that the position of the Q_4–Q_D separation region depends on the lower value of desorbent selectivity for decreasing desorbent strengths. As mentioned above, since zone 4 is almost free of component A, the desorbent selectivity is close to its lower value. The stronger the desorbent, the more the separation region is shifted to the left in the (Q_4, Q_D) plane, i.e. the lower the value of Q_4 is required to achieve the separation with the desired purity.

In the same way, we observe that for two decreasing strength cases ($\alpha_{A/D} = 1.2 \rightarrow 1.6$ and $\alpha_{A/D} = 1.0 \rightarrow 1.9$) the separation regions borderlines are bounded by those of the two constant selectivity cases. This means that in zones 4 and 1, the systems with decreasing desorbent strength $\alpha_{A/D} = 1.2 \rightarrow 1.6$ and $\alpha_{A/D} = 1.0 \rightarrow 1.9$ are weaker than the constant desorbent strength case $\alpha_{A/D} = 1$, and stronger than the constant desorbent strength case $\alpha_{A/D} = 1.3$.

When considering increasing desorbent strength cases (Fig. 6c), we observe that the Q_4–Q_D separation regions obtained for the different cases are very distant one to the others, due to important differences in the higher values of desorbent selectivity among the different studied cases. Indeed, as already mentioned above, the desorbent selectivity in zones 1 and 4 is very close to the value corresponding to low concentration of component A, i.e. the higher value of desorbent selectivity for increasing desorbent strength. Except for the strongest desorbent $\alpha_{A/D} = 1.3 \rightarrow 0.8$, we observe that the studied cases with increasing desorbent strength lead to high desorbent consumption, since the desorbent strength is low in zone 1.

In terms of minimization of desorbent requirement, we see that the best systems are the ones with low desorbent selectivity, hence strong desorbent strength, in zone 1, i.e. $\alpha_{A/D} = 1.0$ for constant desorbent strength, and $\alpha_{A/D} = 1.0 \rightarrow 1.9$ or $\alpha_{A/D} = 0.8 \rightarrow 1.3$ for variable desorbent strength. However the system with $\alpha_{A/D} = 0.8 \rightarrow 3.1$, although the desorbent is strong when it is highly concentrated, is slightly disfavoured by its large selectivity variation extent, which tends to make it weaker in zone 1, where the amount of component A is no more negligible.

Desorbents with increasing strength are never good candidates for minimizing the desorbent requirement, since they are weaker in zones 1 and 4 compared to zones 2 or 3. The desorbent with $\alpha_{A/D} = 1.3 \rightarrow 0.8$ is nevertheless a reasonable candidate, being the strongest among the four desorbents with increasing desorbent strength.

4.3 Desorbent choice for optimization of the 4 zones SMB performance

Feed and desorbent flow-rates are compiled in Table 4. For each type of desorbent strength variation, we can define the

most efficient to maximize robust feed flow-rate and to minimize desorbent consumption:

- the best constant strength desorbent is $\alpha_{A/D} = 1.3$,
- the best decreasing strength desorbent is $\alpha_{A/D} = 1.0 \rightarrow 1.9$,
- the best increasing strength desorbent is $\alpha_{A/D} = 1.3 \rightarrow 0.8$.

It seems that the most efficient among the different studied desorbents is the decreasing strength desorbent $\alpha_{A/D} = 1.0 \rightarrow 1.9$, as it lies at the limit between intermediate and strong desorbent in zone 1, and is intermediate in zones 2 and 3.

This approach is particularly useful for selecting the most efficient desorbent for a given separation. For instance, SMB performances for xylene isomers separation have been calculated, for the two desorbents D$_1$ and D$_2$ exhibiting constant and variable strength as reported in Fig. 2. It was found that the performances are comparable in terms of robust feed flow-rate with both desorbents, but the use of the decreasing strength desorbent D$_2$ allows a reduction of 14% of the desorbent requirement, as compared to the use of the constant strength desorbent D$_1$.

5 Conclusion

In this work, the issue of finding an optimal desorbent along with its associated operating conditions in a SMB process for a given separation has been addressed.

First, process modelling using a detailed TMB model accounting for finite mass transfer resistance and axial mixing allowed to confirm that desorbent strength and its variation with concentrations has an influence on the tuning of all zones.

It has been shown that the maximum feed flow-rate and the minimum desorbent flow-rate depend on desorbent strength. Moreover, it has been observed that the gap between feed flow-rate at vertex and robust feed flow-rate (allowing $\pm 1\%$ zone flow-rates disturbances) highly depends on the shape of the separation region, and thus on desorbent strength.

Variable desorbent strength, in order to have high desorbent strength in zone 1 and weaker desorbent strength in zones 2 and 3, is preferred to optimize SMB process performance, particularly in terms of productivity and desor-

bent consumption for a given purity and recovery. This concept has been illustrated with the desorbent selection in large scale adsorption process for xylene isomers separation.

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