Complete Separation Conditions for a Local Equilibrium TCC Adsorption Unit

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A new technique presented can offer analytical solutions for the local equilibrium true countercurrent model to study the simulated moving-bed (SMB) separation process. This equilibrium theory could be very useful for predicting both optimal and robust operation conditions for the SMB separation process, if the results can be easily calculated. However, analytical solution was available only in the limiting case of binary separation. With this analytical solution for multicomponent systems, the application of equilibrium theory will be more practical. While developing these solutions, a new way of applying the well-known ω-transformation to nonlinear adsorption system was conceived. This approach may have broader applications than are presented here.

Introduction

Adsorption processes have been used in industry for the separation of many bulk mixtures. One of the important examples is the SORBEX process developed by UOP, where a substituted aromatic compound is separated from its isomers. This adsorption process is operated in a continuous mode, where several adsorption columns are connected sequentially to simulate a moving-bed operation.

A simulated moving-bed (SMB) process is very complicated from both practical and theoretical points of view. Achieving a periodical flow switching in large scale is itself an engineering challenge. To design a separation process from limited information on multicomponent adsorption equilibria also requires a lot of experience. To add the design of such a process, a full model, including details such as the delay of flow by switching valves (Tonkovich and Carr 1996), can be used. However, a quick way to estimate the proper operation conditions should also be useful in many occasions. For such purposes, a simple equilibrium model may be of great value.

A steady-state, local-equilibrium, true countercurrent (TCC) adsorption model was employed by Storti et al. (1989, 1993, 1995) and Mazzotti et al. (1994, 1996, 1997) in a series of efforts to study the SMB process. The purpose was to obtain the most important design rules with a simple but adequate model. In this respect, the equilibrium model is relatively easy to work with, and the equivalence between an SMB process and a TCC adsorption unit has been proven (Ruthven and Ching, 1989).

For a given feed to be separated and a known desorbent, the outcome of a four-section TCC adsorption unit is determined by four operation parameters. These operation parameters can be identified as the four normalized fluid/solid flow ratios (m_1 to m_4) in the TCC sections, or as the switching times in the SMB unit (Storti et al., 1995).

Based on the ω-transformation proposed years ago by Rhee et al. (1971), a set of criteria could be obtained that guarantee achieving a complete separation in an equilibrium TCC adsorption unit. Among them, the conditions related to sections 1 and 4, which discuss purification of the desorbent and regeneration of the adsorbent, can be written independently of the others. However, the conditions related to sections 2 and 3, where the separation occurs, are coupled and can only be expressed as a bounded region on the (m_2, m_3) parameter space.

For the separation of a binary mixture, explicit expressions to outline the complete separation region on the (m_2, m_3) plane could be derived (Storti et al., 1993). However, for a multicomponent system, this region had to be determined by trial and error (Mazzotti et al., 1994, 1996). Specifically, a system of constrained nonlinear equations had to be solved for each point on the (m_2, m_3) plane. The results were then checked against the complete separation criteria. To bypass the tedious calculations, a shortcut method that treated a multicomponent feed as a pseudobinary system was proposed (Mazzotti et al., 1994). However, the prediction of the short cut method was not very accurate.

The simple equilibrium theory would be a useful tool for the design of SMB processes, or guideline for process evaluation, if the calculation could be made easier. In this article, a new technique to solve the equilibrium model is demonstrated, with which explicit expressions were obtained to outline the complete separation region on (m_2, m_3) plane.

Theoretical Backgrounds

Following the work of Storti et al. (1993) and Mazzotti et al. (1994), a local-equilibrium, four-section TCC adsorption unit will be employed to model a SMB process. As illustrated in Figure 1, the pure fluid streams connecting the sections will be identified by alphabetical superscripts; the composite solid streams between sections will be indicated by Greek letters; and the TCC sections will be designated by numerical symbols. In addition, capital letters D, F, E, and R will be used to identify the desorbent, the feed, the extract, and the raffinate streams, respectively.

Following the works just cited, we will index the components according to an increasing order of adsorption strength. The set of components to be collected in the extract stream will be referred to as group E. The weakest and the strongest adsorptives in this group will be identified by subscripts Ew and Es, respectively. Similarly, the components to be collected in the raffinate stream belong to the group R, where the subscripts Rw, Rs indicate, respectively, the weakest and the strongest components in this group.

The steady-state material balance in each TCC section can be written as

$$\frac{\partial}{\partial x}[my_i - \theta_i] = 0, \tag{1}$$

where y_i and $\theta_i \equiv \Gamma_i/\Gamma^\infty$ are, respectively, the composition and the fractional coverage in the fluid and the adsorbed phases. The parameter m here is defined, following Mazzotti et al. (1994), as the ratio between the net fluid mass-flow rate and that of the adsorbed phase

$$m \equiv \frac{u_f \rho_f - u_s \epsilon_p \rho_f}{(1-\epsilon_p) u_s \rho_s \Gamma^\infty} \equiv \frac{u_f/u_s - \epsilon_p}{(1-\epsilon_p)\sigma}, \tag{2}$$

where the definitions of the symbols are given in the Notation section. Since $u_f/u_s > 0$, we have $\epsilon_p/[(1-\epsilon_p)\sigma] < m < \infty$.

The term $my_i - \theta_i$ in Eq. 1 represents the normalized net flux in the TCC section. With the same notation, the normalized fluxes carried by the fluid and the solid streams connecting the sections will be, respectively, $(m+\mu)y_i$ and $(-\mu y_i - \theta_i)$, where $\mu \equiv \epsilon_p/[\sigma(1-\epsilon_p)]$ for short.

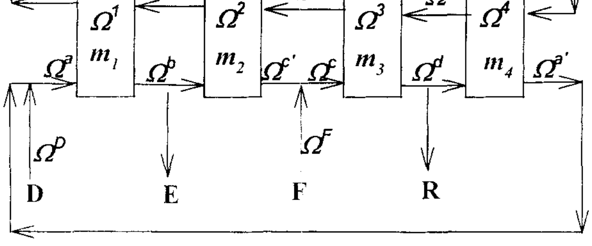

Figure 1. Four-section TCC adsorption model used in this study.

The system variables are indicated in this figure.

Within the TCC section, the solid and the fluid phases are assumed to be in equilibrium at all times. The equilibrium will be described by a constant selectivity stoichiometric relationship.

$$\theta_i = K_i y_i / \sum_{j=1}^{N} K_j y_j, \tag{3}$$

where K_i are the equilibrium constants (selectivity). This relationship is called a stoichiometric model because the sum of the fractional coverage always goes to 1. This is different from the commonly used Langmuir isotherm, and is particularly useful for systems where an upper limit to the overall adsorbable amount is imposed by the adsorbent saturation capacity.

Despite its difference, the ω-transformation (Rhee et al., 1971), originally developed for the Langmuir isotherm, can still be applied to the stoichiometric model. With the ω-transformation, a one-to-one mapping can be established between the equilibrium compositions and a $(N-1)$-dimensional Ω-vector. Given the equilibrium compositions, the Ω-vector components can be found to be the roots to the equation

$$\sum_{i=1}^{N} \frac{K_i y_i}{K_i - \omega} = 0. \tag{4}$$

It is known that these roots satisfy the following inequalities

$$0 < K_1 \le \Omega_2 \le K_2 \le \Omega_3 \cdots \le K_{N-1} \le \Omega_N \le K_N, \tag{5}$$

where K_i is a root if and only if $y_i = \theta_i = 0$. The same set of roots can also be found by the equation

$$\sum_{i=1}^{N} \frac{\theta_i}{K_i - \omega} = \frac{\prod_{j=2}^{N} (\Omega_j - \omega)}{\prod_{i=1}^{N} (K_i - \omega)} = 0. \tag{6}$$

Given the Ω-vector, explicit expressions are available (Storti et al., 1993) to calculate the equilibrium compositions y_i and θ_i. Furthermore, we have

$$\delta \equiv \sum_{i=1}^{N} K_i y_i = \left(\prod_{j=1}^{N} K_j \right) \Big/ \left(\prod_{j=2}^{N} \Omega_j \right). \tag{7}$$

Notice that the index for the Ω-vector components runs from 2 to N. This is different from the convention used by Storti, Mazzotti, and their coworkers. We have taken this indexing scheme to allow for an easier extension to nonstoichiometric systems in the future. Care must be taken when comparing our results with those of the previous workers.

For the steady operation of a local equilibrium TCC adsorption section, a constant state will eventually be reached.

The constant state is characterized by the mass-flow ratio m and the compositions, or the corresponding Ω-vector, in the section. The constant-state Ω-vector of the section is a combination of the Ω-vectors for the fluid and solid incoming streams. The exact way to combine the Ω-vectors depends on the value of the parameter $m\delta$ (Storti et al., 1989; Mazzotti et al., 1994). Taking section 1 as an example, its constant-state Ω-vector is related to that of the incoming streams a and β by one of the following relations;

$$\Omega^1 = \{\Omega_2^\beta, \Omega_3^\beta, \ldots, \Omega_N^\beta\} \qquad m_1\delta_1 \le \min\{\Omega_2^a, \Omega_2^\beta\}$$

$$\Omega^1 = \{\Omega_2^a, \ldots, \Omega_k^a, \Omega_{k+1}^\beta, \ldots, \Omega_N^\beta\}$$

$$\max\{\Omega_k^a, \Omega_k^\beta\} \le m_1\delta_1 \le \min\{\Omega_{k+1}^a, \Omega_{k+1}^\beta\}$$

$$\Omega^1 = \{\Omega_2^a, \Omega_3^a, \ldots, \Omega_N^a\} \qquad \max\{\Omega_N^a, \Omega_N^\beta\} \le m_1\delta_1$$

$$\Omega^1 = \{\Omega_2^a, \ldots, \Omega_k^a, \Omega_{k+1}, \Omega_{k+2}^\beta, \ldots, \Omega_N^\beta\}$$

$$\Omega_{k+1}^\beta < m_1\delta_1 = \Omega_{k+1}^1 < \Omega_{k+1}^a. \quad (8)$$

Because the four TCC sections are connected in our model, their constant-states are not independent. An important theorem has been proved by Storti et al. (1993) concerning the achievable states in a four-section TCC adsorption unit. It states that, under a steady-state operation, the Ω-vector of any fluid or solid stream or that in a TCC section must satisfy the relation

$$\min\{\Omega_j^D, \Omega_j^F\} \le \Omega_j \le \max\{\Omega_j^D, \Omega_j^F\}, \quad (9)$$

where Ω^D and Ω^F are, respectively, the Ω-vectors characterizing the desorbent and the feed streams.

Following Mazzotti et al. (1994), we will assume that the feed to be separated is free of any desorbent, and that the desorbent stream is pure. Therefore, $\Omega_i^D = K_{i-l}$ for $i \le D$ and $\Omega_i^D = K_i$ for $D < i$. At the same time, either Ω_D^F or Ω_{D+1}^F will be equal to K_D. The preceding theorem can then be simplified to

$$K_{i-1} \le \Omega_i \le \Omega_i^F, \qquad 2 \le i \le D$$

$$\Omega_i^F \le \Omega_i \le K_i, \qquad D < i \le N \quad (10)$$

for all the Ω vectors in the unit.

With the pure desorbent, clean feed assumptions, the necessary and sufficient conditions for achieving a complete separation can be written as (Mazzotti et al., 1994)

$$f_E^1 = 0 \qquad f_R^1 = 0$$

$$-Fy_E^F = f_E^2 < 0 \qquad f_R^2 = 0$$

$$f_E^3 = 0 \qquad Fy_R^F = f_R^3 > 0$$

$$f_E^4 = 0 \qquad f_R^4 = 0$$

$$f_D^4 < f_D^3 = f_D^2 < f_D^1, \quad (11)$$

where the subscripts E and R represent, respectively, all components belonging to that group, and $F = m_3 - m_2$ is the normalized feed flow rate.

However, the preceding conditions are not useful because one cannot control the flux of the individual component. Based on Eqs. 1, 8, 10, and 11, Mazzotti et al. (1994) were able to derive the following necessary and sufficient criteria (the Ω-criteria hereafter) on the operation parameters $m_1 \sim m_4$ for:

$$K_{Es} < m_1K_D \qquad \text{if } K_D < K_{Es}$$

$$\Omega_{Es+1}^\beta < m_1K_D \qquad \text{if } K_{Es} < K_D \quad (12)$$

$$m_4 < K_{Rw}/K_D \qquad \text{if } K_{Rw} < K_D$$

$$m_4 < \Omega_2^d/K_D \qquad \text{if } K_D < K_{Rw} \quad (13)$$

$$K_{Rs} < m_2\delta_2 < \Omega_{Ew}^2 = \Omega_{Ew}^{c'}, \qquad K_{Rs} < m_3\delta_3 < \Omega_{Ew}^c$$

$$\text{if } K_D < K_{Rs}$$

$$\Omega_D^\gamma < m_2\delta_2 < \Omega_{Ew}^2 = \Omega_{Ew}^{c'}, \qquad \Omega_D^\gamma = \Omega_D^3 < m_3\delta_3 < \Omega_{Ew}^c$$

$$\text{if } K_{Rs} < K_D < K_{Ew}$$

$$\Omega_{Ew}^\gamma < m_2\delta_2 < K_{Ew}, \qquad \Omega_{Ew}^\gamma = \Omega_{Ew}^3 < m_3\delta_3 < K_{Ew}$$

$$\text{if } K_{Ew} < K_D. \quad (14)$$

Equations 12 and 13 are explicit if $K_{Rs} < K_D < K_{Ew}$. However, the conditions in Eq. 14 are coupled and cannot be separated. Together they define a closed region on the (m_2, m_3) plane. The purpose of this article is to show that explicit expressions can be obtained to outline the complete separation region on the (m_2, m_3) plane.

Extensions to the Equilibrium Theory

The ω-transformation can also be applied to the normalized net flux $f_i \equiv m_i - \theta_i$ (hereafter the net flux for short) in the TCC sections. Let us define a function

$$T(\omega) \equiv \sum_{i=1}^{N} \frac{K_i f_i}{K_i - \omega} + 1. \quad (15)$$

It can be shown (see Appendix A) that

$$T(\omega) = (m\delta - \omega)\left[\sum_{i=1}^{N} \frac{\theta_i}{K_i - \omega}\right] = (m\delta - \omega)\frac{\prod_{i=2}^{N}(\Omega_i - \omega)}{\prod_{i=1}^{N}(K_i - \omega)}. \quad (16)$$

In other words, the normalized net fluxes can be mapped to an N-dimensional space of $(m\delta, \Omega)$, with Ω-vector determined by the compositions and m determined by the normalized overall net flux. Excluding the trivial case with all f_i equal to zero, the function $T(\omega)$ just defined is a piecewise continuous function with singularities at those K_i where f_i does not vanish.

By our definition, f_i can also be written as $f_i = (m\delta - K_i)\theta_i/K_i$. This suggests that either θ_i or $m\delta - K_i$ should be zero when $f_i = 0$. On the other hand, $m\delta$ is larger than K_i if and only if f_i is positive, while it is smaller than K_i if and only if f_i is negative. Since we have indexed the components according to increasing K values, all positive f_i should appear before negative ones.

For the case with $K_N < m\delta$, all nonvanishing f_i are positive, and therefore

$$\frac{dT}{d\omega} = \sum_{i=1}^{N} \frac{K_i f_i}{(K_i - \omega)^2} > 0. \tag{17}$$

Likewise, if $m\delta < K_1$, all nonvanishing f_i are negative and thus $dT/d\omega < 0$.

If $m\delta$ falls within the interval $[K_k, K_{k+1}]$, we have $dT/d\omega > 0$ for $\omega < \min\{m\delta, \Omega_{k+1}\}$ and $dT/d\omega < 0$ for $\omega > \max\{m\delta, \Omega_{k+1}\}$. In other words, $T(\omega)$ is a convex function in the interval $[K_k, K_{k+1}]$ with two zeros at $m\delta$ and Ω_{k+1}. In the special case where $m\delta = \Omega_{k+1}$, we have $d^2T/d\omega^2 = 0$ at $m\delta$. These properties can be proved by knowing that $\sum \theta_i/(K_i - \omega)$ is a monotonously increasing function, while $(m\delta - \omega)$ is a monotonously decreasing function.

The ω-transformation can also be applied to the normalized fluxes carried by the fluid and solid streams. For example, a flux function $S^\alpha(\omega)$ can be defined for the solid stream α as

$$S^\alpha(\omega) \equiv \sum_{i=1}^{N} \frac{K_i[-\mu y_i^\alpha - \theta_i^\alpha]}{K_i - \omega} + 1$$

$$= (-\mu\delta^\alpha - \omega)\frac{\prod_{i=2}^{N}(\Omega_i^\alpha - \omega)}{\prod_{i=1}^{N}(K_i - \omega)}, \tag{18}$$

with Ω^α characterizing the compositions in the solid stream.

Similarly, a flux function $H^\alpha(\omega)$ can be defined for the fluid stream a as

$$H^a(\omega) \equiv \sum \frac{K_i(m+\mu)y_i^a}{K_i - \omega} = \delta^a(m+\mu)\frac{\prod_{i=2}^{N}(\Omega_i^a - \omega)}{\prod_{i=1}^{N}(K_i - \omega)}, \tag{19}$$

with Ω^a characterizing the compositions in the fluid stream.

The material balance at the left boundary of section 1 can now be written as

$$T^1(\omega) = S^\alpha(\omega) + H^a(\omega) \tag{20}$$

or

$$(m_1\delta_1 - \omega)\prod_{i=2}^{N}(\Omega_i^1 - \omega) + (\mu\delta^\alpha + \omega)\prod_{i=2}^{N}(\Omega_i^\alpha - \omega)$$

$$- \delta^a(m+\mu)\prod_{i=2}^{N}(\Omega_i^a - \omega) = 0. \tag{21}$$

The zeroth and Nth-order coefficients of this polynomial equation are always zero. From the rest of the coefficients, $N-1$ equalities can be written that relate the parameters m_1, μ, Ω^1, Ω^α, and Ω^a.

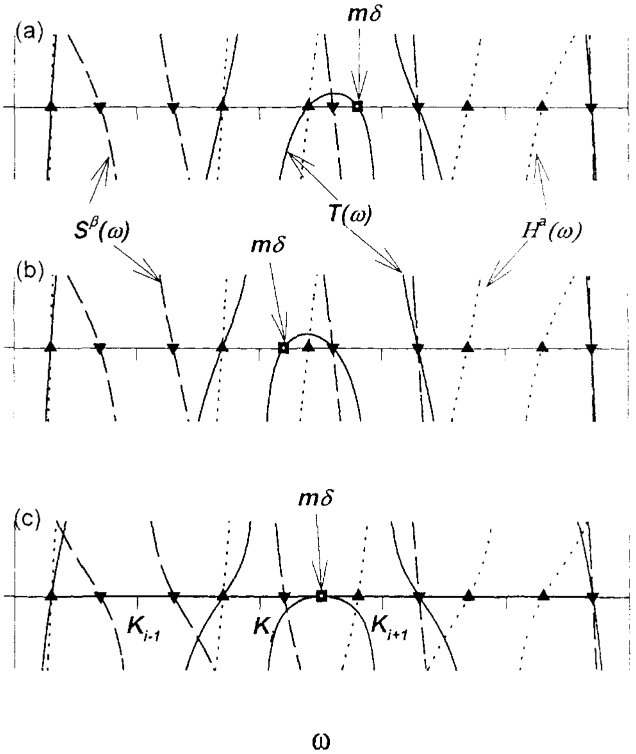

Figure 2. Constant-state relationship in terms of the flux functions $T(\Omega)$, $S^R(\Omega)$, and $H^L(\Omega)$.

With these flux functions, the constant-state relations given previously can be understood graphically as showed in Figure 2. In this figure we have plotted the flux functions $T^1(\omega)$, $S^\beta(\omega)$, and $H^a(\omega)$ over the range of interest. Notice that $S^\beta(\omega)$ is a piecewise-continuous function with negative slope, while $H^a(\omega)$ is a piecewise-continuous function with positive slope. The function $T^1(\omega)$, on the other hand, has positive slope below $\min\{m_1\delta_1, \Omega_{k+1}^1\}$ and negative slope above $\max\{m_1\delta_1, \Omega_{k+1}^1\}$.

With the help of this figure, we can rephrase the constant-state relations as follows: all Ω^1 smaller than $m_1\delta_1$ were inherited from the left input stream, and those larger than $m_1\delta_1$ were inherited from the right input stream. If $\Omega_k^1 = m_1\delta_1$, then $d^2(T^1)/d\omega^2 = 0$ at $m_1\delta_1$ and $\Omega_k^\beta \le \Omega_k^1 \le \Omega_k^a$.

From the material balance equation and the known slopes of $S(\omega)$ and $H(\omega)$, general inequalities between the zeros of $T^1(\omega)$, $S^\beta(\omega)$, and $H^a(\omega)$ can be written. If $T^1(\omega)$ has only one zero Ω_j between $[K_{j-1}, K_j]$, one of the following inequalities must be true:

$$\min\{\Omega_j^\beta, \Omega_j^1\} \le \Omega_j^b \le \max\{\Omega_j^\beta, \Omega_j^1\},$$

$$\Omega_j^a = \Omega_j^\alpha = \Omega_j^1 \le K_j < m_1\delta_1$$

$$\min\{\Omega_j^a, \Omega_j^1\} \le \Omega_j^\alpha \le \max\{\Omega_j^a, \Omega_j^1\},$$

$$m_1\delta_1 < K_{j-1} \le \Omega_j^b = \Omega_j^\beta = \Omega_j^1. \tag{22}$$

If $T^1(\omega)$ has two zero $\omega_j^\oplus$ and $\omega_j^\ominus$ between $[K_{j-1}, K_j]$, then one among the following is true:

$$\min\left\{\omega_j^{\oplus}, \Omega_j^{\beta}\right\} \le \Omega_j^{b} \le \max\left\{\omega_j^{\oplus}, \Omega_j^{\beta}\right\} \le \omega_j^{\ominus} = m_1\delta_1,$$

$$\Omega_j^{a} = \Omega_j^{\alpha} = \Omega_j^{1} = \omega_j^{\oplus}$$

$$m_1\delta_1 = \omega_j^{\oplus} \le \min\left\{\Omega_j^{a}, \omega_j^{\ominus}\right\} \le \Omega_j^{\alpha} \le \max\left\{\Omega_j^{a}, \omega_j^{\ominus}\right\},$$

$$\Omega_j^{\beta} = \Omega_j^{b} = \Omega_j^{1} = \omega_j^{\ominus}$$

$$\Omega_j^{\beta} \le \Omega_j^{b} \le \omega_j^{\oplus} = \Omega_j^{1} = m_1\delta_1 = \omega_j^{\ominus} \le \Omega_j^{\alpha} \le \Omega_j^{a}. \quad (23)$$

These are the relations that Storti et al. (1993) employed to derive the theorem of achievable states.

Two material balance equations can be written for each section, leading to $2(N-1)$ equalities. The constant-state relations provide another $N-1$ conditional equalities for each section. On top of the $12(N-1)$ equalities obtained from the four sections, the material balances at the feed and desorbent stream junctions give another $2(N-1)$ equalities. We have therefore a total of 14 $(N-1)$ conditional equalities involving 4 m's and 16 Ω-vectors, as indicated in Figure 1. These variables can be solved if the mass-flow ratios and the Ω-vectors of the feed and desorbent streams were assigned.

However, as we will demonstrate, it is not necessary to solve all these equations if we are only interested in the complete separation operation. In fact, under such conditions two equations are enough to determine the states in sections 2 and 3.

New Technique to Solve the Equilibrium Model

Logic of the procedures

In the following discussion, we assume that the Ω-criteria have already been satisified in sections 1 and 4, and concentrate only on sections 2 and 3. We want to convert the Ω criteria for these sections to the (m_2, m_3) plane without solving the entire system.

Since we are looking for the necessary and sufficient conditions for complete separation, the results should also satisfy the flux conditions in Eq. 11. With this understanding, the normalized net fluxes in sections 2 and 3 should satisfy the equalities

$$f_D \equiv f_D^2 = f_D^3 = (m_2 - 1)\Sigma_{i\epsilon R} y_i^F + (m_3 - 1)\Sigma_{i\epsilon E} y_i^F$$

$$f_E^2 = -F y_E^F = -(m_3 - m_2) y_E^F$$

$$f_R^3 = F y_R^F = (m_3 - m_2) y_R^F. \quad (24)$$

Conversely speaking, given a pair of f_D and F values that guarantee complete separation, we can always find the corresponding m_2 and m_3 values by

$$m_2 = f_D + 1 - F\sum_E y_i^F$$

$$m_3 = f_D + 1 + F\sum_R y_i^F. \quad (25)$$

In other words, if a complete separation region on the (f_D, F) plane could be found, one would have no trouble converting it to the (m_2, m_3) space. The problem now is to find the complete separation region on the (f_D, F) plane.

In terms of f_D and F, the flux functions $T^2(\omega)$ and $T^3(\omega)$ can be written as

$$T^2(\omega) = \frac{K_D f_D}{K_D - \omega} + 1 - F\cdot E(\omega) \quad (26)$$

$$T^3(\omega) = \frac{K_D f_D}{K_D - \omega} + 1 - F\cdot R(\omega), \quad (27)$$

where $E(\omega) \equiv \Sigma_E K_i y_i^F/(K_i - \omega)$, $R(\omega) \equiv \Sigma_R K_i y_i^F/(\omega - K_i)$ are completely determined by the known feed compositions. If we were given two zeros $\omega_3^{\oplus}$ and $\omega_3^{\ominus}$ of the function $T^3(\omega)$, f_D and F can be solved as

$$-\left(\frac{f_D}{F}\right) = R_1(\omega_3^{\oplus}, \omega_3^{\ominus}) \equiv \sum_R \left(\frac{\omega_3^{\oplus} - K_D}{\omega_3^{\oplus} - K_i}\right)\left(\frac{\omega_3^{\ominus} - K_D}{\omega_3^{\ominus} - K_i}\right)\frac{K_i y_i^F}{K_D} \quad (28)$$

and

$$\frac{1}{F} = R_2(\omega_3^{\oplus}, \omega_3^{\ominus}) \equiv \sum_R \frac{K_i y_i^F (K_D - K_i)}{(\omega_3^{\oplus} - K_i)(\omega_3^{\ominus} - K_i)}. \quad (29)$$

Similarly, if two zeros $\omega_2^{\oplus}$ and $\omega_2^{\ominus}$ are given for the function $T^2(\omega)$, we will have

$$\frac{f_D}{F} = E_1(\omega_2^{\oplus}, \omega_2^{\ominus}) \equiv \sum_E \left(\frac{K_D - \omega_2^{\oplus}}{K_i - \omega_2^{\oplus}}\right)\left(\frac{K_D - \omega_2^{\ominus}}{K_i - \omega_2^{\ominus}}\right)\frac{K_i y_i^F}{K_D} \quad (30)$$

$$\frac{1}{F} = E_2(\omega_2^{\oplus}, \omega_2^{\ominus}) \equiv \sum_E \frac{K_i y_i^F (K_i - K_D)}{(K_i - \omega_2^{\oplus})(K_i - \omega_2^{\ominus})}. \quad (31)$$

At this point, our original problem has been replaced by finding the complete separation region on some $(\omega^{\oplus}, \omega^{\ominus})$ plane. Questions remain to determine whether the zeros of $T^2(\omega)$ or $T^3(\omega)$ should be used, and to locate the range of these zeros that guarantees a complete separation. For that, we can go back to the Ω-criteria given by Mazzotti et al. (1994).

Case I: Strong−Intermediate or Strong Desorbent. Let us first consider the case where $K_{Rs+1} = K_{Ew} < K_D$. The Ω-criteria for this case are $\Omega_{Ew}^3 < m_2\delta_2 < K_{Ew}$, $\Omega_{Ew}^3 \le m_3\delta_3 < K_{Ew}$, and the theorem of achievable state requires that $K_{Rs} \le \Omega_{Ew}^3 \le \Omega_{Ew}^F$.

Since f_E^2 are negative according to the necessary flux condition, and positive f_i should appear before negative ones, f_D must also be negative. Because the net fluxes in section 2 are all negative, we have $m_2\delta_2 < K_{Ew}$ and $dT^2/d\omega < 0$. On the other hand, positive f_R^3 and a negative f_D imply that $T^3(\omega)$ has two zeros $\omega_3^{\oplus} \le \omega_3^{\ominus}$ in the interval $[K_{Rs}, K_D]$. One of them is Ω_{Ew}^3 and the other is $m_3\delta_3$. Also, we have $dT^3/d\omega \ge 0$ at $\omega_3^{\oplus}$ and ≤ 0 at $\omega_3^{\ominus}$.

With the Ω-criteria we can identify that $\Omega_{Ew}^3 = \omega_3^{\oplus}$ and $\omega_3^{\ominus} = m_3\delta_3$. The achievable state condition and the Ω-criterion on $m_3\delta_3$ can then be written as

$$\Omega_{Ew}^{3} = \omega_3^{\oplus} \le \omega_3^{\ominus} = m_3\delta_3 \le K_{Ew} \tag{32}$$

and

$$K_{Rs} < \Omega_{Ew}^{3} = \omega_3^{\oplus} \le \min\{\Omega_{Ew}^{F}, \omega_3^{\ominus}\}. \tag{33}$$

Notice that $\Omega_{Ew}^{3} \neq K_{Rs}$ since component *Rs* must exist in section 3.

The Ω-criterion on $m_2\delta_2$ does not need to be repeated because it is already implied by the preceding inequalities and the necessary flux conditions. It is easy to see that the upper limit of $m_2\delta_2$ is implied by the necessary flux conditions. To prove that the lower bound is also satisfied, we use the material balance $T^2(\omega) + H^F(\omega) = T^3(\omega)$. Since $dT^3/d\omega \ge 0$ at Ω_{Ew}^{3} and $\Omega_{Ew}^{3} \le \Omega_{Ew}^{F}$, we can conclude that $T^3(\Omega_{Ew}^{F}) = T^2(\Omega F_{Ew}) \ge 0$. On the other hand, we have $T^2(m_2\delta_2) = 0$ and $dT^2/d\omega < 0$. Thus $\Omega_{Ew}^{F} \le m_2\delta_2$ is always satisified if $T^2(\Omega_{Ew}^{F}) \ge 0$.

As demonstrated, the necessary and sufficient conditions for the zeros $\omega_3^{\oplus}$ and $\omega_3^{\ominus}$ can be arrived at very easily from the Ω-criteria. If these criteria were not available, one would have to go through the constant state relations (Eq. 8) and inequalities 22 and 23 to obtain these conditions.

Based on Eqs. 32 and 33, the complete separation region on the ($\omega_3^{\oplus}$, $\omega_3^{\ominus}$) plane can be found as indicated by the region A-B-R-Ws in Figures 3a and 4a. With ($\omega_3^{\oplus}$, $\omega_3^{\ominus}$) values limited in this region, the complete separation region on the (f_D, F) plane can be constructed from Eqs. 28 and 29, as shown in Figures 3b and 4b. We have marked the corresponding points on both planes, so that the mapping can be easily visualized.

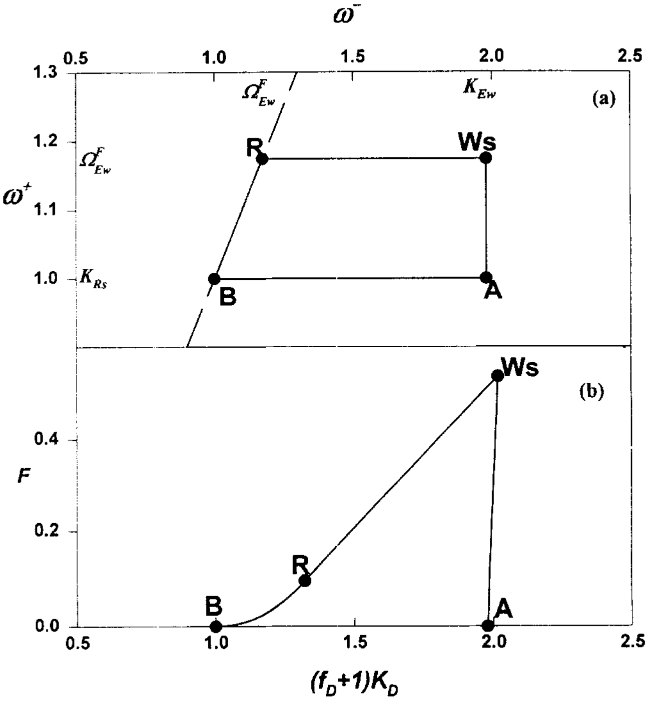

Figure 3. Complete separation regions on ($\omega_3^{\oplus}$, $\omega_3^{\ominus}$) and (f_D^2, F) planes for a strong-intermediate desorbent case.

$K_{Rs} = 1.0$, $y_{Rs}^F = 0.25$. For group E, K_i and y_i^F are 1.98, 2.59, 3.11 and 0.25, 0.1, 0.4, respectively. $K_D = 2.27$ and $\Omega_{Ew}^F = 1.1737$. These are the parameters used in Figure 8 of Mazzotti et al. (1994).

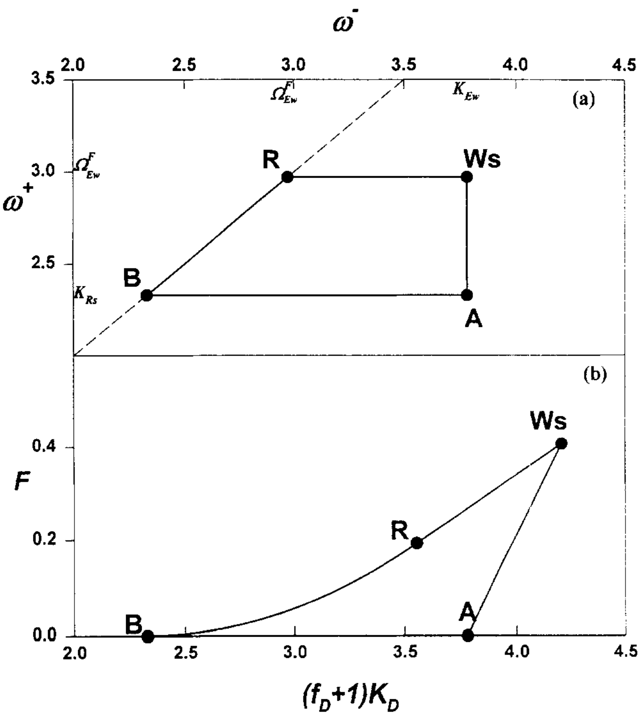

Figure 4. Complete separation regions on ($\omega_3^{\oplus}$, $\omega_3^{\ominus}$) and (f_D^2, F) planes for a strong desorbent case.

For group R, the K_i and y_i^F are 1, 1.11, 2.33 and 0.4, 0.1, 0.25, respectively. For group E, we have $K_{Ew} = 3.78$ and $y_{Ew}^F = 0.25$. $K_D = 5.56$ and $\Omega_{Ew}^F = 2.972$. These are the parameters used in figure 9 of Mazzotti et al. (1994).

Notice that the region boundary on the (f_D, F) plane can be directly calculated from that on the ($\omega^{\oplus}$, $\omega^{\ominus}$) plane. For example, the line Ws-A is obtained with $K_{Rs} < \omega_3^{\oplus} \le \Omega_{Ew}^F$ and $\omega_3^{\ominus} = K_{Ew}$. The line R-Ws is obtained with $\omega_3^{\oplus} = \Omega_{Ew}^F \le \omega_3^{\ominus} \le K_{Ew}$. The curve B-R is obtained with $K_{Rs} < \omega_3^{\oplus} = \omega_3^{\ominus} \le \Omega_{Ew}^F$. At the limit of $\omega_3^{\oplus} \to K_{Rs}$, both $R_1(\omega_3^{\oplus}, \omega_3^{\ominus})$ and $R_2(\omega_3^{\oplus}, \omega_3^{\ominus})$ go to ∞, and we have $f_D \to \omega_3^{\ominus}/K_D - 1$ and $F \to 0$.

The corresponding regions on the (m_2, m_3) plane were given in Figures 5 and 6. To compare our results with that of Mazzotti et al. (1994), the equilibrium constants used in their figures 8 and 9 were taken for our Figures 5 and 6, respectively. The results of our explicit expressions match exactly with their region boundaries found by trial-and-error.

The most important point in these figures is Ws, which corresponds to the optimal operation conditions predicted by the equilibrium theory. Its (m_2, m_3) coordinates can be explicitly given as

$$\left[\frac{R_3(\Omega_{Ew}^F, K_{Ew}) - 1}{R_2(\Omega_{Ew}^F, K_{Ew})}, \frac{R_3(\Omega_{Ew}^F, K_{Ew})}{R_2(\Omega_{Ew}^F, K_{Ew})}\right], \tag{34}$$

where

$$R_3(\omega_3^{\oplus}, \omega_3^{\ominus}) \equiv \frac{\omega_3^{\oplus}\omega_3^{\ominus}}{K_D} \sum_R \frac{y_i^F (K_D - K_i)}{(\omega_3^{\oplus} - K_i)(\omega_3^{\ominus} - K_i)}. \tag{35}$$

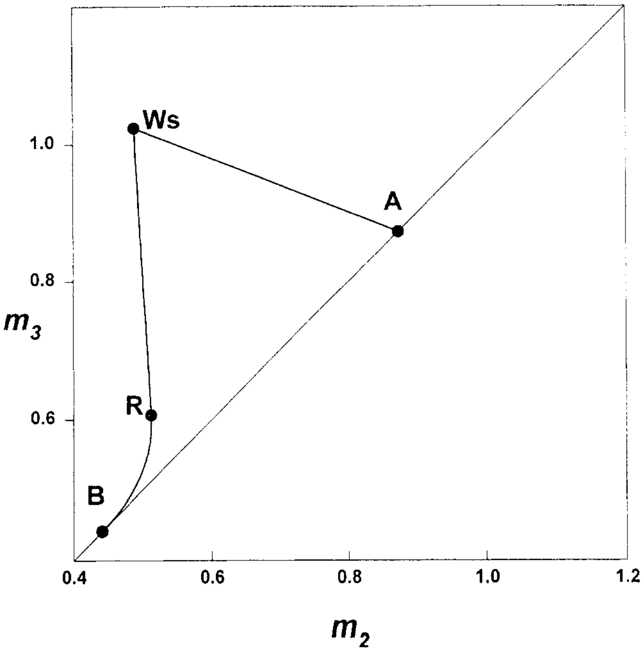

Figure 5. Mapping of the regions in Figure 3 on the (m_2, m_3) plane.

Case 2: Weak or Weak – Intermediate Desorbent. For a weak or a weak–intermediate desorbent, we have $K_D < K_{Rs} = K_{Ew-1}$. For this case, the Ω-criteria are $K_{Rs} < m_2\delta_2 < \Omega^2_{ew} = \Omega^{c'}_{Ew}$ and $K_{Rs} < m_3\delta_3 < \Omega^c_{Ew}$, while the theorem on achievable state requires that $\Omega^F_{Ew} \le \Omega^2_{Ew} \le K_{Ew}$.

According to the new index order, all net fluxes in section 3 should be positive. Therefore, $K_{Rs} < m_3\delta_3$ and $dT^3/d\omega \ge 0$. At the same time, section 2 has both positive net flux f_D and negative net fluxes f^2_E. Therefore, $T^2(\omega)$ has two zeros $\omega^\oplus_2 \le \omega^\ominus_2$ in the interval $[K_D, K_{Ew}]$. One of them is Ω^2_{Rs} and the other $m_2\delta_2$. According to the Ω-criteria, we have $m_2\delta_2 = \omega^\oplus_2$ and $\omega^\ominus_2 = \Omega^2_{Ew}$.

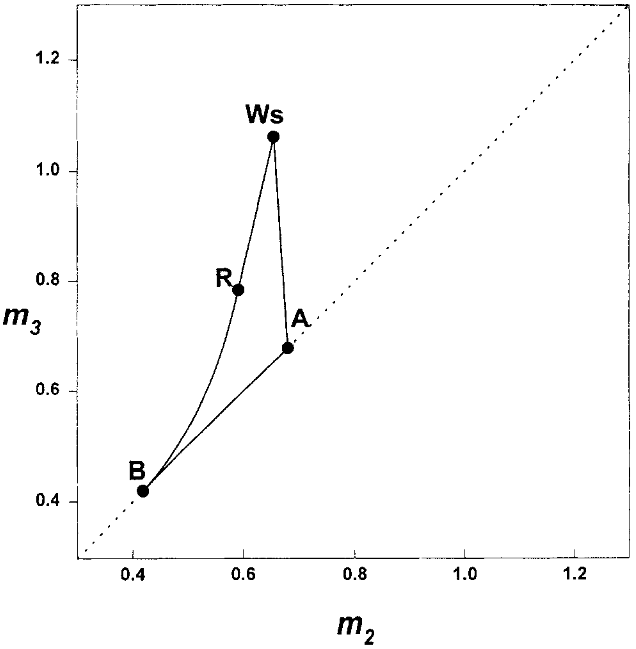

Figure 6. Mapping of the regions in Figure 5 on the (m_2, m_3) plane.

Again we can prove (see Appendix B) that $K_{Rs} < m_3\delta_3 < \Omega^c_{Ew}$ is implied by the necessary flux conditions and the inequalities

$$K_{Rs} \le m_2\delta_2 = \omega^\oplus_2 \le \omega^\ominus_2 = \Omega^2_{Ew} \tag{36}$$

$$\max\{\omega^\oplus_2, \Omega^F_{Ew}\} \le \omega^\ominus_2 = \Omega^2_{Ew} < K_{Ew}. \tag{37}$$

The complete separation region defined by these inequalities can again be mapped to the (f_D, F) plane by Eq. 30 and 31, then to the (m_2, m_3) plane by Eqs. 25.

Case 3: Intermediate Desorbent. The situations are a little more complicated when $K_{Rs} < K_D < K_{Ew}$. The Ω-criteria are $\Omega^3_D < m_2\delta_2 < \Omega^2_{Ew}$ and $\Omega^3_D < m_3\delta_3 < \Omega^c_{Ew}$. The theorem of achievable states requires that $K_{Rs} \le \Omega^j_D \le \min\{\Omega^F_D, K_D\}$ and $\max\{K_D, \Omega^F_{Ew}\} \le \Omega^j_{Ew} \le K_{E\omega}$. Depending on the feed compositions, we may have either $\Omega^F_D = K_D < \Omega^F_{Ew}$, or $\Omega^F_D < \Omega^F_{Ew} = K_D$. At the same time f_D can be positive, negative, or exactly zero.

When $f_D < 0$, all net fluxes in section 2 are negative, while $f^3_R > 0$ and $f_D < 0$ in section 3. The analysis is similar to the strong desorbent case. We have

$$K_{Rs} < \omega^\oplus_3 = \Omega^3_D \le \min\{\omega^\ominus_3, \Omega^F_D\} \tag{38}$$

$$\omega^\oplus_3 \le \omega^\ominus_3 = m_3\delta_3 < K_D, \tag{39}$$

which is enclosed in the region S-B-R-W in Figure 7a.

When $f_D > 0$, all net fluxes in section 3 are positive, thus $K_{Rs} < m_3\delta_3$. At the same time, in section 2, we have $f_D > 0$ but $f^2_E < 0$. By the same analysis as the weak desorbent case, we find

$$K_D < \omega^\oplus_2 = m_2\delta_2 \le \omega^\ominus_2 \tag{40}$$

$$\max\{\omega^\oplus_2, \Omega^F_{Ew}\} \le \omega^\ominus_2 = \Omega^2_{Ew} < K_{Ew}, \tag{41}$$

which is enclosed in the region A-T-S in Figure 7a.

Each of the $\omega^\oplus_3$, $\omega^\ominus_3$ and $\omega^\oplus_2$, $\omega^\ominus_2$ regions in figure 7a can be mapped into a region on the (f_D, F) plane, as shown in Figure 7b. On the (f_D, F) plane, these two regions are connected and share the $f_D = 0$ (or $(f_D + 1)K_D = K_D$) line as a common boundary. The combined (f_D, F) region can then be mapped to the (m_2, m_3) plane, as shown in Figure 8. The parameters used in these figures are the same as that in Figure 7 of Mazzotti et al. (1994). For this case the feed compositions are such that $\Omega^F_D < K_D = \Omega^F_{Ew}$.

Again, the point W in Figure 8 corresponds to the optimal operation conditions predicted by the equilibrium theory. Its coordinates in the (m_2, m_3) plane can be found explicitly as

$$m_2 = 1 + \left[\sum_E y^F_i\right] \Big/ \left[\sum_E \frac{K_i y^F_i}{\Omega^F_* - K_i}\right] \tag{42}$$

$$m_3 = 1 + \left[\sum_R y^F_i\right] \Big/ \left[\sum_R \frac{K_i y^F_i}{\Omega^F_* - K_i}\right], \tag{43}$$

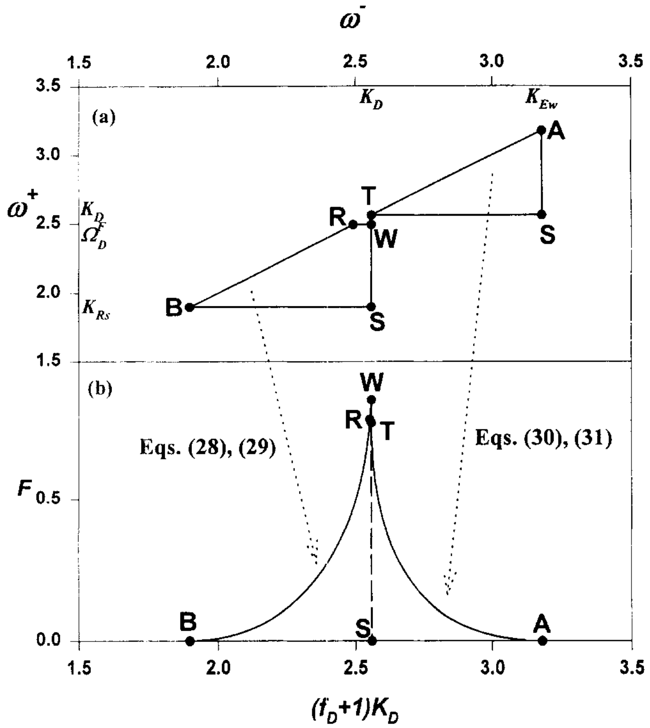

Figure 7. Complete separation regions on $(\omega_3^{\oplus}, \omega_3^{\ominus})$ and (f_D^2, F) planes for an intermediate desorbent case.

For group R, K_i and y_i^F are 1, 1.18, 1.90 and 0.4, 0.1, 0.25, respectively. For group E we have $K_{Ew} = 3.18$, $y_{Ew}^F = 0.25$, $K_D = 2.56$ and $\Omega_D^F = 2.4935$. These are the parameters used in Figure 7 of Mazzotti et al. (1994).

where Ω_*^F is the one between Ω_D^F and Ω_{Ew}^F that is different from K_D.

Note that the point W, calculated by our exact solution, is higher than that suggested by Mazzotti and coworkers. This is because the complete separation region becomes very narrow near this point. It would be very difficult for them to find such a narrow region through trial-and-error.

Discussions

As we have mentioned, the equilibrium theory is a convenient model for predicting the robust and optimal operation conditions for the SMB processes. Now that the tedious numerical procedures have been replaced by explicit expressions, the equilibrium theory will be easier to use.

Let us recapitulate the technique used to derive these explicit expressions. First, new flux functions were defined by applying the ω-transformation to the normalized net fluxes. Several important properties of these functions were also identified.

The flux conditions for achieving complete separation were then taken as the basic requirements. With these requirements, only two unknowns, m_2 and m_3, were left in the flux functions $T^2(\omega)$ and $T^3(\omega)$. These unknowns can be solved if we know the two zeros for $T^2(\omega)$ or for $T^3(\omega)$. The problem of finding the complete separation region on the (m_2, m_3) plane was thus transformed to finding that on the $(\omega^{\oplus}, \omega^{\ominus})$ plane. The complete separation region on the $(\omega^{\oplus}, \omega^{\ominus})$

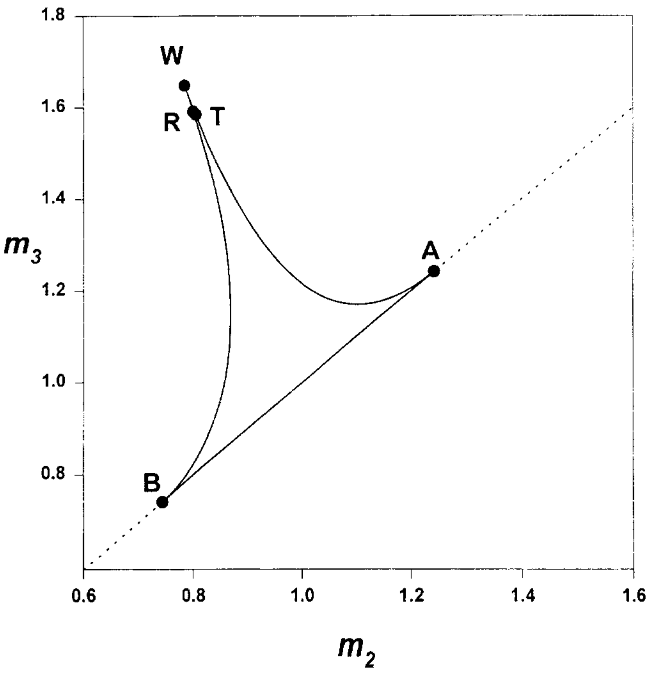

Figure 8. Mapping of the regions in Figure 7 on the (m_2, m_3) plane.

$\omega^{\ominus}$) plane can be obtained, with slight modifications, from the Ω-criteria given by Mazzotti and coworkers (1994).

The procedures just described will also work if there were two kinds of desorbents in the desorbent stream, or if there were more or fewer sections in the TCC unit. It is also possible to extend this approach to finding explicit expressions for regions on the (m_2, m_3) plane that lead to partial separation, as discussed by Storti et al. (1995) and Mazzotti et al. (1996). The extension to systems with nonstoichiometric Langmuir isotherm also seems possible. All these extensions will be discussed in future articles.

The application of the ω-transformation to the normalized equilibrium net fluxes in a TCC adsorption section was an important step in the preceding developments. With this transformation, the material balance equation could be written in the $(m\delta, \Omega)$ space, where the system equations may be easier to solve. This approach could be useful on more occasions than finding the complete separation region of a TCC adsorption unit. For example, the complete dynamic solution of a TCC section could be solved much more easily, as shown in Appendix C. It could even be extended to the steady-state solution of nonequilibrium models if the mass-transfer coefficients were assumed the same for all components.

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Notation

f_i^j = normalized net flux of component i in stream (section) j
F = normalized total flux of the feed stream
L = the length of a TCC adsorption section
t = time

u = superficial fluid-phase velocity
u_s = superficial solid-phase velocity
z = axial coordinate
δ = equilibrium theory parameter, $\delta = \Sigma\, K_i y_i$
ϵ = external void fraction
ϵ_p = intraparticle void fraction
ϵ^* = overall void fraction, $\epsilon^* = \epsilon + \epsilon_p(1-\epsilon)$
Γ^∞ = adsorbed phase saturation capacity
μ = shorthand for $\epsilon_p/[\sigma(1-\epsilon_p)]$
Ω = equilibrium theory parameter defined by Eqs. 4 and 6
ρ_f = fluid-phase density
ρ_s = bulk solid mass density
σ = capacity ratio, $\sigma = \rho_s \Gamma^\infty/\rho_f$
τ = dimensionless time, $\tau = tu_s/L$

Literature Cited

Mazzotti, M., G. Storti, and M. Morbidelli, "Robust Design of Countercurrent Adsorption Separation Processes: 2. Multicomponent Systems," *AIChE J.*, **40**(11), 1825 (1994).

Mazzotti, M., G. Storti, and M. Morbidelli, "Robust Design of Countercurrent Adsorption Separation Processes: 3. Non-Stoichiometric Systems," *AIChE J.*, **42**(10), 2784 (1996).

Mazzotti, M., G. Storti, and M. Morbidelli, "Robust Design of Countercurrent Adsorption Separation Processes: 4. Desorbent in the Feed," *AIChE J.*, **43**(1), 64 (1997).

Rhee, H. K., R. Aris, and N. Amundson, "Multicomponent Adsorption in Continuous Countercurrent Exchangers," *Philos. Trans. Roy. Soc. London*, **A269**, 187 (1971).

Ruthven, D. M., and C. B. Ching, "Countercurrent and Simulated Countercurrent Adsorption Separation Process," *Chem. Eng. Sci.*, **44**(5), 1011 (1989).

Storti, G., M. Masi, S. Carra, and M. Morbidelli, "Optimal Design of Multicomponent Countercurrent Adsorption Separation Processes Involving Nonlinear Equilibria," *Chem. Eng. Sci.*, **44**(6) 1329 (1989).

Storti, G., M. Mazzotti, M. Morbidelli, and S. Carra, "Robust Design of Binary Countercurrent Adsorption Separation Processes," *AIChE J.*, **39**(3), 471 (1993).

Storti, G., R. Baciocchi, M. Mazzotti, and M. Morbidelli, "Design of Optimal Operation Conditions of Simulated Moving Bed Adsorptive Separation Units," *Ind. Eng. Chem. Res.*, **34**, 288 (1995).

Tonkovich, A. L. Y., and R. W. Carr, "Experimental Evaluation of Designs for the Simulated Countercurrent Moving Bed Separator," *AIChE J.*, **42**(3), 683 (1996).

Appendix A

According to the definition, we have $K_i f_i = (m\delta - K_i)\ \theta_i$, thus

$$T(\omega) - 1 = \Sigma\frac{(m\delta - K_i)}{K_i - \omega} = m\delta\Sigma\frac{\theta_i}{K_i - \omega} - \Sigma\theta_i - \omega\Sigma\frac{\theta_i}{K_i - \omega}. \tag{A1}$$

Since $\Sigma\ \theta_i = 1$, we have

$$T(\omega) = (m\delta - \omega)\Sigma\frac{\theta_i}{K_i - \omega}. \tag{A2}$$

Appendix B

According to the necessary flux conditions, all net flux in section 3 is positive. Therefore, $K_{Rs} < m_3\delta_3$ should always be satisified, and we have $dT^3/d\omega > 0$. With two zeros for $T^2(\omega)$ in the same interval, we have $dT^2/d\omega \le 0$ at $\Omega^2_{Ew} = \omega_2^\ominus$. This and $\Omega^F_{Ew} \le \Omega^2_{Ew}$ lead to the conclusion that $T^2(\Omega^F_{Ew}) = T^3(\Omega^F_{Ew}) \ge 0$, which, with $dT^3/d\omega > 0$, gives

$$m_3\delta_3 \le \Omega^F_{Ew} \le \Omega^2_{Ew} = \Omega^{c'}_{Ew}. \tag{B1}$$

Because $H^{c'}(\omega) = H^c(\omega) + H^F(\omega)$, and the H functions have positive slopes, we have the inequality

$$\min\{\Omega^F_{Ew}, \Omega^c_{Ew}\} \le \Omega^{c'}_{Ew} \le \max\{\Omega^F_{Ew}, \Omega^c_{Ew}\}. \tag{B2}$$

Combining this with Eq. B1, we can prove that $m_3\delta_3 \le \Omega^F_{Ew} \le \Omega^{c'}_{Ew} \le \Omega^c_{Ew}$. In other words, $K_{Rs} < m_3\delta_3 < \Omega^c_{Ew}$ is always satisified if the necessary flux conditions and Inequalities 36 and 37 are obeyed.

Appendix C

If we divide the transient material balance equation by $K_i - \omega$ and sum over all components and multiply by the factor $\Pi(K_i - \omega)$, we will obtain

$$\frac{\partial}{\partial\xi}\left[(m\delta - \omega)\prod_{i=2}^{N}(\Omega_i - \omega)\right] - \frac{\partial}{\partial\tau}\left[(-\lambda\delta - \omega)\prod_{i=2}^{N}(\Omega_i - \omega)\right] = 0, \tag{C1}$$

where $\xi \equiv z/L$, $\tau \equiv tu_s/L$, $\lambda \equiv \epsilon^*/[\sigma(1-\epsilon_p)] > 0$ and ϵ^* is the total void fraction.

After expanding the derivatives and substituting Ω_k for ω, we have

$$[m\delta - \Omega_k]\frac{\partial\Omega_k}{\partial\xi} + [\lambda\delta + \Omega_k]\frac{\partial\Omega_k}{\partial\tau} = 0 \tag{C2}$$

or

$$\left.\frac{d\xi}{d\tau}\right|_{\Omega_k} = \frac{m\delta - \Omega_k}{\lambda\delta + \Omega_k}. \tag{C3}$$

This describes the movement of the constant Ω_k characteristic line on the $\xi - \tau$ plane.

If $m\delta > \Omega_k$, then the constant characteristic traces back to the $\xi = 0$ boundary. If $\Omega_k < m\delta$, then the constant characteristic line traces back to the $\xi = 1$ boundary. Thus, all $\Omega_j < m\delta$ were inherited from the left, and all $\Omega_j > m\delta$ were inherited from the right.

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