



## Adsorptive separation of gas mixtures: Mechanistic view, sharp separation and process intensification

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### ABSTRACT

We present here a mechanistic view of adsorption processes for separation of gas mixtures. The moving-bed adsorber (abandoned due to practical difficulties) is shown to offer orders of magnitude higher productivity than the conventional pressure swing adsorption (PSA) and yields 'perfect separation'. To realize its potential in fixed beds, simulated moving bed (SMB) with pressure or thermal swing and 3-bed and 4-bed PSAs that emulate moving-bed adsorbers have been proposed. Based on their characteristics of phase equilibria and separating agents employed, a classification of adsorption processes has been proposed as 'absorption like', 'distillation like' and 'chromatographic' processes, which provides insight into these processes and a rational basis for their design. The mechanism of separation in moving bed, SMB and the conventional PSA are shown to be similar to that of either absorption or distillation. On the other hand, the duplex, molecular-gate and rapid PSAs are shown to share the same separation mechanism that is akin to heat-transfer mechanism in heat regenerators. Subtle but significant differences in the role of 'reflux' in absorption-like and distillation-like processes and their implications in process design have been highlighted. Though process intensification in molecular-gate PSA and duplex PSA is modest compared to the SMB, they appear to hold promise since they are based on a proven technology. Their adaptability for absorption and extraction using immobilized solvent has been presented.

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### 1. Introduction

Skarstrom [1,2] whose work led to the commercialization of pressure swing adsorption (PSA), employed the same PSA cycle for drying of air as well as for fractionation of air, though the adsorption equilibrium characteristics of the mixtures were different. Numerous variants of this cycle were proposed with the same approach to improve the performance of PSA processes. After examining 16 such PSA cycles proposed in the literature on CO<sub>2</sub> capture from flue gas, Reynolds et al. [3] lament, "... it is still not clear why the authors chose the cycles they did and, more importantly, why one PSA cycle outperformed another one. . .". An insight into the separation mechanism and interrelations of adsorption processes among themselves and with other separation processes would provide a rational basis to improve the performance of the existing processes and to devise new ones.

The particulate characteristic of the adsorbent and the use of additional separating agents (mechanical energy, thermal energy, eluent or combination of these) lead to a variety of processes for separating gas as well as liquid mixtures compared to the other

separation processes. These can be classified based on the combination of characteristics of adsorption equilibria (*single component, competing or co-adsorption*), the nature of separation (equilibrium or kinetic controlled), the modes of contact of the phases (*moving-beds, simulated moving-beds, rotating beds, fixed beds and layered beds*), the methods of regeneration (*pressure swing, thermal swing, elution and combination of these*), the types of operation (*steady-state or cyclic*), and the state of feed mixture (*gas or liquid*) lead to a rich variety of processes. Therefore the scope for innovation is high unlike in the case of distillation and absorption.

Separation of a binary mixture of components *A* and *B* into pure components (the perfect separation) is in principle feasible in some adsorption processes. In others, either pure *A* as extract product (perfect enrichment) or pure *B* as raffinate product (perfect cleanup) is feasible. The feasibility of 'sharp separation', which is set arbitrarily in this work if both product purities are greater than 97.5 mol%, is of interest.

Process intensification (PI) is a design philosophy, which aims at reducing the size of equipment by orders of magnitude and the energy requirement for the same production objective. The industrial scale PSA units are bulky. Successful attempts have been made in the development of adsorbents to improve selectivity [4–7]. However PI as an objective has not received much attention in adsorptive gas separation.

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The objectives of this work are:

- To present a mechanistic view that provides insight into different adsorption processes.
- To propose the ways for achieving PI.
- To examine the feasibility of perfect and sharp separations and determine the criteria to achieve them.

We confine our attention mainly to the separation of gas mixtures. However, we have made passing references to the separation of liquid mixtures for the sake of completeness. The kinetic-controlled separation of gas mixtures is out of the scope of this work. For clarity, we restrict the analysis to binary gas mixtures in this work. The extension to multicomponent mixtures is rather involved and is not considered here.

## 2. Classification of adsorption equilibria

Let us consider the adsorption characteristics of a binary mixture of heavy component, *A*, and light component, *B* (for brevity they are referred to as *A* and *B*). Fig. 1a depicts a typical phase diagram of the systems in which only *A* is adsorbed. It is similar to the phase diagrams of the gas–liquid (absorption) equilibria. Fig. 1b shows a phase diagram for co-adsorption of both components, wherein the amount of *A* adsorbed does not influence the amount of *B* adsorbed. This is similar to the absorption of two solutes from an insoluble gas into a solvent, which forms an ideal solution with *A* and *B*. Fig. 1c shows a phase diagram for competing adsorption in which the adsorption of one component affects the other. The diagram is similar to the phase diagrams of the vapor–liquid (distillation) equilibria. The *X*–*Y* diagram contains only partial information and need to be supplemented by the  $Q_T$ – $Y_A$  (Fig. 1d), where  $Q_T$  is the amount of adsorbate per unit mass of adsorbent. The latter is similar to the enthalpy–concentration diagram.

The selectivity,  $S_{AB}$ , defined as

$$S_{AB} = \frac{Y_A X_B}{X_A Y_B}$$

is greater than one. Higher the separation factor, ‘easier’ is the separation. As  $S_{AB} \rightarrow \infty$ , the equilibria tend to the absorption-like equilibria (Fig. 1a). The objective of some of the attempts reported in literature is to increase the selectivity; with an ultimate goal of achieving an absorption-like equilibria. The details can be found elsewhere [4]. The selectivity is also similarly defined for co-adsorption.

## 3. Classification of processes

In those processes, in which single-component adsorption prevails, unidirectional transfer of *A* takes place as in absorption. We refer to them as *absorption-like* processes due to the lack of an appropriate name. These are similar to absorption, stripping, drying, evaporation, and liquid extraction (immiscible systems) in which reflux is not employed [8]. In those processes with competing adsorption, the counter exchange of *A* and *B* prevails as in distillation. These are referred to as *distillation-like* processes. These processes are similar to fractional distillation, fractional extraction, fractional crystallization and foam fractionation, in which reflux is employed at both ends of the separator [8]. In the case of non-competing adsorption of both *A* and *B*, unidirectional transfer of both *A* and *B* takes place and these too can be treated like absorption-like processes.

In the above processes, the adsorbent acts as the separating agent in separation of *A* and *B*. The regeneration of the saturated adsorbent could be accomplished using an energy separating agent

(pressure swing or thermal swing or both) and therefore it is possible to obtain nearly pure *A* and pure *B* as products [9]. Alternately, the regeneration could be accomplished using a non-adsorbing component *C*, referred to as eluent. However, the extract product would be a mixture of *A* and *C*, and the raffinate product would be a mixture *B* and *C*. Such processes where two mass separating agents are used, namely an adsorbent and an eluent, are referred to as chromatographic processes. As the products of chromatographic processes are contaminated with the eluent, two other separation processes are required to separate the eluent from raffinate and extract products to obtain pure *A* and pure *B*.

Notwithstanding the requirement of additional separation processes, chromatographic processes have been commercialized long ago for the separation of liquid mixtures and the well-known examples are the Sorbex™ processes of UOP and increasingly finding applications in pharmaceutical industries [10]. Currently, the chromatographic processes are used commercially for the separation of only liquid mixtures. However, the separations of gas as well as vapor mixtures have been demonstrated [11–17]. These processes are similar to the fractionation of a liquid mixture by extraction using two solvents which are mutually insoluble [18].

Chromatographic processes can be used for both competing and non-competing adsorption of *A* and *B*. However, they are of no use for the single-component adsorption as *B* itself acts as the eluent.

The following sections deal with separation mechanisms in different types of adsorbers.

## 4. Mechanistic view of separation in moving-bed adsorbers

We propose here mechanistic views of separation in moving-bed adsorbers for absorption-like, distillation-like and chromatographic processes. Fig. 2a–c shows the schematic diagrams of the three processes. The flow of solids is downward whereas the gas flow is upward. The separation of *A* and *B* takes place in the shaded blocks. The regeneration of adsorbent takes place in the bottommost blocks (regenerators). The presaturation of adsorbent with raffinate, required in distillation-like and chromatographic processes, takes place in the topmost blocks (presaturators). The adsorbent could be regenerated by thermal swing (as in hypersorbent [19]), by pressure swing [20] or by eluent [21].

Fig. 2a'–c' depicts the mechanistic views of separation at molecular level in those three processes. The different sections of the adsorbers are identified by the broken lines. The gas and adsorbate phases are shown as streams flowing side by side. The streams are depicted by solid circles ‘●’ for molecules of *A* and open circles ‘○’ for *B*. The adsorbent and the eluent (if any) are visualized as carriers of *A* and *B* facilitating exchange of *A* and *B* between the gas and adsorbate phases. The adsorbent and eluent, after their regeneration, are recycled as shown in the figures. The phases are visualized as distinct streams flowing side by side but in opposite directions separated by a gap. The horizontal arrows in the gap between the streams indicate the directions of transfer of molecules of *A* and *B* across the phases. The variations of the width of the streams along the section depict the variation in the flow rates of gas and adsorbate. The separation mechanisms of these three processes are described below.

### 4.1. Absorption-like processes

There are only two sections in the absorption-like process (see Fig. 2a), namely adsorption and regeneration sections. Transfer of *A* takes place from the gas phase to the adsorbate phase. Note the adsorbate flow rate increases as the solids moves down. The unidirectional mass transfer leads to temperature variation along the moving bed, if the feed is rich in *A*. If the adsorbent fed to the section

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