PSA Performance of Densely Packed Adsorbent Beds

Arthur I. Shirley and Alberto I. LaCava
The BOC Group Technical Center, New Providence, NJ 07974

The separation of air by pressure swing adsorption is improved by filling the interparticle voids in kinetically selective adsorbent beds with fine particles of the adsorbent or inert material. The ratio of the average diameter of the coarse adsorbent particles to the average diameter of the fine particles, the size of the fine particles themselves, and the percent of volume of the fine particles in the bed are all critical to optimum PSA performance.

Introduction

Pressure swing adsorption (PSA) is a method used to selectively adsorb certain components of a feed gas mixture, thereby separating and purifying a desired product gas, for example, nitrogen from air. The preferred adsorbent for nitrogen PSA is carbon molecular sieve (CMS), an activated carbon made by depositing carbon into the pores with a pyrolyzing gas during manufacturing (Juntgen et al., 1981). This process is practiced commercially worldwide.

The sieving action of CMS causes oxygen to be more quickly adsorbed than nitrogen. This result is believed to be due to the interactions of the individual gas species with the pore structure of the carbon. The deposited carbon forms apertures called "slits" between the cavities in the carbon structure where adsorption takes place (Nandi and Walker, 1976). The potential energy that a molecule experiences as it passes through a slit determines the rate of adsorption for that molecular species (Rao et al., 1985a,b), such that each gas species will have a different adsorption rate.

Separation based on a large difference in adsorption rates between components of a gas mixture is called a "kinetic" separation. By contrast, a separation based on a difference in adsorption capacities is called an "equilibrium" separation. If the PSA cycle time is much shorter than the longest adsorption "half-time" (the length of time for an adsorbent to adsorb 50% of its capacity for a particular gas species) for any gas component, a kinetic separation can result. If the cycle time is longer, only an equilibrium separation will be possible.

Although PSA techniques have been refined to some degree, PSA still suffers some disadvantages inherent in being a cyclic process. For example, the regeneration step of the PSA cycle serves the desirable function of removing the adsorbed component from the adsorbent, but is also accompanied by an undesirable loss of the nonadsorbed component that is contained in the interparticle void space of the bed. The interparticle voidage of a typical adsorbent bed is about 40% of the total bed volume, resulting in significant losses.

Filling the interstitial space between the adsorbent particle with much smaller particles is one way of reducing the void volume in the bed. Since a greater mass of particles will be packed into the same total volume, the mixture of particles will have a higher packed density than either the large (coarse) or small (fine) component alone. Mixing adsorbent particle sizes has been shown to improve an equilibrium separation (Ma, 1973) or increase the amount of gas that can be stored in a given volume of adsorbent (Greenbank, 1990). As the magnitude of the size ratio of the particles increases, so does the increase in packing density and the improvement in the separation.

For a kinetic separation, however, other factors come into consideration that may negate the benefit of reduced voidage. Reducing the particle size of kinetic adsorbents also may reduce their adsorption half-times. For normal PSA cycles this brings the separation closer to equilibrium, making a kinetic separation more difficult. The same reasoning should also hold true for a mixture of coarse and fine kinetically selective adsorbent since, as the difference in average particle size of the mix increases, a larger variance in adsorption rates will result. One might expect that mixing coarse and fine particles of a kinetically selective adsorbent could adversely affect the separation in some situations.

Correspondence concerning this article should be addressed to A. I. Shirley.

Filling the interstitial spaces between the adsorbent particles with a fine inert (nonadsorbing) material would also reduce void losses, but the inert fines could affect the separation in other ways; in particular, by taking up some space otherwise occupied by CMS.

In this article experimental results on the PSA performance of mixtures of coarse and fine CMS particles are reported. For comparison, experiments were also performed using coarse CMS and an inert filler. Surprisingly, it has been found that there exists a size range of mixtures of particles where air separation is improved over that of the coarse CMS alone. The critical parameters determining which mixtures will have a performance improvement are outlined below.

Experimental Apparatus and Procedure

A PSA system for enriching nitrogen from air generally has two adsorption beds filled with CMS, each being subjected to a series of processing steps in cyclic fashion. In the first step of the cycle, one adsorption bed is pressurized with air while cocurrently producing nitrogen gas, and the other bed is desorbed and regenerated, such as by venting to atmosphere or vacuum. In a second step called pressure equalization, the adsorption beds are placed in fluid communication and brought to an intermediate pressure. In a third step, the first adsorption bed is regenerated, sometimes with a countercurrent flow of product-quality gas (the "purge") to enhance the regeneration, while the second bed is pressurized with air while cocurrently producing nitrogen gas. In the last step of the cycle the beds are again equalized, and the cycle returns to step 1. During each cycle pressures in the beds will typically vary from about 1 to 8 kg/cm^2.

The apparatus for performing the PSA process is shown schematically in Figure 1. Here the valves controlling flow of feed into the system, product withdraw, and waste gas venting from adsorbent beds A and B are numbered 1 through 10. Typical timing and valve positions are shown in Figure 2 for a cycle time of 120 s.

With both coarse and fine particles, the critical size dimension is the weight-averaged diameter. This is equal to the extruded diameter for commercial pellets, while for special or irregularly shaped fines is the geometric average of the screen openings for the upper and lower mesh sizes. These mesh ranges are indicated in the text, tables, and figures as $-XX/+YY$, that is, all particles will pass an XX-mesh U.S. Standard sieve and be retained on a YY-mesh U.S. Standard sieve, where XX and YY are mesh numbers between 20 and 200. For example, a fines cut indicated $-40/+60$ mesh would mean all the fine particles will pass a 40-mesh sieve and be retained on a 60-mesh sieve.

Fine CMS material was comminuted in a kitchen grinder or ball mill from commercial 2.5-mm average diameter CMS pellets of approximately 6-mm length. Different fines cuts were separated on a mechanical sieve shaker. Coarse and fine particles were mixed in a V-blender to assure homogeneity and packed into adsorbent vessels in thin layers to avoid settling of the fines. A compressible packing was added at both ends of the adsorbent beds to prevent movement and segregation of the adsorbent during pressure cycling. Densities were measured for the coarse and fine components as well as their mixtures.

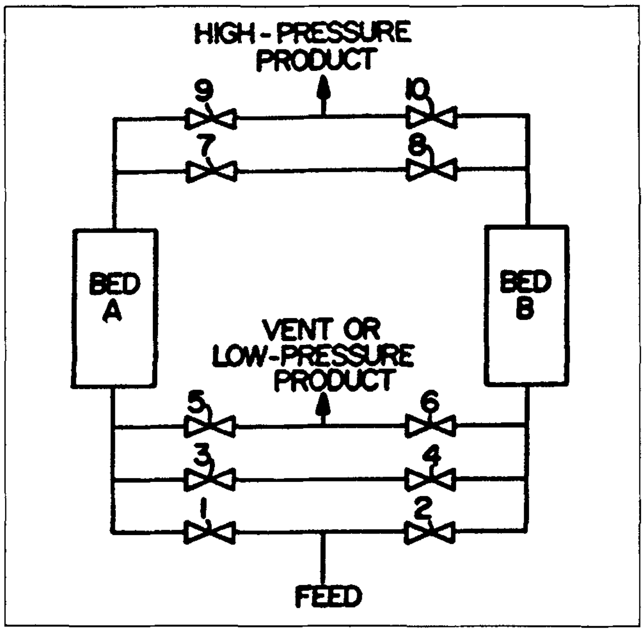

Figure 1. Conventional PSA system comprising two adsorbent beds.

Baseline air separation experiments were conducted using the PSA unit with adsorbers containing only the coarse CMS and a range of cycle times of from 90 to 480 s, according to the cycle shown in Figure 2. Steady-state product purity was set at 1.0% O_2 at a production pressure of 6.6 kg/cm^2·g. For comparison, additional experiments were conducted under the same conditions utilizing a bed packing of about 60% of the commercial CMS material and about 40% of different cuts of ground CMS fines. The ground CMS had particle size ranges of $-40/+60$, $-40/+80$, $-60/+120$ and $-60/+200$ mesh.

For the adsorbent mixtures containing inert fine material, glass blasting beads of roughly spherical shape were used. These were purchased by mesh range and so did not have to be ground or sieved. Bulk densities for the glass beads were approximately 1.5 g/mL for each mesh range. The fine glass beads had particle size ranges of $-30/+40$, $-40/+60$, $-50/+70$, $-40/+80$, $-60/+120$, and $-60/+200$. Because the glass beads were so much heavier than the coarse CMS

		FULL CYCLE SEQUENCE			
VALVE POSITION \ TIME(SEC)		4	56-116	4	56-116
FEED TO BED A	01		▨		
FEED TO BED B	02				▨
BOTTOM BALANCE	03	▨		▨	
BOTTOM BALANCE	04	▨		▨	
BED A VENT	05				▨
BED B VENT	06		▨		
TOP BALANCE A	07	▨		▨	
TOP BALANCE B	08	▨		▨	
PRODUCT FROM BED A	09		▨		
PRODUCT FROM BED B	10				▨

▨ OPEN
☐ CLOSED

Figure 2. Sequence of steps in the PSA cycle using the PSA system shown in Figure 1.

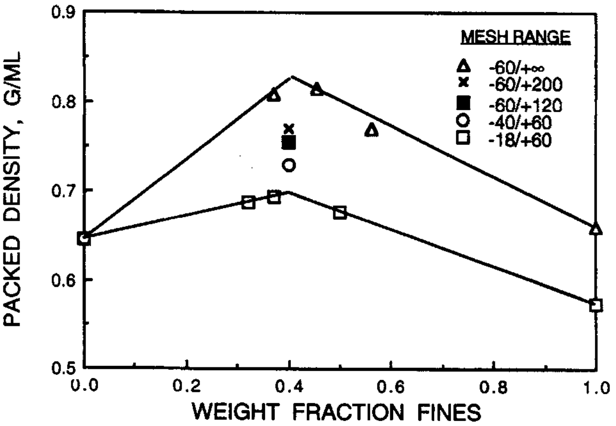

Figure 3. Packed density for mixtures of coarse and fine CMS as a function of the weight percentage of fine CMS in the mixture.

△ = −60/∞; × = −60/+200; ■ = −60/+120; ○ = −40/+60; □ = −18/+60.

pellets they could not be mixed in the V-blender; instead, they were mixed by hand in small batches that were added individually to the adsorbers.

Experimental Results—CMS Fines

The addition of fine particles to a bed of coarse particles will affect the packing density in a manner that is well understood. If there are no segregation effects in the blending process, then the highest packed densities are achieved when the particles are uncorrelated (Williams, 1976). Also, as the particle-size distribution becomes broader, the bed voidage becomes smaller (White and Walton, 1936), leading to higher packed densities.

Figure 3 shows the effect on packed density of mixing various cuts of fine ground CMS with coarse unground pellets. As would be expected, the greatest density increase is found with mixtures containing ~40 wt. % fines. This is close to the theoretical optimum of 37.5% for spherical particles of equal bulk densities (White and Walton, 1936). The fines cuts with the broadest particle-size distributions (such as −60/+∞) give the greatest density increases, in keeping with the expectations. In general, the larger the upper mesh number (the "XX" in −XX/+YY), the greater the density increase; likewise, for a given upper mesh number, the larger the lower mesh number (the "YY" in −XX/+YY), the greater the density increase. The maximum packed density increase by mixing coarse and fine particles is approximately 26%, close to that predicted by theory for mixtures of large and small spheres of equal true densities (Ziolkowski and Michalski, 1992).

During the adsorption tests it was discovered that the fines that would pass a 200-mesh screen caused excessive pressure drop and dust problems in the PSA unit. Fines that were retained on a 40-mesh screen were produced in insufficient quantities for testing. Consequently, no mixtures having fines that would pass a 200-mesh screen or be retained on a 40-mesh screen were used in the PSA experiments.

Although it would be expected from equilibrium PSA theory that decreased bed voidage would lead to increased product throughput and yield, PSA experiments with mixtures of coarse and fine CMS in the optimum ratio have shown that this is true only for a particular range of particle sizes. Figure 4 shows the change in specific product (rate of product-gas production divided by the mass of the adsorbent) and product yield (product-gas rate divided by feed-gas rate) as the packing density increases due to fines addition. Increases in performance are found for densities up to about 0.75 g/mL, while higher densities result in decreasing performance. The higher densities are achieved by the addition of fines that would pass a 60-mesh sieve; consequently, the performance loss may not actually be due to high packing densities, but instead may be due to the adsorption kinetics of the small fines being different from those of the large (unground) particles.

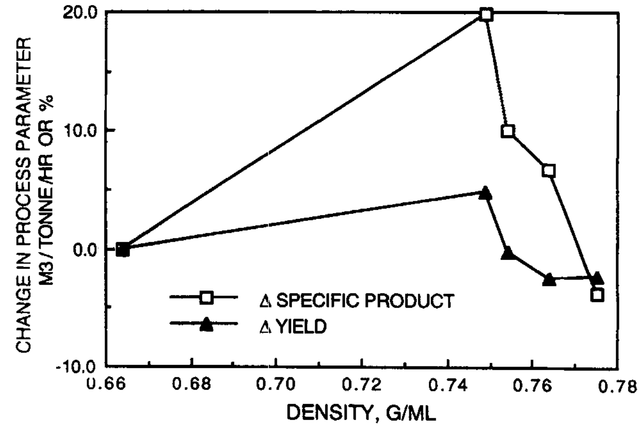

Figure 4. Change in process parameter as a function of packed density.

□ = change in specific product; ▲ = change in yield.

Evidence for this is found in Figure 5. Plotted here are the change in specific product and yield (relative to the baseline unground CMS) for different cycle times between 90 and 480 s using a PSA bed packing of 40% fine material with a mesh range of −40/+60. At a cycle time of 120 s, the specific product rate passes through a maximum; longer cycle times result in decreasing performance. Although any CMS-based

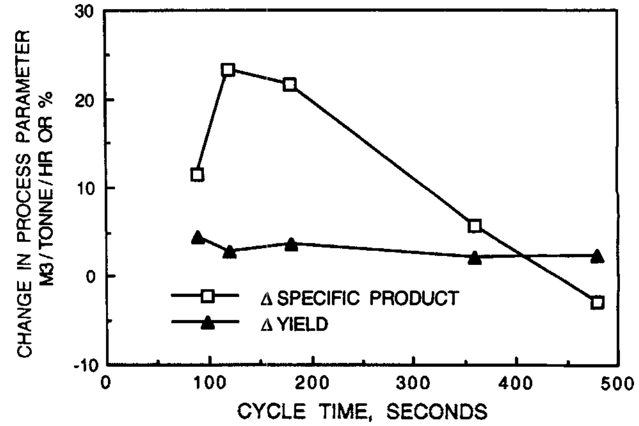

Figure 5. Change in process parameter as a function of PSA cycle time.

□ = change in specific product; ▲ = change in yield.

separation will display an "optimum" cycle time, the optimum for the fines mixture occurs at a shorter cycle time than that for coarse CMS alone.

This behavior is consistent with an increase in the adsorption rates of O_2 and N_2 as the particle size decreases. The increase in adsorption rates could be due to the breakdown of the macrostructure of the carbon as the pellets are ground into smaller particles. Shearing the macropores would open up large areas to adsorption. In the unground CMS admission of gas molecules to these macropores is controlled by small pore throats, but in the ground CMS some of these macropores would now be open and unrestricted. This would cause the uptake rates to increase, such that the CMS fines would lose the ability to separate air as the particle size becomes infinitely small.

As a consequence, the adsorption kinetics become faster for smaller particle (Figure 6), and the differentiation between oxygen and nitrogen by the CMS is reduced. This would explain the loss of specific product with fines having extremely small particle sizes (or large densities) as shown in Figure 4. The fine CMS cannot contribute to the separation of air due to its fast adsorption kinetics, so only the coarse particles are able to produce the product. The amount of product produced per total mass of CMS (both coarse and fine) is therefore reduced.

In the same manner, for a given mixture of coarse and fine particles, it would be expected that as the PSA cycle time increases the improvement in PSA performance by the CMS mix will decrease. The behavior shown in Figure 5 is consistent with this view, as the change in specific product (again for a fines size range of −40/+60) goes through a maximum of around a cycle time of 120 s. At cycle times shorter than 120 s, there may be insufficient time for O_2 adsorption, and so the improvement caused by mixing coarse and fine CMS is not maximized. Above 120 s the cycle time is becoming larger than the N_2 adsorption half-time, meaning that the fine material is not helping in the separation process, so the size of the improvement in specific product becomes smaller, ultimately becoming negative as the kinetics of the fine material becomes much faster than the cycle time.

The effect of the faster kinetics of the fine CMS on the product yield is quite different from their effect on the product rate. As the adsorption half-time for nitrogen decreases, the uptake rate of nitrogen increases, meaning that the overall adsorption rate is increased. For a given cycle time this would mean that more gas per cycle is adsorbed as the half-time decreases. Since the more rapid nitrogen uptake would be expected to decrease the selectivity of the adsorbent, the overall effect would be to decrease the yield for a given amount of purified product recovered (Figure 7).

Experimental Results—Inert Fines

Although replacing the fine CMS material with an inert fine material overcomes the problem of fast adsorption kinetics, it introduces new aspects to the adsorption behavior. The presence of inerts will reduce the number of active adsorption sites per volume, and any difference in true density between coarse and fine material may result in segregation and nonuniform flow. Although the coarse CMS and fine inerts may be initially mixed in a very uniform fashion, subsequent PSA operations may lead to separation of the fractions.

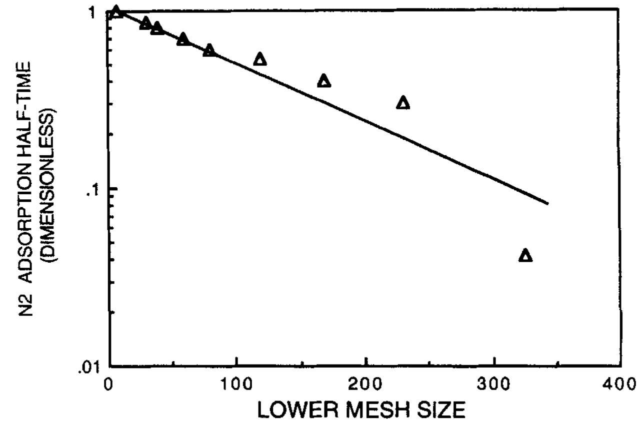

Figure 6. Nitrogen adsorption half-time as a function of the lower mesh size of the fines range.

Figure 8 shows the CMS density (defined as the weight of carbon per total volume of a mixture of CMS and inert fines) as a function of the weight fraction of inerts in the mixture. The two sizes of inert fines, −40/+60 and −50/+70, correspond to mean particle sizes of 300 and 250 μm, respectively, or CMS:fines size ratio (= D/d) of 8 and 10, respectively. White and Walton (1936) computed for packings of cylinders that minimum voidage is achieved by using fines with D/d of at least 6.5. The results of Figure 8 show that the fines are indeed displacing the CMS pellets in the low-weight-fraction range (below 0.4), indicating that random packing or size variation may require that D/d be much larger than 6.5 for efficient packing. Above a weight fraction of 0.4, the initial voidage of the CMS has been completely filled with inert packing, and the CMS density drops toward zero as the amount of fines is increased. The breakpoint of 0.4-weight-fraction inert fines was taken as the upper limit for mixtures in this study.

Although the smaller inert fines give improved packing, they can adversely affect the flow characteristics of the mixture. Flow behavior was measured for mixtures of CMS with various sizes of inert fines, and the resultant pressure gradient-superficial velocity data are plotted in Figure 9. The largest beads, −30/+40 mesh, give a pressure drop of slightly

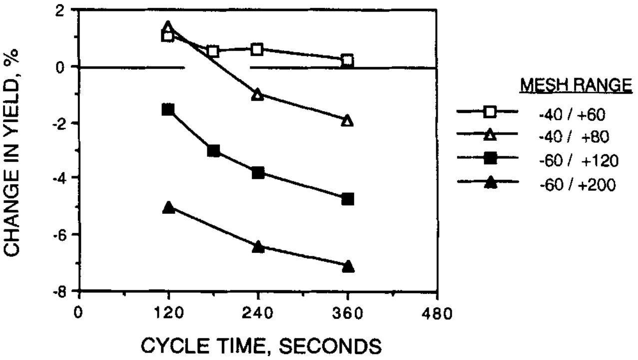

Figure 7. Change in yield as a function of the cycle time of process.

□ = −40/+60; △ = −40/+80; ■ = −60/+120; ▲ = −60/+200.

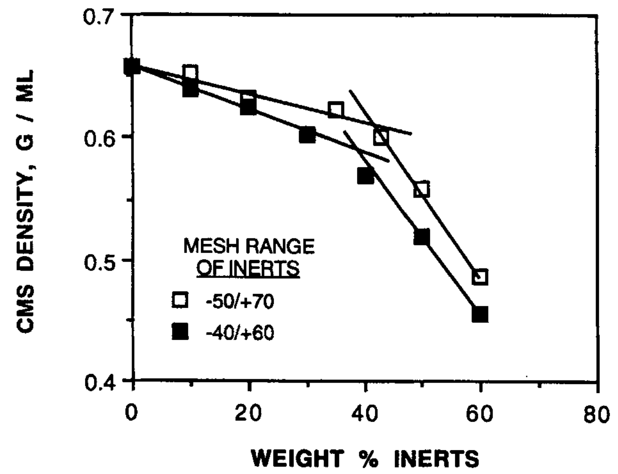

Figure 8. Packed density of CMS for mixtures of coarse CMS and fine inert glass beads as a function of the weight percentage of fine inert glass beads in the mixture.

□ = −50/+70; ■ = −40/+60.

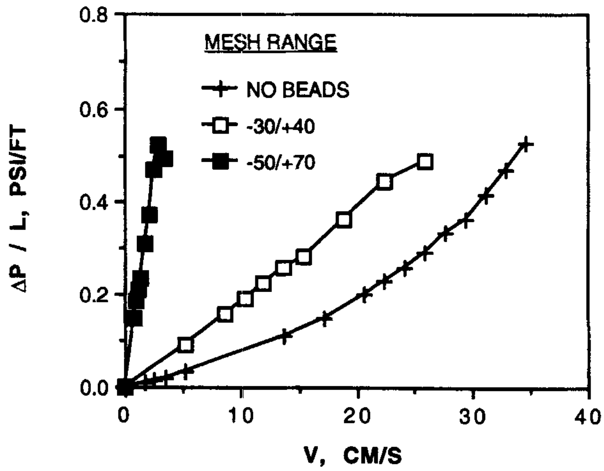

Figure 9. Pressure gradient for mixtures of coarse CMS and fine inert glass beads as a function of the apparent gas velocity.

+ = No beads; □ = −30/+40; ■ = −50/+70.

greater than CMS alone, while a smaller size of beads (−50/+70) gives a very large pressure gradient. This increase in pressure gradient is due, of course, to the smaller void fraction in the mix with the −50/+70 mesh fines as compared to that in the −30/+40 mesh fines. The −30/+40 mesh fines have a *D/d* ratio of only about 5, less than the 6.5 required to pack the fines in the interstitial spaces of the coarse CMS. The −50/+70 mesh fines, on the other hand, pack very nicely in these interstitial spaces, leading to much lower voidages and higher pressure gradients.

The superficial velocity where fluidization occurs, *Vf*, is also affected by the inert fines size. The *Vf* for each mixture shown in Figure 9 is indicated by the highest velocity on each curve, except for the coarse CMS alone, which fluidizes at velocities greater than about 50 cm/s. The −50/+70 beads were found to fluidize at $Vf < 4$ cm/s in the interstitial spaces of the CMS, while the −30/+40 mesh beads would only fluidize as a mixture at about $Vf > 25$ cm/s. The fluidization of bidisperse mixtures has been analyzed in the literature (Ziolkowski and Michalski, 1992), and these results are within the bounds of expected performance.

Fluidization presents a problem in that any vessels designed to contain the fines/CMS mixture must have sufficient transverse area to keep gas velocities below *Vf*. If the fines are fluidized, they will exert a grinding action that reduces the size and effectiveness of the coarse particles, thereby creating a fine dust. Dust is very undesirable in PSA operation both as a product contaminant and because of detrimental effects, for example, plugging of valves, analytical instrumentation, and the like.

Although the smaller beads suffer from fluidization limitations, they are more effective at improving PSA performance. In Figure 10 the smaller beads (−40/+80 and −50/+70) are seen to give an increase in specific product (relative to that of CMS alone) of as much as 9 h^{-1}. The larger beads (−30/+40 and −40/+60) give essentially no change in product rate, however. Presumably this is because any gains in performance due to void reduction are offset by having less CMS per unit volume of adsorbent bed. The yield of product, on the other hand, is improved in all cases of bead size, although the smallest beads give the greatest yield increases (Figure 11). These trends hold true up to about 45–50 wt. % inerts, above which both the specific product and yield drop sharply. This point roughly corresponds to the breakpoint in Figure 7, where increasing wt. % inert fines begin to displace the CMS, leading to lower CMS densities.

In Figure 12, the effect of PSA cycle time on the performance improvement of CMS containing approximately 40% of −40/+80 mesh inert fine material is shown. Here the performance is taken relative to that of the unmixed CMS at the same product purity (1% O_2) and cycle time. When compared with data for the coarse/fine CMS mixture of similar weight fraction and size as shown in Figure 5, there is a strong similarity between the two graphs. In both graphs there appears to be a maximum in specific product at a cycle time

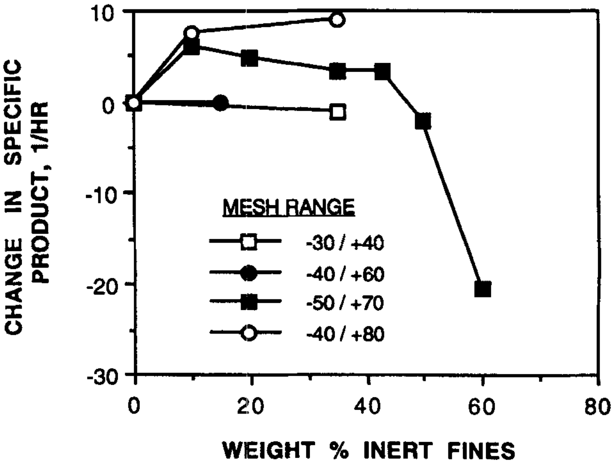

Figure 10. Change in specific product as a function of the weight % fines in the mix.

□ = −30/+40; ● = −40/+60; ■ = −50/+70; ○ = −40/+80.

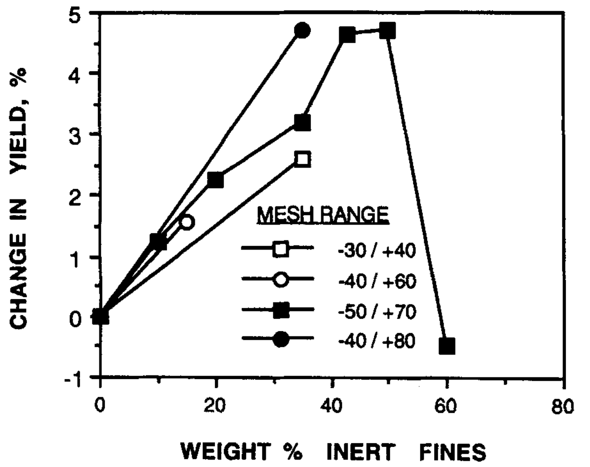

Figure 11. Change in yield as a function of the weight % fines in the mixture.

□ = −30/+40; ○ = −40/+60; ■ = −50/+70; ● = −40/+80.

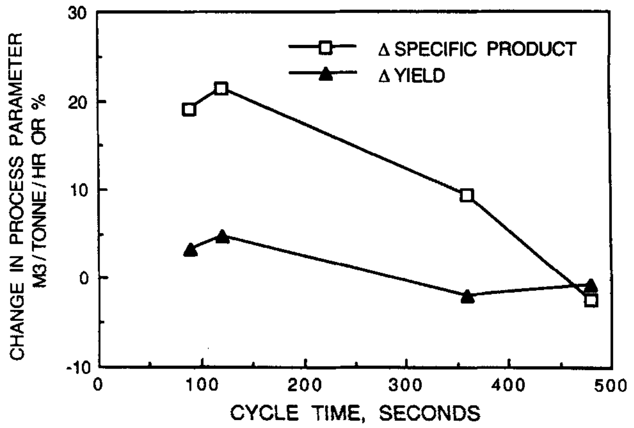

Figure 12. Change in process parameter as a function of PSA cycle time.

□ = change in specific product; ▲ = change in yield.

around 120 s. Likewise the yield parameter tends to be small and to decrease slightly with increasing time. It is true that the coarse/fines CMS mixtures yield a relatively steady 3% to 5% yield increase compared to the coarse CMS alone, while the coarse CMS/inert fines mixtures exhibit a steadily decreasing yield, becoming negative at cycle times above 240 s, but it should be remembered from Figure 6 that most of the coarse/fine CMS mixtures exhibited a decreasing yield with increasing cycle time.

Although it appears from Figure 11 that there is little or no difference between the PSA performance of the mixtures with inert fines and that of the mixtures with CMS fines, there is a distinct difference between the two. The specific product data are reported on a mass-of-CMS basis; consequently, for the same specific product rate the mixtures with CMS fines must produce more product (per unit of mixture volume) than the mixtures with inert fines. This carries over to the yield since, as the yield is the ratio of product rate to feed rate, the mixtures with inert fines adsorb less feed gas (per unit of mixture volume) than the mixtures with CMS fines.

Conclusions

Measurement of PSA performance using mixtures of coarse CMS with either fine CMS or inerts has shown that they can provide an improvement over the PSA performance of coarse CMS alone for a narrow range of fines sizes and PSA cycle times. The difference between the behavior of the mixtures with CMS fines and those of the inert fines lies in their effect on the kinetic separation. The inert fines reduce void gas contamination of the product, leading to higher product rates for short cycle times, while the CMS fines do this as well as contribute to the separation. The smaller the size of the CMS fines, the faster the adsorption kinetics; consequently, there is a decrease in yield as the CMS fine size decreases.

Two aspects of using fine materials in adsorbent packings are the effect of increased pressure drop and the potential for segregation of the coarse and fine components. Although these have been touched upon in the discussion of the experimental results, it is appropriate to comment more about them here. For coarse and fine particles of the same true density, segregation will occur on a size-basis only; by sifting when the diameter ratios are greatly different or by fluidization of the mixture during adsorption cycle operation. For coarse and fine particles of differing true densities the situation is complicated by the gravity settling of the more dense fine particles. This will be aggravated if there is movement of the adsorbent beds during cycling. Care must be taken to choose fine materials nearly matching the true density of the coarse adsorbent; likewise, the adsorbent packing should be constrained to prevent interparticle movement, and pressure and flows should be selected so as to avoid fluidizing the fine material.

Notation

d = diameter of fine particles, mm
D = diameter of coarse particles, mm

Literature Cited

Greenbank, M., "Preparation of a Dense Pack Particulate Gas Adsorbent," U.S. Patent 3,757,490 (Nov. 27, 1990).

Juntgen, H., K. Knoblach, and K. Harder, "Carbon Molecular Sieves: Production from Coal and Application in Gas Separation," *Fuel*, **60**, 817 (1981).

Ma, J. C. N., "Chromatographic Adsorbents," U.S. Patent 3,757,490 (Sept. 11, 1973).

Nandi, S. P., and P. L. Walker, "Separation of Oxygen and Nitrogen Using 5A Zeolite and Carbon Molecular Sieves," *Sep. Sci.*, **11**, 441 (1976).

Rao, M. B., R. G. Jenkins, and W. A. Steele, "Potential Functions for Diffusive Motion in Carbon Molecular Sieves," *Langmuir*, **1**, 137 (1985a).

Rao, M. B., R. G. Jenkins, and W. A. Steele, in *Proc. 17th Biennial Conference on Carbon, Extended Abstracts and Program*, Lexington, KY, p. 114 (June 16–21, 1985).

White, H. E., and S. F. Walton, "Particle Packing and Particle Shape," Amer. Cer. Soc. Meeting, Columbus, OH (Apr. 1, 1936).

Williams, J. C., *Powder Tech.*, **15**, 245 (1976).

Ziolkowski, D., and J. Michalski, "Onset of Fluidization in an Organized System Within Voids of Packings Formed by Spherical Elements," *Chem. Eng. Sci.*, **47**, 4007 (1992).

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