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Purification of Hydrogen by Pressure Swing Adsorption

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ABSTRACT

Pressure swing adsorption (PSA) processes are used for the production of high purity hydrogen from steam methane reforming off-gas (SMROG) and refinery off-gases (ROG). A variety of commercial PSA processes for the production of H₂ with or without a by-product (CO₂ from SMROG), as well as PSA processes for direct production of ammonia synthesis gas (from SMROG), are reviewed. The equilibrium ad(de)sorption characteristics of the components of SMROG and ROG feed gas on an activated carbon, a zeolite, and a silica gel are reported, and the criteria for adsorbent selection in these PSA processes are discussed. Recent ideas to increase the H₂ recovery from these PSA processes by integrating them with selective surface flow membranes or other PSA units are reviewed.

INTRODUCTION

Production of pure hydrogen from a gas mixture containing 60–90 mol% hydrogen by using pressure swing adsorption (PSA) processes has become the state-of-the-art technology in the chemical and petrochemical industries. Several hundred PSA–H₂ process units have been installed around the world. The two most common gas streams used for this application are (a) the steam-methane reformer off-gas (SMROG) after it has been further treated in a water-gas shift reactor, and (b) the refinery off-gas (ROG) from various sources. The typical feed gas compositions to the PSA system for these cases are (a) 70–80% H₂, 15–25% CO₂, 3–6% CH₄, 1–3% CO, and

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trace N_2 ; and (b) 65–90% H_2 , 3–20% CH_4 , 4–8% C_2H_6 , 1–3% C_3H_8 , and less than 0.5% C_4+ hydrocarbons. Both feed gases are generally available at a pressure of 8 to 28 atm (1 atm = 101.3 kPa) and at a temperature of 21 to 38°C (70–100°F), and they are generally saturated with water. The PSA processes are designed to produce a dry hydrogen-rich product stream at the feed gas pressure containing 98–99.999 mol% H_2 with a H_2 recovery of 70–90%. A waste gas stream containing the unrecovered H_2 and all of the impurities of the feed gas is also produced at a pressure of 1.1 to 1.7 atm. Several specially designed PSA processes simultaneously produce a secondary product stream containing 99+ mol% CO_2 at a near ambient pressure when the SMROG is used as the feed gas. Other PSA processes are designed to directly produce an ammonia synthesis gas containing a N_2 – H_2 mixture in a mole ratio of 1:3 from the SMROG feed gas with or without a by-product stream of CO_2 .

The research and development activities in this field have been very extensive during the last thirty years. Figure 1 shows the year-by-year breakdown of the number of US patents issued on H_2 -PSA processes between 1978 and 1998 (1). A total of 177 basic patents were granted to 65 corporations around the world. The research goals consisted of developing new H_2 -PSA processes for (a) increasing the primary and secondary product recoveries while maintaining their high purities, and (b) reducing the adsorbent inventory and the associated hardware costs. A considerable effort was also made to develop new adsorbents or to modify existing adsorbents in order to achieve these research goals. It became a common practice to use more than one type of adsorbents in these PSA processes (as layers in the same adsorbent vessel or as single ad-

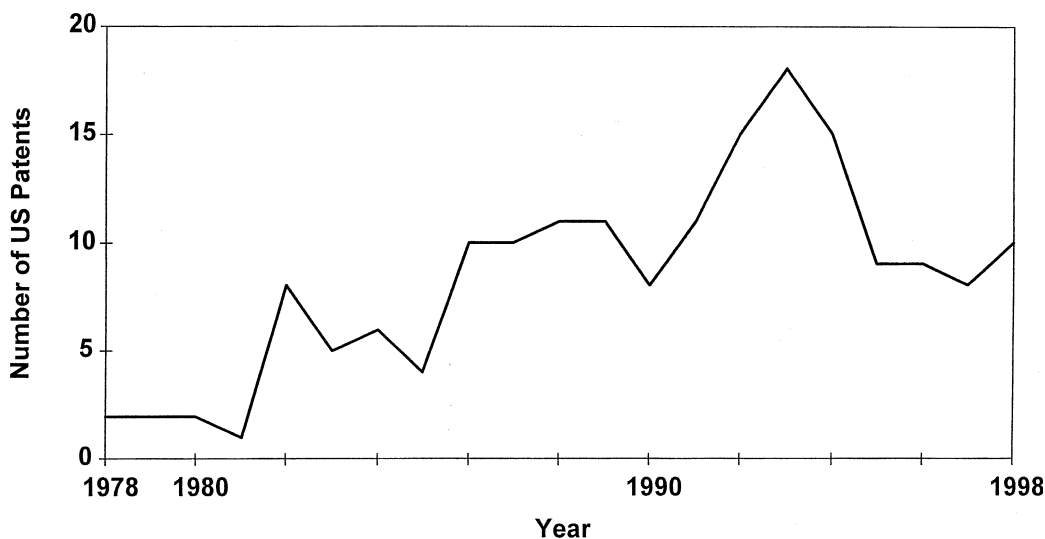


FIG. 1 Survey of US patents.



sorbents in different vessels) in order to obtain optimum adsorption capacity and selectivity for the feed gas impurities while reducing the coadsorption of H_2 , as well as for their efficient desorption under the operating conditions of the PSA processes.

The purpose of this paper is to (a) review several key commercial H_2 -PSA processes and compare their separation performances, (b) describe the adsorption characteristics of key adsorbents used in these processes, and (c) summarize the recent research efforts to improve hydrogen recovery by these processes.

PSA PROCESSES FOR PRODUCTION OF HYDROGEN ONLY

The most frequently used PSA process concept in this area is patented by Union Carbide Corporation of U.S.A. (2). One version of this process consists of 11 cyclic steps as follows:

- (a) *Adsorption*: The feed gas is passed at pressure P^F through an adsorber and an essentially pure H_2 stream is produced through the product end at the feed gas pressure. A part of this gas is withdrawn as the primary H_2 -product stream. The step is stopped when the impurity mass transfer zones are somewhere in the middle of the adsorber and the rest of the adsorber is essentially clean.
- (b) *Cocurrent Depressurization I*: The adsorber is then cocurrently depressurized to a pressure level of P_1 . An essentially pure H_2 stream is again produced through the product end which is used to pressurize a companion adsorber undergoing Step (h).
- (c) *Cocurrent Depressurization II*: The adsorber is further depressurized cocurrently to a pressure level of P_2 . The effluent gas through the product end is again a high purity H_2 stream which is used to pressurize another companion adsorber undergoing Step (g).
- (d) *Cocurrent Depressurization III*: The adsorber is again depressurized cocurrently to a pressure level of P_3 . The effluent gas through the product end is still a high purity H_2 stream which is used to countercurrently purge another companion adsorber undergoing Step (f).
- (e) *Countercurrent Depressurization*: The adsorber is then countercurrently depressurized to the lowest pressure level of the cycle (P^D). The effluent gas from this step, which contains a part of the desorbed gases and most of the column void gases, is wasted.
- (f) *Countercurrent Purge*: The adsorber is then countercurrently purged with a gas stream of essentially pure H_2 at pressure P^D obtained from a companion column undergoing Step (d). The effluent gas from this step contains the remaining part of the desorbed impurities and it is wasted.



- (g) *Countercurrent Pressurization I*: The adsorber is then pressurized from pressure P^D to P_2 by countercurrently introducing the gas produced by a companion column undergoing Step (c).
- (h) *Countercurrent Pressurization II*: The adsorber is further pressurized from P_2 to P_1 by countercurrently introducing the effluent gas from Step (b).
- (i) *Countercurrent Pressurization III*: Finally, the adsorber is countercurrently pressurized from P_1 to P^F with a part of the H_2 product gas produced by a companion column undergoing Step (a). The adsorber is now ready to start a new cycle.

Other modifications to the above described PSA cycle with only two cocurrent depressurization steps (which produce the high purity H_2 effluent gases for only one countercurrent pressurization step and the countercurrent purge step) are also practiced (3). Typically, a multicolumn PSA unit containing 4 to 12 parallel columns is used to accommodate these steps. Several adsorbers can be simultaneously receiving the feed gas mixture (Step a) when the H_2 production capacity is very large. Figure 2 is a schematic flow sheet for a 10-column PSA process using the 11-step process. This process is generally known as the Polybed process.

The most distinguishing features of the Polybed process consist of (i) stopping the adsorption Step (a) while a substantial adsorption capacity for the feed gas impurities remain unused near the product end of the adsorber and then (ii) carrying out the series of cocurrent depressurization Steps (b)–(d). The feedlike void gas from the section of the column which holds the feed im-

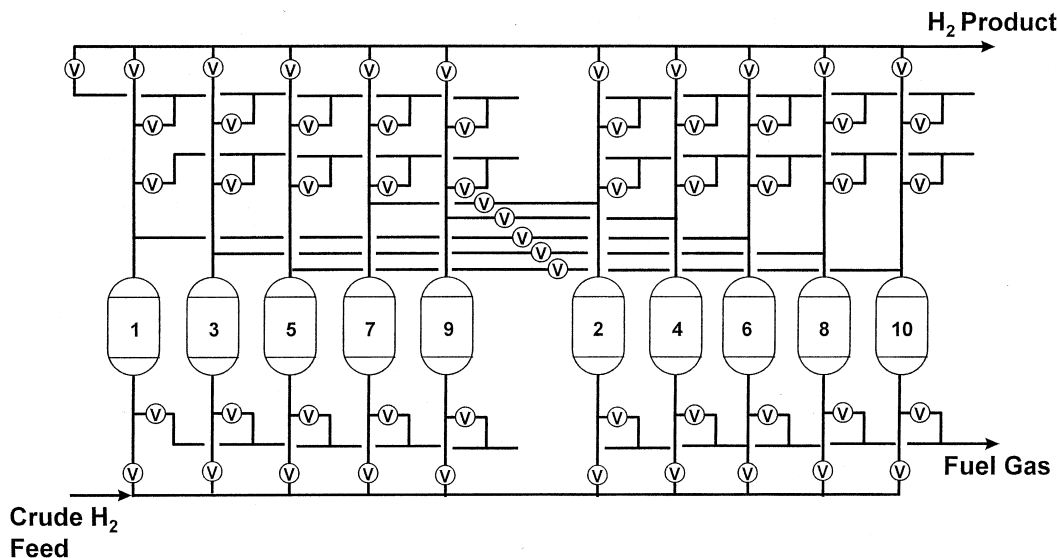


FIG. 2 Schematic flow diagram for the Polybed PSA process.



purities at the end of Step (a) expands toward the product end during Steps (b)–(d), and the impurities are adsorbed in the clean section of the column. Consequently, high purity H₂ streams at different pressure levels are produced from the column during these steps which are used to countercurrently purge (Step f) and pressurize (Steps g and h) other companion columns. These sequences of steps extract valuable H₂ from the column void gas at the end of Step (a) as pure H₂ and use it efficiently for impurity desorption and partial pressurization steps. The net result is higher H₂ recovery from the feed gas. This is, however, done at the cost of increased adsorbent inventory per unit amount of feed processed because the entire adsorber is not used to process the feed gas in Step (a).

A polybed system consisting of 10 parallel columns, each containing a layer of activated carbon in the feed end and a layer of 5A zeolite in the product end, could process a SMROG (77.1% H₂, 22.5% CO₂, 0.35% CO, and 0.013% CH₄) at 20.7 atm and 21°C to produce a 99.999% pure H₂ product at near the feed gas pressure with a H₂ recovery of 86.0% (2). The lowest desorption pressure (P^D) for the process was 1 atm, and the composition of the waste gas was 32.0% H₂, 66.8% CO₂, 1.0% CO, and 0.04% CH₄. The volume fractions of the carbon and the zeolite layers in the adsorbers were 0.762 and 0.238, respectively. The total cycle time (11 steps) used was 13.33 minutes, and the feed processing capacity for the process was 34.9 ft³ of feed gas (1 atm, 15°C)/ft³ of total adsorbent in the system/cycle.

A very interesting variation of the above described process is patented by Toyo Engineering Corporation of Japan (4). It consists of nine sequential steps as follows:

- (a) *Adsorption*: This step is identical to Step (a) of the Polybed process. It produces a high purity H₂ stream at feed gas pressure (P^F), a part of which is withdrawn as the primary H₂ product.
- (b) *Cocurrent Depressurization I*: This step is identical to Step (b) of the Polybed process. The column pressure at the end of this step is P_1 and the effluent gas is high purity H₂ which is used to pressurize a companion column undergoing Step (h).
- (c) *Cocurrent Depressurization II*: The effluent gas from this step is initially high pressure H₂ but the step is continued until some of the less strongly adsorbed impurities from the feed gas break through the product end. The column pressure at the end of this step is P_2 . The entire effluent gas from Step (c) is stored in a separate tank packed with non-porous inert solids. As this effluent gas enters the storage tank, it displaces the previously stored gas from the tank [received from another column which underwent Step (c)]. The previously stored gas leaves the tank through the same end which was used to introduce the gas into the tank. Thus, the effluent gas from the tank during this step initially



contains a H_2 stream containing some impurities of the feed gas followed by an essentially pure H_2 stream. This gas is used to purge a column countercurrently at pressure P^D for removal of the adsorbed impurities. Thus, the gas is introduced into the tank through one end during Step (c) for one cycle and then through the other end for the next cycle and so on.

- (d) *Cocurrent Depressurization III*: The column is then further depressurized cocurrently to a pressure of P_3 and the effluent gas is used to pressurize a companion column undergoing Step (g).
- (e) *Countercurrent Depressurization*: The column is depressurized to a pressure of P^D . The effluent gas forms a part of the waste gas from this process.
- (f) *Countercurrent Purge*: The column is purged with the effluent gas from the storage tank at pressure P^D . The column effluent is wasted.
- (g) *Countercurrent Pressurization I*: The column is pressurized to pressure P_3 using the effluent gas from a companion column undergoing Step (d).
- (h) *Countercurrent Pressurization II*: The column is pressurized to a pressure level of P_1 by introducing the effluent from a companion column undergoing Step (b).
- (i) *Countercurrent Pressurization III*: The column is finally pressurized to P^F by using a part of the H_2 product being produced by a companion column undergoing Step (a).

The distinguishing feature of this process is described by Step (c). The countercurrent purge gas is produced by allowing some impurities to break through the column (substantially increases purge gas quantity) but the purge efficiency is maintained by reversing the order of flow of this gas into the column being purged. This process is thus called the Lofin process (last out, first in). The use of a larger quantity of purge gas, partly with slightly impure H_2 , increases the overall H_2 recovery by the process and reduces the adsorbent inventory (5).

Figure 3 is a schematic process diagram for the Lofin process using four parallel adsorbers and a gas storage tank. It could produce a 99.96% H_2 product at feed gas pressure from a ROG containing 78.8% H_2 , 15.3% CH_4 , 4.0% C_2H_6 , 1.4% C_3H_8 , 0.3% C_4H_{10} , and 0.1% C_5H_{12} (dry basis) at a pressure of 28 atm and $15^\circ C$ with a H_2 recovery of 86.3% (4). The adsorbers were packed with a layer of silica gel (25%) near the feed end and a layer of activated carbon (75%) near the product end. The total cycle time (9 steps) for the process was 30.0 minutes, and the feed processing capacity for the process was 153.0 ft^3 of feed gas/ ft^3 of total adsorbent in the system/cycle. A waste gas containing 33.8% H_2 , 47.9% CH_4 , 12.5% C_2H_6 , 4.4% C_3H_8 , and 1.25 C_4+ hydrocarbons was produced at a pressure of 1.3 atm.



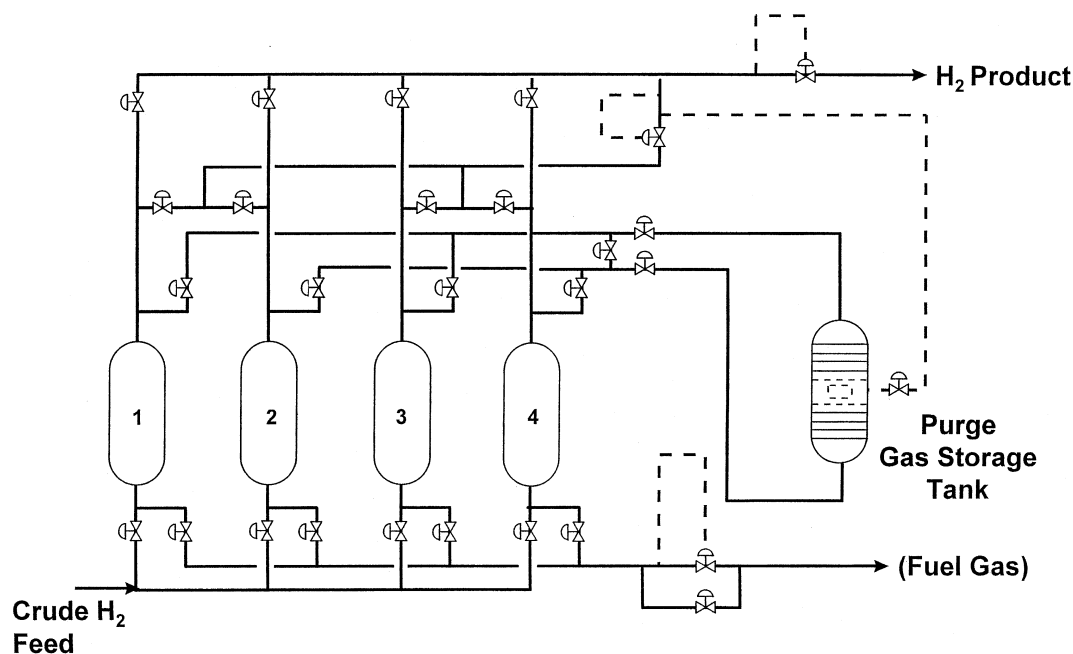


FIG. 3 Schematic flow diagram for the Lofin PSA process.

PSA PROCESS FOR SIMULTANEOUS PRODUCTION OF HYDROGEN AND CARBON DIOXIDE

A specially designed PSA process for the simultaneous production of pure H_2 and CO_2 from the SMROG was patented by Air Products and Chemicals of U.S.A. (6). Figure 4 shows a schematic flow diagram for the process. It consists of six parallel adsorbers (called A beds) in series connection with three other parallel adsorbers (called B beds). The A and B beds undergo the following six- and seven-step cycles, respectively.

Cycle Steps for A Beds

- (a) *Adsorption*: The SMROG is passed through a train of A and B beds in series and a stream of pure H_2 at feed pressure (P^F) is produced through the product end of the B bed. A part of this gas is withdrawn as the primary H_2 product.
- (b) *Cocurrent CO_2 Rinse*: The A and B beds are then disconnected and a stream of essentially pure CO_2 at feed gas pressure is cocurrently passed through the A bed. The effluent gas from the A bed is recycled as feed gas to another A bed. The A bed is saturated with CO_2 at the end of this step.



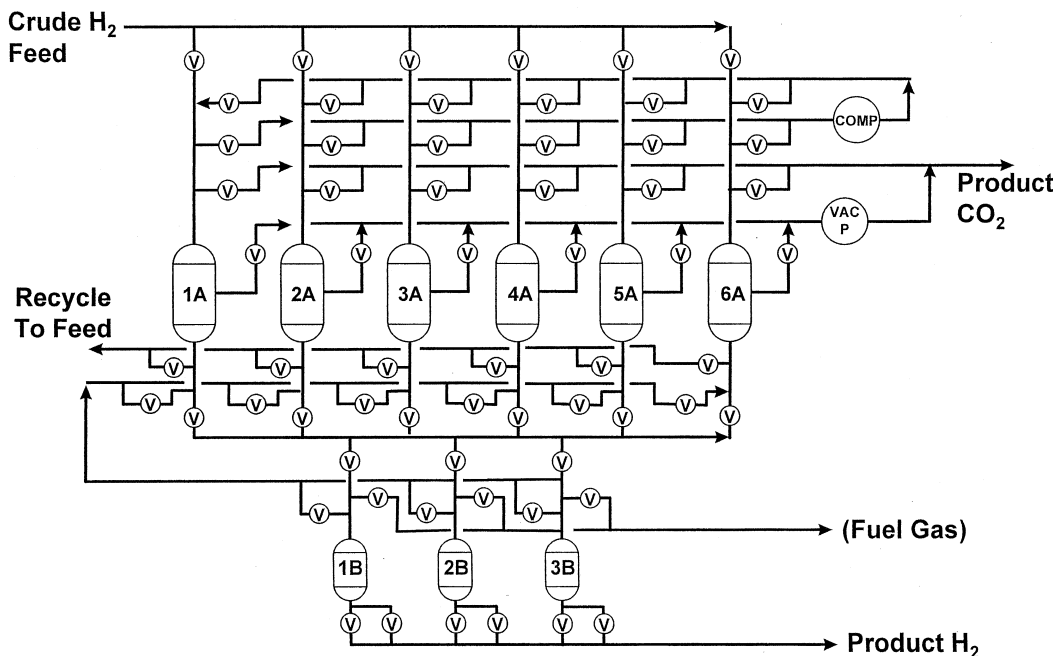


FIG. 4 Schematic flow diagram for the Gemini PSA process.

- (c) *Countercurrent Depressurization*: The A bed is then depressurized to a near ambient pressure level. The effluent gas is pure CO₂. A part of this gas is recompressed to P^F and used as CO₂ rinse gas to a companion A bed. The balance is withdrawn as the secondary CO₂ product.
- (d) *Countercurrent Evacuation*: The A bed is then evacuated to the lowest subatmospheric pressure level of the cycle (P^D). The effluent is again pure CO₂ which is withdrawn as the secondary product.
- (e) *Countercurrent Pressurization I*: The column is then pressure equalized to a pressure level of P_1 with a B bed which has just finished its adsorption Step (a).
- (f) *Countercurrent Pressurization II*: The A bed is finally repressurized with a part of the H₂-rich gas produced by an A-B tandem in series undergoing Step (a) by introducing the gas to the A bed through a companion B bed in series.

Cycle Steps for B Beds

- (a) *Adsorption*: The B bed is connected with an A bed in series undergoing Step (a).
- (b) *Countercurrent Depressurization I*: The B bed is connected with an A bed which has just finished Step (d) in order to pressure equalize the two beds.



- (c) *Countercurrent Depressurization II*: The B bed is connected with another B bed which has completed Step (f) in order to pressure equalize those beds.
- (d) *Countercurrent Depressurization III*: The B bed is depressurized to near ambient pressure level and the effluent gas is wasted.
- (e) *Countercurrent Purge*: The B bed is purged with essentially pure H₂ obtained from another B bed undergoing Step (a). The effluent is wasted.
- (f) *Cocurrent Pressurization*: The B bed is then connected with another B bed undergoing Step (c) in order to pressure equalize the two beds.
- (g) *Countercurrent Pressurization*: The B bed is finally pressurized to P^F by introducing a part of H₂-rich gas produced by another B bed undergoing Step (a). The B bed is connected with an A bed undergoing Step (f) during this step.

The A beds are packed with activated carbons which selectively remove CO₂ and H₂O from the SMROG. The B beds are packed with zeolites for selective removal of the remaining CO₂, CH₄, CO and N₂ from H₂. The process is designed in such a fashion that very little CO₂ breaks through the A beds during Step (a).

The most distinguishing features of this process are (i) cocurrent CO₂ rinse at feed pressure, (ii) separation of A and B beds during column regeneration steps, (iii) use of different regeneration methods for A (depressurization and evacuation) and B (depressurization and purge) beds, and (iv) pressure equalization between A and B and B and B beds to conserve the void gases. These features permit production of two pure products (CO₂ and H₂) from SMROG with high recoveries of both components. The process, however, requires rotating machinery (vacuum pumps and CO₂ recycle compressor) for its operation.

The process is called Gemini because of its ability to produce two products from a multicomponent feed gas. It simultaneously produced a primary H₂ product at a purity of 99.999% with a H₂ recovery of 87.1% and a secondary CO₂ product at a purity of 99.4% with a CO₂ recovery of 94.0% from a SMROG feed gas containing 75.4% H₂, 19.9% CO₂, 0.96% CO, and 3.73% CH₄ at a pressure of 18 atm at 21°C (7). The H₂ product was produced at the feed gas pressure and the CO₂ product was produced at ambient pressure. The final evacuation level in Step (d) of A beds was 0.13–0.20 atm. The waste gas was produced at near ambient pressure and consisted of 8.1% CO₂, 5.6% CO, 20.8% CH₄, and 65.4% H₂. The absence of large amounts of CO₂ in the waste gas of the Gemini process compared to those for the Polybed and the Lofin processes makes it a fuel gas with a higher calorific value. More detailed information about the operation and performance of this process can be found elsewhere (7).



PSA PROCESSES FOR PRODUCTION OF AMMONIA SYNTHESIS GAS

A very important modification of the Polybed and Gemini process cycles described above can be used to produce an ammonia synthesis gas (a N_2 and H_2 mixture in the molar ratio of 1:3) directly from SMROG as feed to the PSA systems.

For the case of the Polybed process this is achieved by using N_2 from an external source to countercurrently purge (Step f) and pressurize the adsorbers (Step i). This introduces weakly adsorbing N_2 into the adsorbers before the adsorption Step (a) begins. This N_2 is expelled from the adsorber in conjunction with H_2 from the feed gas as the effluent stream during Step (a) of the polybed system (8).

For the Gemini process the ammonia synthesis gas can be produced as the effluent gas from Step (a) by (i) carrying out the final countercurrent repressurization (Step f) of the A beds by introducing N_2 from an external source, (ii) eliminating Steps (c) and (f) for the B beds, and (iii) countercurrently purging (Step e) and repressurizing (Step g) the B beds with an external source of N_2 (9, 10). The A and B beds remain disconnected during Step (g) in this case. Thus, the modified Gemini process simultaneously produces an ammonia synthesis gas stream at feed gas pressure and a by-product CO_2 stream. Only four A beds and two B beds are needed to operate the modified cycle (10). The A beds are again filled with an activated carbon and the B beds are filled with a zeolite. A H_2 recovery of 95% in the ammonia synthesis gas and a by-product CO_2 recovery of 94% at a CO_2 purity of 99.4% can be achieved by this process using SMROG feed gas (same composition as that for the Gemini process) at a pressure of 18 atm at 21°C. The ammonia synthesis gas is free of carbon oxides. About 75% of the N_2 used in pressurizing and purging the A and B beds is recovered in the ammonia synthesis gas (9, 10). The waste gas has a composition of 6.9% CO_2 , 5.5% CO, 21.3% CH_4 , 45.7% N_2 , and 20.6% H_2 . The process is especially attractive for urea production by reacting NH_3 and CO_2 .

The above examples demonstrate the variety and flexibility of PSA processes designed for purification of H_2 from a bulk feed gas containing 70 to 90% H_2 . All of these processes are designed to meet certain product specifications and to increase the product recoveries at high purities.

ADSORBENTS FOR HYDROGEN PSA PROCESSES

The selection of adsorbents is critical for determining the separation performance of the above described PSA processes for hydrogen purification. The separation of the feed gas impurities from hydrogen by the adsorbents used in these processes is generally based on their thermodynamic properties.



The kinetics of adsorption is not a critical issue. Thus, the multicomponent adsorption equilibrium capacities and selectivities, the multicomponent isosteric heats of adsorption, and the multicomponent equilibrium-controlled desorption of the feed gas impurities under the conditions of operation of the ad(de)sorption steps of the PSA processes dominate the adsorbent selection.

Figures 5 and 6 show the pure gas adsorption isotherms of the components of SMROG at 30°C on the BPL activated carbon (Calgon Corp.) and the 5A zeolite (UOP Corp.), respectively. The amounts adsorbed are given in milligram moles per gram of the adsorbents. Table 1 shows the Henry's law selectivities (at the limit of zero pressure) of the binary pairs of the SMROG components at 30°C on the same adsorbents (11). These data were measured in a laboratory using a conventional volumetric adsorption apparatus (12).

CO₂, which has a large permanent quadrupole moment, is very strongly and selectively adsorbed on the zeolite with a very large adsorption capacity at low partial pressures of CO₂. However, it is also very difficult to desorb the CO₂ from the zeolite under the conditions of operation of the PSA processes. Figure 7 shows the isothermal desorption characteristics of CO₂ by H₂-purge from the BPL carbon and the 5A zeolite. It plots the fraction of CO₂ originally present in a column packed with the adsorbent that is desorbed by H₂ purge as a function of the amount of H₂ leaving the column. These plots were gener-

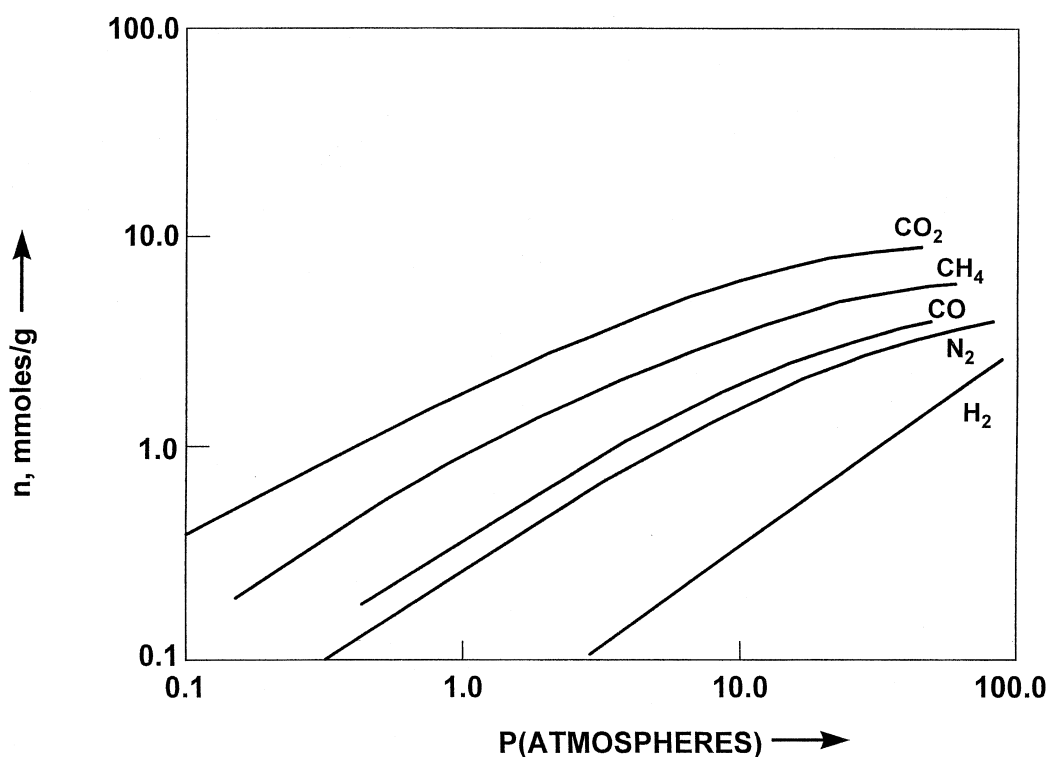


FIG. 5 Adsorption isotherms of CO₂, CO, CH₄, N₂, and H₂ on BPL activated carbon at 30°C.



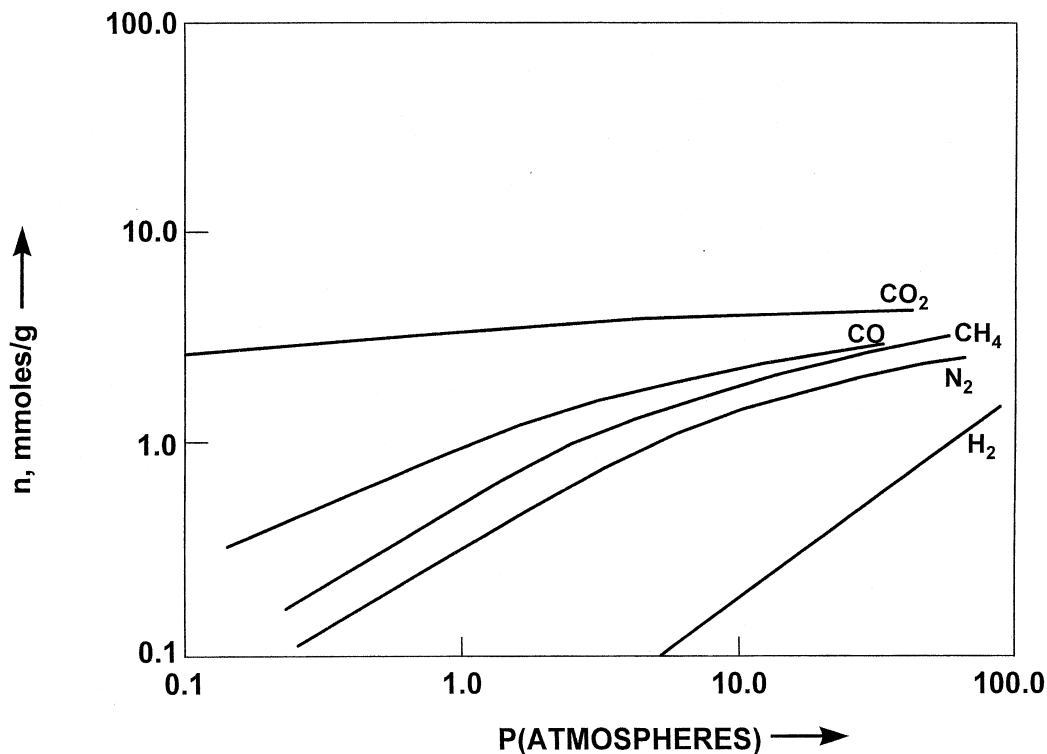


FIG. 6 Adsorption isotherms of CO₂, CO, CH₄, N₂, and H₂ on 5A zeolite at 30°C.

TABLE 1
Henry's Law Selectivity on BPL Carbon and 5A
Zeolite at 303 K

Gas mixture	Selectivity	
	BPL	5A
CO ₂ -CH ₄	2.5	195.6
CO ₂ -CO	7.5	59.1
CO ₂ -N ₂	11.1	330.7
CO ₂ -H ₂	90.8	7400.0
CO-CH ₄	0.33	3.3
CO-N ₂	1.48	5.6
CO-H ₂	12.11	125.0
CH ₄ -N ₂	4.5	1.7
CH ₄ -H ₂	36.6	37.8
N ₂ -H ₂	8.2	22.3



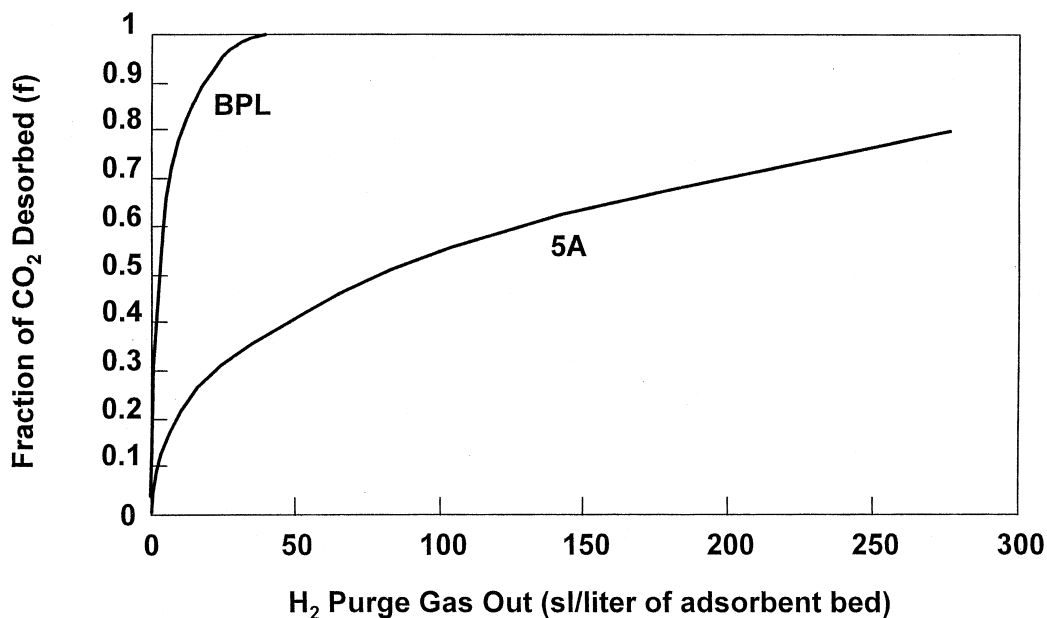


FIG. 7 Equilibrium-controlled desorption characteristics of CO₂ by H₂ purge.

ated using the local equilibrium model of desorption by purge (13). It was assumed that the packed column was initially saturated with pure CO₂ at ambient pressure and 30°C and then the column was isothermally purged with pure H₂ under the same conditions. It may be seen from Fig. 7 that a much smaller quantity of H₂ purge is needed to desorb the CO₂ efficiently from the BPL carbon than from the 5A zeolite. Thus, the ease of desorption of CO₂ from the activated carbon makes it the preferred adsorbent for CO₂ removal even though the CO₂ capacities and selectivities on the carbon are moderate compared to those on the zeolite.

Figure 5 and 6, and Table 1, on the other hand, show that the 5A zeolite exhibits a much larger capacity for adsorption of dilute CO and N₂ than the BPL carbon. The selectivities of adsorption of these gases over H₂ on the zeolite are also much larger than those on the carbon. The polar natures of CO (permanent dipole and quadrupole moments) and N₂ (permanent quadrupole moment) molecules are responsible for these behaviors. At the same time, the desorption of CO and N₂ from 5A zeolite by H₂ purge is relatively much more favorable than that for CO₂ as shown by Fig. 8. Thus, the zeolite is the favored adsorbent for removal of these gases from H₂ by the PSA processes.

The capacity of adsorption of nonpolar CH₄ and its selectivity of adsorption over H₂ are about the same on both materials. However, CH₄ is selectively adsorbed over CO on the carbon and CO is selectively adsorbed over CH₄ on the zeolite. Thus, both zeolite and carbon can be used to remove CH₄ from the SMROG.



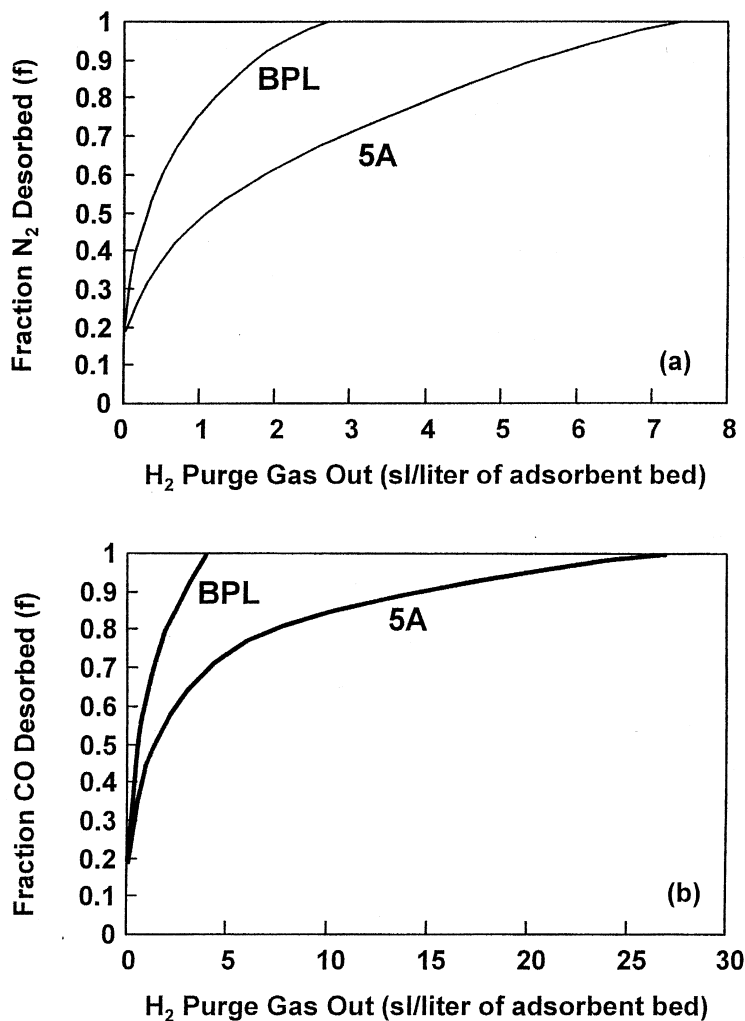


FIG. 8 Equilibrium-controlled desorption characteristics of CO and N₂ by H₂ purge.

All PSA processes use activated carbons for removal of CO₂ and CH₄ and zeolites for removal of CO, CH₄, and N₂ from SMROG. However, different types of activated carbons (pore size, source, surface polarity) and different types of zeolites (framework structure, cations, levels of ion exchange) may be employed for process optimizations.

Figures 9 and 10 show the pure gas adsorption isotherms of the components of ROG at 30°C on BPL activated carbon and a silica gel sample (Sorbead H, Mobil Corp.), respectively. Table 2 reports the corresponding Henry's law selectivities of the binary pairs of ROG components at 30°C on the same adsorbents. These data were also measured in our laboratory.

It may be seen from these data that the carbon adsorbs C₃+ hydrocarbons very strongly. Consequently, their desorption from carbon by H₂ purge be-



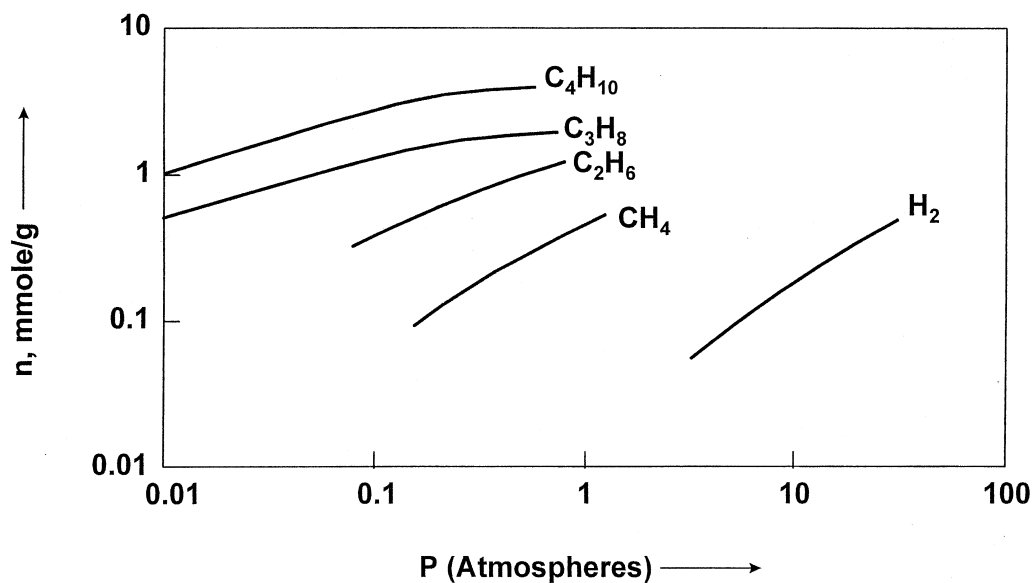


FIG. 9 Adsorption isotherms of C_4H_{10} , C_3H_8 , C_2H_6 , CH_4 , and H_2 on BPL activated carbon at $30^\circ C$.

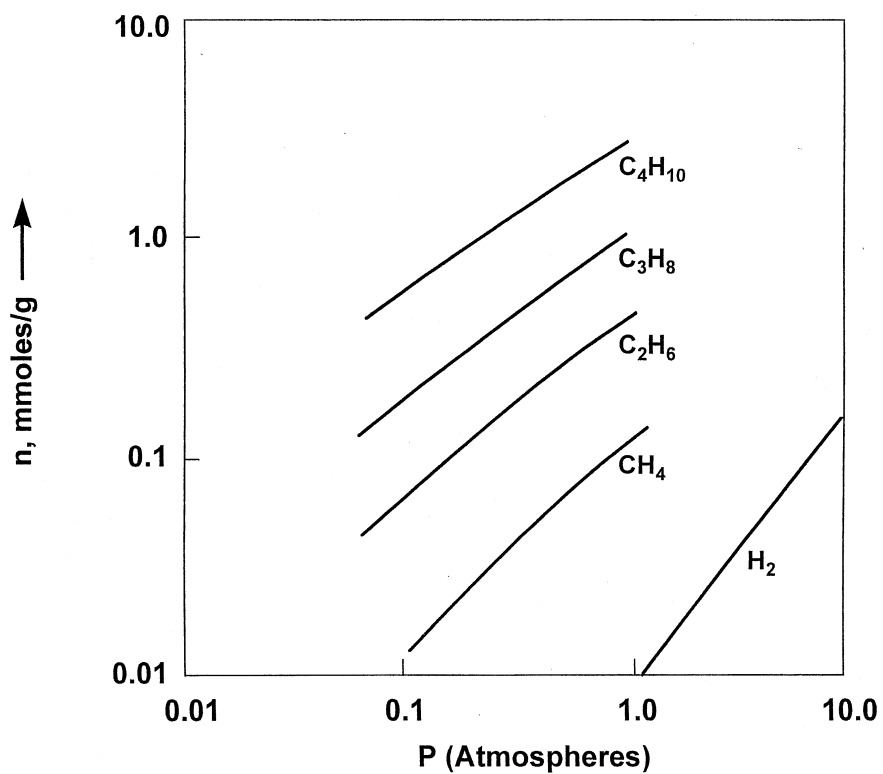


FIG. 10 Adsorption isotherms of C_4H_{10} , C_3H_8 , C_2H_6 , CH_4 , and H_2 on Sorbead H silica gel at $30^\circ C$.



comes rather impractical. Figure 11 compares the isothermal desorption characteristics of C_3H_8 by H_2 purge from BPL carbon and the silica gel samples. These data were also generated in the same fashion as those for the components of the SMROG. Thus, the silica gel, which offers relatively lower adsorption capacities and selectivities over H_2 for C_3+ hydrocarbons than the BPL carbon, is a preferred material for removal of the higher hydrocarbons from the ROG. Carbon, on the other hand, is favored for removal of CH_4 and C_2H_6 from H_2 because it exhibits relatively higher capacities and selectivities of adsorption over H_2 for these gases and yet these gases are not very strongly adsorbed on carbon. The use of silica gel in H_2 purification from ROG has been addressed in a recent publication (14).

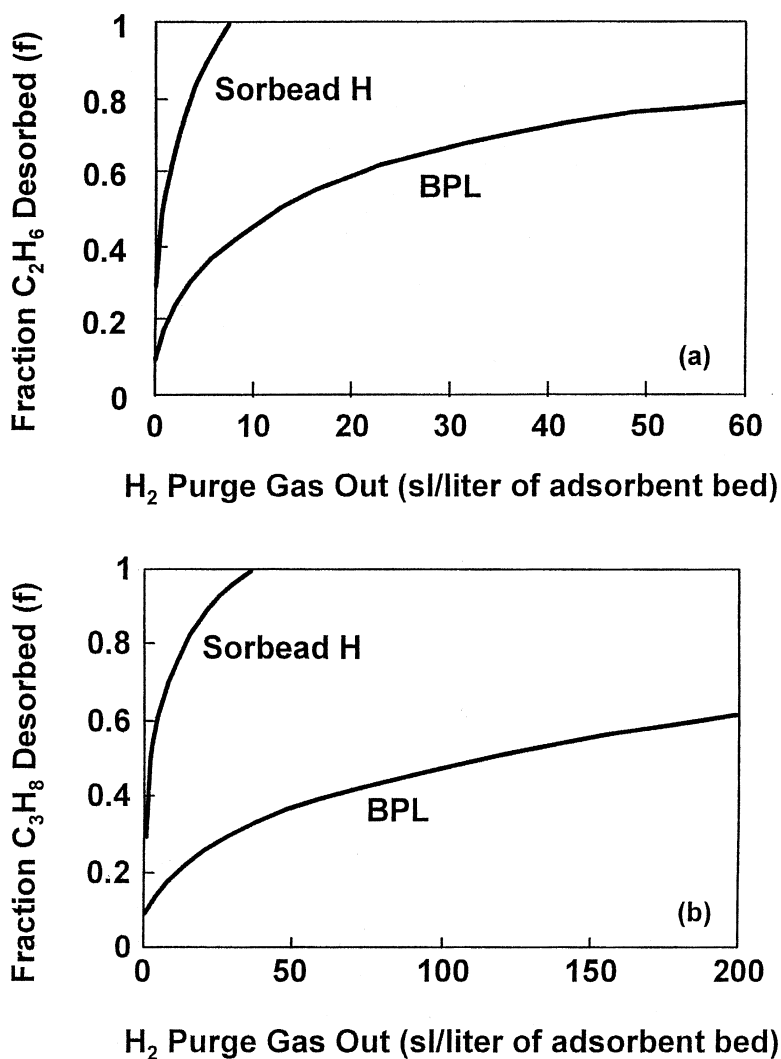


FIG. 11 Equilibrium-controlled desorption characteristics of C_3H_8 by H_2 purge.



Again, various forms of activated carbons and silica gels can be employed for the production of H_2 from ROG.

IMPROVED HYDROGEN RECOVERY BY PSA PROCESSES

The waste gases from the above described and other H_2 PSA processes contain low to medium purity H_2 (25–60%) and are produced at a pressure of 1.1–1.7 atm. About 15–30% of the feed gas H_2 is wasted in these streams (19). It is not generally attractive to recover H_2 from these waste gases because H_2 is often a minor component in these gases and its partial pressure is low. Consequently, these waste gases are combusted to recover their fuel values.

An earlier proposal to partially recover H_2 from these waste gases was to recompress the gas to a pressure of 7.8 atm and to employ a two-column, four-step Skarstrom PSA cycle consisting of adsorption, countercurrent depressurization, countercurrent purge, and pressurization with a part of the pure H_2 product (15). About 60–70% of H_2 from the main PSA waste gases can be recovered as pure H_2 by this route, and the recovered H_2 can be used to purge the main PSA adsorbers (10, 16). The net result is increased overall H_2 recovery by the integrated process. For example, the H_2 recovery of the Gemini process described earlier can be increased from 87% to 95% by this option (10).

More recently, it has been shown that the selective surface flow (SSF) membrane, which was developed and patented by Air Products and Chemicals, can be integrated with a H_2 -PSA process to increase the overall H_2 recovery by the hybrid system (17). The SSF membrane consists of a thin nanoporous carbon membrane layer supported on a macroporous alumina tube. The pore diameters of the carbon membrane are in the 5 to 7 Å range (18). When the PSA waste gases (SMROG or ROG feed) are passed through the high pressure side of the SSF membrane, the larger and more polar molecules (CO_2 , CO, C_1 – C_5 hydrocarbons) are selectively adsorbed over H_2 on the pore walls. The adsorbed molecules then selectively diffuse toward the low pressure side of the membrane where they desorb into the permeate stream. Thus the SSF membrane produces a H_2 -enriched gas stream as the high pressure effluent gas (retentate). This gas can be compressed to the feed gas pressure level of the main H_2 -PSA process and recycled by mixing it with the fresh feed to the PSA system in order to increase overall H_2 recovery by the hybrid process.

The adsorption–surface diffusion–desorption mechanism of transport through the SSF membrane can simultaneously provide high separation selectivity between H_2 and the impurities of the PSA waste gas and high flux for the impurities, even when the gas pressure in the high pressure side of the membrane is low to moderate (3–4.4 atm).



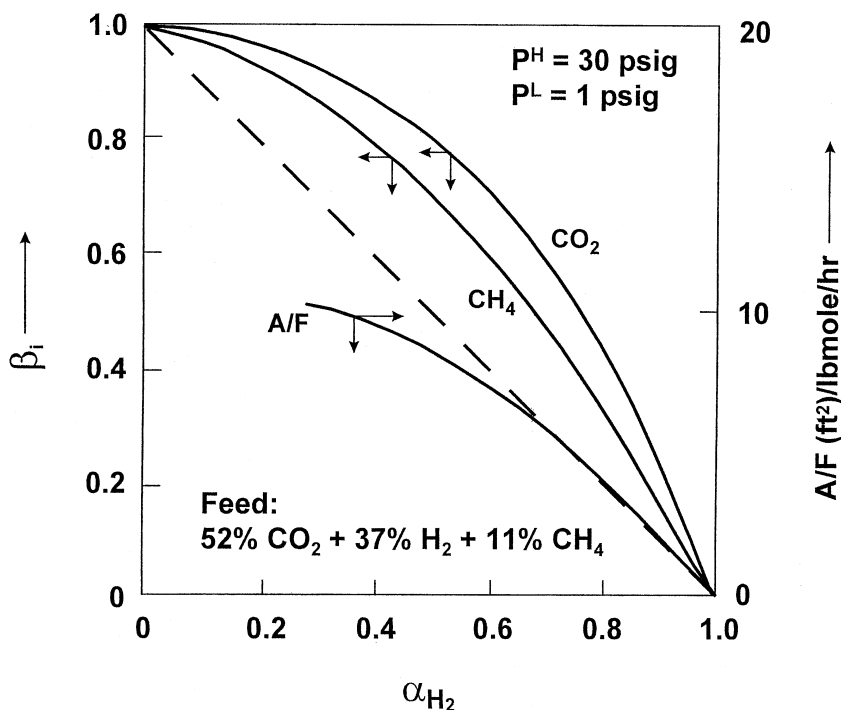


FIG. 12 Separation performance of SSF membrane for PSA waste gas (SMROG feed).

Figure 12 shows an example of the separation efficiency of the SSF membrane for SMROG-PSA waste gas (19). It plots the rejection (β_i) of the more selectively adsorbed components of the gas mixture ($i = CO_2, CH_4/CO$) as a function of H_2 recovery (α_{H_2}). The rejection of component i is defined by the ratio of the molar flow rate of that component in the low pressure permeate stream to that in the feed stream. The recovery of H_2 is defined by the ratio of the molar flow rate of H_2 in the high pressure effluent stream to that in the feed stream. The plot also shows the ratio of the membrane area (A) needed to process a given flow rate (F) of the feed gas. These data are sufficient to design the membrane for a given feed gas composition and flow rate (20).

The data of Fig. 12 were measured using a feed gas composition of 52% CO_2 , 37% H_2 , and 11% CH_4 at a pressure of 3 atm. There is practically no difference between the separation characteristics of CH_4 and CO by this membrane. Thus, this gas composition represents a typical H_2 -PSA waste gas. It may be seen from Fig. 12 that about 90% CO_2 and 80% ($CH_4 + CO$) can be rejected by the SSF membrane from the above described feed gas at a very moderate feed gas pressure when the H_2 recovery is 40%. The corresponding (A/F) value is about 10 $ft^2/lb \cdot mol/h$ ($1 ft^2/lb \cdot mol/h = 0.20 m^2/kg \cdot mol/h$). The high pressure effluent gas composition from the membrane under these conditions will be 25.7% CO_2 , 1.1% ($CH_4 + CO$), and 73.2% H_2 , which is comparable to that of the fresh feed to the PSA system.



It can be shown that an increase in the overall H₂ recovery of 7 to 10 percentage points can be achieved by using the hybrid PSA–SSF membrane system (19). The compression duty and the membrane area for the hybrid process can be significantly reduced by (i) fractionating the PSA depressurization waste gas; (ii) directly passing the initial part of the PSA depressurization waste gas, which is richer in H₂, through the SSF membrane without additional compression; and (iii) compressing the PSA purge waste gas to the pressure level needed to process it through the same membrane (19).

Figure 13 shows a schematic flow diagram for the PSA–SSF hybrid concept for increased H₂ recovery using the process scheme described above. The fresh feed to the PSA process is SMROG containing 72.8% H₂, 22.6% CO₂, and 4.6% (CH₄ + CO) at a pressure of 19.4 atm. The PSA process cycle is similar to that for the Polybed process except that only two cocurrent depressurization steps are used [eliminate Steps (e) and (g)]. The H₂ recovery by the PSA process is 77.6%. The countercurrent depressurization (Step e) effluent gas is fractionated. The initial part of this gas, which is richer in H₂, is directly fed to a SSF membrane at a pressure of 3 atm. The countercurrent purge (Step f) effluent gas is compressed to 3 atm and sent to the same membrane. The H₂-enriched high pressure effluent gas from the membrane is recompressed to 19.4 atm and recycled as feed gas to the PSA process. This increases the overall H₂ recovery of the hybrid process to 84.0%. A more detailed description of this concept can be found elsewhere (19).

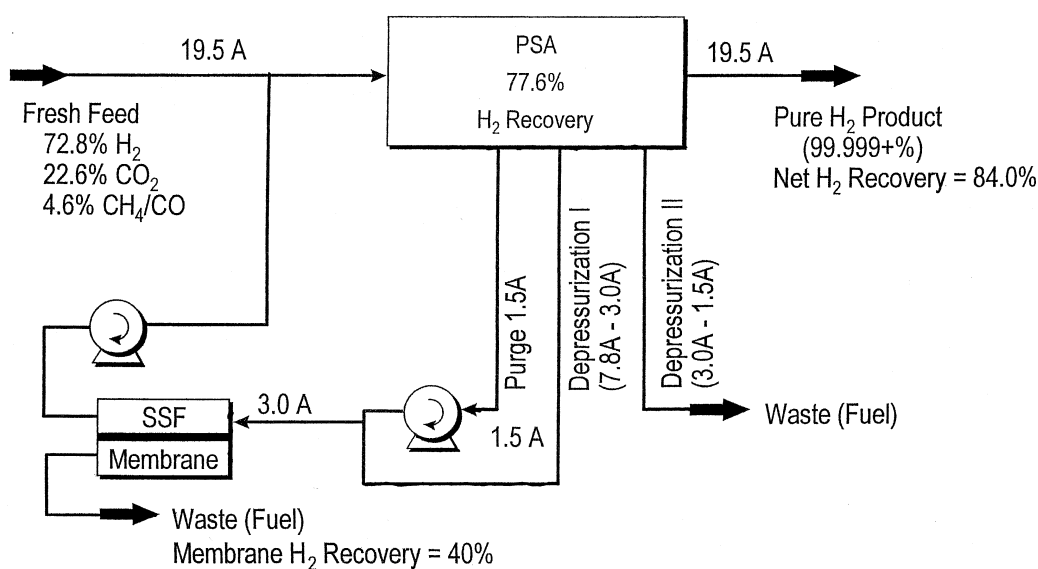


FIG. 13 Schematic flow diagram for hybrid PSA–SSF membrane separation system.



The SSF membrane can also be used to enrich and recycle H_2 from the waste gas of a PSA process which uses ROG as feed (21).

SUMMARY

Production of high purity hydrogen from a gas containing 70–90% H_2 using a pressure swing adsorption (PSA) process has become a common industrial practice. Numerous PSA processes have been developed for this purpose. The commonly used feed gases to the PSA processes are the steam methane reforming (SMR) off-gas (SMROG) and refinery off-gases (ROG). The basic research and development objectives in this area are (a) increasing hydrogen recovery at high purity (99.999% H_2) and (b) decreasing the adsorbent inventory and the hardware costs.

Three commercially developed PSA processes are described, and their key distinguishing features and separation performances are reviewed. Some of these processes are designed to produce a by-product stream (CO_2 from SMROG) along with the primary product stream (H_2). Several of these processes can also be modified to produce an ammonia synthesis gas directly as the primary product (from SMROG feed) with or without the production of CO_2 .

The pure gas equilibrium ad(de)sorption characteristics of the components of the SMROG and ROG feed streams on BPL activated carbon, 5A zeolite, and Sorbead H (silica gel) are reported, and the criteria for their selection in these PSA processes are briefly described.

Recent ideas for further improving H_2 recovery from H_2 -PSA processes are reviewed. These concepts extract additional H_2 from the PSA waste gases by integrating the PSA system with (a) additional PSA units or (b) selective surface flow (SSF) membrane systems. An example of the PSA-SSF membrane hybrid process is described.

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