This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Production of Hydrogen and Ammonia Synthesis Gas by Pressure Swing Adsorption

Shivaji Sircar[a]
[a] AIR PRODUCTS AND CHEMICALS, INC., ALLENTOWN, PENNSYLVANIA

To cite this Article Sircar, Shivaji(1990) 'Production of Hydrogen and Ammonia Synthesis Gas by Pressure Swing Adsorption', Separation Science and Technology, 25: 11, 1087 — 1099

To link to this Article: DOI: 10.1080/01496399008051839

URL: http://dx.doi.org/10.1080/01496399008051839

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SEPARATION SCIENCE AND TECHNOLOGY, 25(11 & 12), pp. 1087–1099, 1990

Production of Hydrogen and Ammonia Synthesis Gas by Pressure Swing Adsorption

SHIVAJI SIRCAR
AIR PRODUCTS AND CHEMICALS, INC.
ALLENTOWN, PENNSYLVANIA 18195-1501

Abstract

Two new pressure swing adsorption processes for the simultaneous production of hydrogen or ammonia synthesis gas and carbon dioxide from a reformer off-gas feed are described. Both products are produced at high purity and recovery. Performance data for these processes are reported.

INTRODUCTION

Pressure swing adsorption (PSA) has become the state-of-the-art technology for the production of ultrapure (99.99+ mol%) hydrogen from many different crude hydrogen sources containing 40–95 mol% H_2 such as steam reformer off-gas, catalytic reformer off-gas, ethylene off-gas, etc. (*1*). A large variety of PSA process concepts have been patented to achieve this goal (*2*). These processes selectively remove CO_2, CO, N_2, H_2O, CH_4, C_2H_4, and other hydrocarbon impurities which are present in bulk or dilute quantities in the crude H_2 source. The product gas is essentially pure H_2 at nearly the feed gas pressure with moderate to high (65–90%) H_2 recovery from the feed gas. Increasing H_2 recovery and reducing adsorbent inventory are the key goals of these processes.

More recently, a PSA process was developed by Air Products and Chemicals which produces two pure products from a multicomponent feed gas with high recoveries of both product components (*3*). For example, this process (hereafter called Process A) can simultaneously produce a stream of 99.999+ mol% H_2 with a recovery of 87.0% and a stream of 99.4 mol% CO_2 with a recovery of 94.0% from a crude feed gas (reformer off-gas) containing 20.0% CO_2, 1.0% CO, 4.0% CH_4, and 75.0% H_2 at 200–300 psig.

The purpose of this paper is to describe two new evolutionary variations of Process A developed by Air Products and Chemicals which can further increase H_2 recovery to about 95.0% (Process B) or directly produce an ammonia synthesis gas (Process C) from the above-described feed gas while maintaining the high purity and recovery of the by-product CO_2. These examples will also demonstrate the flexibility and the complexity of modern PSA processes.

PROCESS B: AN IMPROVED PSA PROCESS FOR SIMULTANEOUS PRODUCTION OF HYDROGEN AND CARBON DIOXIDE FROM REFORMER OFF-GAS

A multicolumn PSA system is used to achieve the goals of high purity and recovery of both H_2 and CO_2 products from the reformer off-gas (*4*). Figure 1 shows a schematic flow diagram for the process. It contains three sets of adsorbent beds designated *A*, *B*, and *C*. The *A* beds (six in parallel) contain an adsorbent for selective adsorption of CO_2 and H_2O from H_2, CO, and CH_4. The *B* beds (three in parrallel) and the *C* beds (two in parallel) contain one or more layers of adsorbents for selective removal of CO_2 from CO, CH_4, and H_2 and for selective removal of CO and CH_4 from H_2. Each bed of each set goes through a cyclic sequence of adsorption,

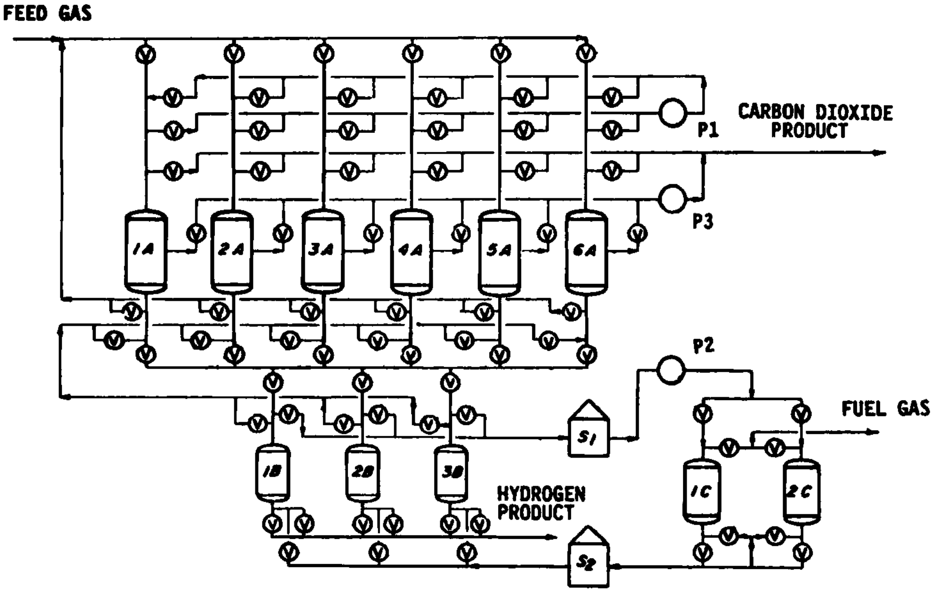

FIG. 1. Schematic flow diagram for PSA Process B.

desorption, and other complementary steps. One *A* bed and one *B* bed are connected in series during the adsorption step of the cycle, but then they undergo two entirely different sequences of desorption and complementary steps. The *C* beds operate as a satellite of the *B* beds. A detailed description of the cycle steps for this process is given below.

Cycle Steps for A Beds

(Aa) Adsorption Step. The feed gas is passed through an *A* bed at the highest pressure level (P_A) of the cycle. The bed has been previously pressurized to the feed gas pressure level with a H_2-rich gas. The CO_2-depleted effluent from the *A* bed is passed through a *B* bed for removal of the dilute impurities (CO, CH_4, N_2) in the feed gas along with any CO_2 that has slipped through the *A* bed. The adsorption step is continued until the CO_2 mass transfer zone (MTZ) reaches the exit end of the *A* bed without substantially breaking through it.

(Ab) Carbon Dioxide Rinse Step. At the end of the adsorption step, the connection between the *A* and *B* beds is closed and a stream of high purity CO_2 is passed through the *A* bed in the same direction as the feed gas flow (cocurrent) at feed gas pressure. The effluent from the bed has a feed-gas-like composition, and it is produced at the feed gas pressure. This gas is recycled as feed to another adsorber by mixing it with fresh feed. The rinse step is continued until the adsorber is essentially saturated with high purity CO_2.

(Ac) Countercurrent Depressurization Step. The *A* bed is then depressurized to the near-ambient pressure level by withdrawing gas from the feed end (countercurrent). The effluent is a high purity CO_2 gas, a part of which is compressed to P_A and used as the CO_2 rinse gas to another column undergoing Step (*Ab*), and the remainder of this gas is withdrawn as part of the CO_2 product gas. A CO_2 compressor is needed for this step.

(Ad) Countercurrent Evacuation Step. Following Step (*Ac*), the bed is evacuated through the feed end (countercurrent) to the lowest pressure level (P_D) in the cycle by using a vacuum pump. The effluent gas is high purity CO_2, a part of which may be used to supply the CO_2 rinse gas in Step (*Ab*) while the remainder forms a part of the CO_2 product gas.

(Ae) Countercurrent Pressurization Step I. After evacuation, the *A* bed is again connected with a *B* bed then undergoing Step (*Bb*) below to transfer a part of the void and desorbed gases from the *B* bed to the *A* bed through the product end of that bed (countercurrent), thus raising the pressure of the *A* bed to a level of P_1 ($P_D < P_1 < P_A$).

(Af) Countercurrent Pressurization Step II. Finally, the *A* bed is brought back to the adsorption pressure (P_A) by introducing a H_2-rich gas into the bed through the product end (countercurrent). The gas is obtained from the effluent of a *B* bed undergoing the adsorption Step (*Ba*), and it flows into the *A* bed via a *B* bed undergoing Step (*Bg*) below. The *A* bed is now ready to start a new adsorption step in series with a *B* bed which is also ready for that step.

Cycle Steps for B Beds

(Ba) Adsorption Step. The *B* bed in series with an *A* bed during its adsorption Step (*Aa*) receives the CO_2-depleted gas from the *A* bed at feed gas pressure, and it removes the remaining CO_2 and other dilute impurities from that gas to produce a very high purity H_2-rich effluent. The bed is pressurized to P_A with a H_2-rich gas prior to the start of this step. A part of the effluent is withdrawn as the H_2 product gas, and the balance is used to pressurize the *B* (Step *Bg*) and the *A* (Step *Af*) beds. The adsorption step is continued until the leading impurity MTZ in the bed is just short of breakthrough at the H_2 product end.

(Bb) Countercurrent Depressurization Step I. At the termination of the adsorption step, the *B* bed is connected with an *A* bed undergoing Step (*Ae*) above, and a portion of the void and desorbed gases are transferred through the feed end (countercurrent) of the bed to the *A* bed, thus lowering the pressure of the *B* bed from P_A to P_1.

(Bc) Countercurrent Depressurization Step II. Following Step (*Bb*), the *B* bed is connected with another *B* bed undergoing Step (*Bf*), and more void and desorbed gases are removed from the *B* bed through the feed end (countercurrent). The *B* bed pressure drops from P_1 to P_2 during this step.

(Bd) Countercurrent Depressurization Step III. The *B* bed is now depressurized from P_2 to a near-atmospheric pressure level by withdrawing gas from it through the feed end (countercurrent). The effluent gas contains a portion of the feed gas impurities along with some H_2 which is compressed to a pressure level of P_C and fed to a *C* bed undergoing Step (*Ca*) below.

(Be) Countercurrent Purge Step. After Step (*Bd*) the bed is purged at near-ambient pressure with a high purity H_2 stream introduced into the bed through the H_2 product end (countercurrent) in order to further desorb the impurities from the bed. The purge gas is obtained from the effluent of a *C* bed undergoing Step (*Ca*) below. The effluent of this step is also compressed to P_C and fed to a *C* bed by mixing it with the effluent of step (*Bd*).

(Bf) Cocurrent Pressurization Step. Following the purge step, the pressure in the *B* bed is raised from a near-ambient pressure level to P_2 by connecting it with another *B* bed undergoing Step (*Bc*). The pressurization gas is introduced into the bed through the feed end (cocurrent).

(Bg) Countercurrent Pressurization Step. Finally, the *B* bed is brought back to the feed gas pressure level by introducing a high purity H_2 stream through the H_2 product end (countercurrent) of the bed. This gas is obtained from the effluent of another *B* bed undergoing the adsorption Step (*Ba*). During this step the *B* bed is connected in series with an *A* bed undergoing Step (*Af*), and both beds are simultaneously pressurized to P_A by using a part of the high purity H_2 gas. The *B* bed is now ready to start a new adsorption step by being placed in series with an *A* bed which is also ready for that step.

Cycle Steps for C Beds

(Ca) Adsorption Step. The effluent gas from Steps (*Bd*) and (*Bc*) are mixed and compressed to a pressure level of P_C ($< P_A$). The gas mixture is then passed through one of the *C* beds which was previously pressurized to P_C with a hydrogen-rich gas. The CO_2, CO, and CH_4 impurities are adsorbed and a stream of ultrapure H_2 is produced at pressure P_C at the effluent end of the *C* bed. A portion of this gas is used to purge one of the *B* beds then undergoing Step (*Be*). Another portion of this effluent is used to purge the companion *C* bed undergoing Step (*Cc*) below. A third portion of this gas is used to pressurize the companion *C* bed undergoing Step (*Cd*) below.

(Cb) Countercurrent Depressurization Step. At the end of Step (*Ca*), the *C* bed is depressurized from P_C to P_W by withdrawing gas through the feed end (countercurrent). The effluent gas at pressure $P_W < P_C$ forms a part of the reject gas from this process.

(Cc) Countercurrent Purge Step. After depressurization, the *C* bed is purged at pressure P_W with a stream of essentially pure H_2 then being produced by the companion *C* bed undergoing Step (*Ca*) above. The purge gas is introduced into the *C* bed through the effluent end (countercurrent) of the bed. The purge effluent gas at pressure P_W is mixed with the effluent of Step (*Cb*) and they form the total reject gas from the PSA Process B.

(Cd) Countercurrent Pressurization Step. After step (*Cc*), the *C* bed is pressurized from P_W to P_C by introducing pure H_2 through the effluent end (countercurrent). The pressurization gas is obtained from the effluent of the companion *C* bed then undergoing Step (*Ca*). The *C* bed is now ready to begin a new cycle starting from Step (*Ca*).

The compressors (P1) and (P2) in Fig. 1 are used to compress the effluent gases from Steps (*Ac*) and (*Bd*) + (*Be*), respectively, while the vacuum pump (P3) is used to evacuate the *A* bed (Step *Ad*). A surge tank (S_1) may be necessary to collect the effluents of Steps (*Bd*) and (*Be*) for mixing the gases prior to compression and supply to the *C* beds as feed.

Figure 2 shows a synchronized time sequence for the steps of Process B

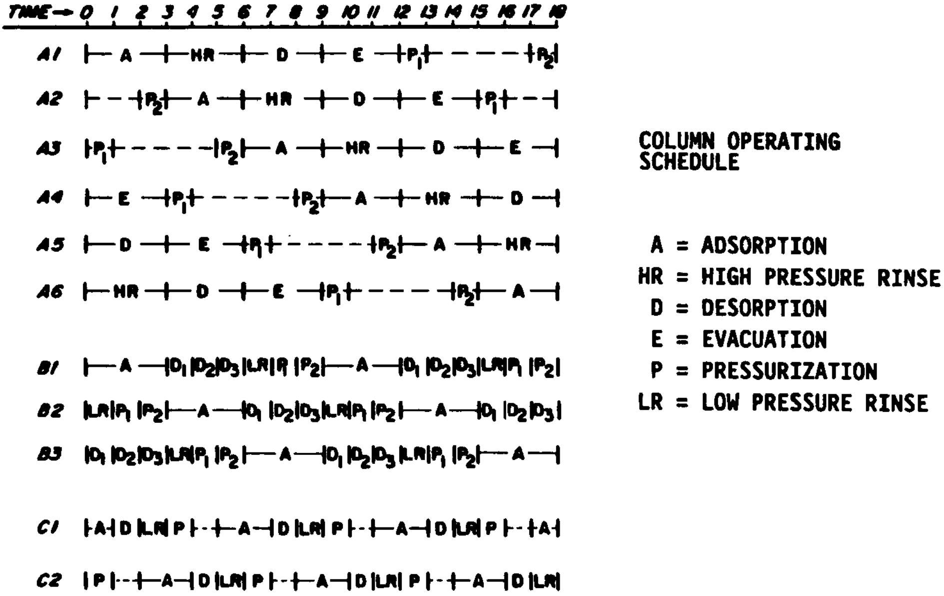

FIG. 2. Column operation schedule for PSA Process B.

for an arbitrarily chosen total cycle time of 18 units. It may be seen that each *B* bed goes through two complete cycles (Steps *Ba*–*Bg*) while each *A* bed completes one cycle (Steps *Aa*–*Af*). Each *C* bed goes through three complete cycles (Steps *Ca*–*Cd*) for each cycle of an *A* bed. This design significantly reduces the adsorbent inventory for the *B* and *C* beds.

Process Performance

The above described PSA process was tested in a multibed pilot unit by using a feed gas composition identical (see Table 1) to that used for testing Process A. The beds were packed with several different proprietary adsorbents. The feed gas pressure was 250 psig ($= P_A$). The *A* beds were evacuated to a pressure level of 150 torr ($= P_D$) at the end of Step (*Ad*). The *B* beds were depressurized to 0 psig at the end of Step (*Bd*) and then they were purged at a near-ambient pressure with pure H_2 produced by the *C* beds (Step *Be*). The effluents from a *B* bed during Steps (*Bd*) and (*Be*) were mixed and compressed to a pressure level of 100 psig ($= P_C$) before feeding the mixture to a *C* bed. The *C* beds were depressurized to 4.5 psig ($= P_W$) at the end of Step (*Cb*) and purged with pure H_2 at that

TABLE 1

Performance of Three PSA Processes for Treatment of Reformer Off-Gas[a]

	Primary H_2 product					Secondary CO_2 product			Fuel gas					
		Purity (mol %)		Recovery (%)						Purity (mol %)				
	Amount	H_2	N_2	H_2	N_2	Amount	Purity (Mol %)	Recovery (%)	Amount	CO_2	CO	CH_4	N_2	H_2
Process A	0.657	99.999+	—	87.1	—	0.188	99.4	94.0	0.155	7.7	6.2	24.1	—	61.9
Process B	0.717	99.999+	—	95.1	—	0.188	99.4	94.0	0.095	12.6	10.1	39.3	—	37.9
Process C	0.956	75.0	25.0	95.1	74.7	0.188	99.4	94.0	0.175	6.9	5.5	21.3	45.7	20.6

[a] The feed gas to the PSA system contains 75.4% H_2, 19.9% CO_2, 0.96% CO, and 3.73% CH_4 at 250 psig and 18.0°C.

pressure during Step (*Cc*). Thus, the effluents from *C* beds during Steps (*Cb*) and (*Cc*), which constitute the reject gas from this process, were available at a positive pressure of 4.5 psig. The H_2 recovery from the *C* beds was about 62% of the feed H_2 to those beds.

A summary of the overall performance of this process is given in Table 1, which also reports the performance of Process A under comparable conditions of operation. The amounts of gases reported in the table are quantities per unit amount of fresh feed gas to the PSA system. It may be seen from Table 1 that Process B provides a much higher H_2 recovery (~95.0%) than Process A (~87.0%) while maintaining the H_2 purity (99.999+ %) and the purity (99.4%) and recovery (94.0%) of product CO_2 intact. This is a significant improvement over Process A because H_2 is an expensive product. The higher H_2 recovery by Process B more than offsets the extra cost of feed gas compression to *C* beds and the capital investment for the *C* beds required by this process. On the other hand, for a given H_2 production demand, the higher H_2 recovery of Process B significantly reduces the feed gas requirement to the PSA system and the sizes of the *A* and *B* beds. It should be noted that the adsorption pressure for the *C* beds (P_C) is much lower than that (P_A) for the *A* and *B* beds, and the feed gas quantity to the *C* beds is about 15% of that to the *A* beds. Thus, the cost of compression of the feed gas to the *C* beds is not very high. In fact, P_C is an optimization variable for this process which introduces a considerable amount of flexibility to the overall operation and economics of the process.

Another major advantage of Process B over Process A is that the waste gases produced from Process B are at a positive pressure (P_W = 4.5 psig) which can be delivered as a fuel gas to the reformer without further compression, yet the *B* beds of the PSA system can be purged with H_2 (Step *Be*) at near-ambient pressure which minimizes the H_2 purge requirement for that step. This could not be done with Process A where the H_2 purge effluent from the *B* beds form a part of the reject gas and, therefore, purging the *B* beds of Process A at ambient pressure would require compression of the waste gases for further use. Alternatively, a larger quantity of H_2 purge gas would be necessary in Process A if the purge step were to be carried out at a positive pressure in order to avoid the compression, and that would result in a significant reduction of H_2 recovery.

The recovery of some H_2 from the reject gases of *B* beds by removal of the impurities from that gas in *C* beds of Process B and partial use of the recovered H_2 to purge the *B* beds at ambient pressure introduces flexibility in the operating conditions of *B* beds and improves H_2 recovery of the overall process. The inefficiency in the operation of the *C* beds due to execution of the H_2 purge Step (*Cc*) at a superatmospheric pressure is small because of the relatively small quantity of the feed gas to those beds and relatively smaller sizes of the beds. Table 1 also gives the amounts and compositions of the reject (fuel) gases from PSA Processes A and B. The reject gas from Process B is leaner in H_2 but richer in CH_4 than that from Process A.

One interesting application of these processes is in the manufacture of urea. The H_2 produced by these processes can be reacted with N_2 to form NH_3 which can then be reacted with the by-product CO_2 from these processes to form urea. The use of ultrapure H_2 can virtually eliminate the need for an ammonia purge loop, which is often a nuisance. Clearly, the new Process B would be a preferred candidate for this application because of higher H_2 recovery.

PROCESS C: PSA PROCESS FOR SIMULTANEOUS PRODUCTION OF AMMONIA SYNTHESIS GAS AND CARBON DIOXIDE FROM REFORMER OFF-GAS

The second new PSA process concept (*5*) is designed for simultaneous and direct production of an ammonia synthesis gas (H_2/N_2 mixture in the molar ratio 3:1) and pure carbon dioxide from a reformer off-gas. Earlier PSA processes in this area could only produce an ammonia synthesis gas from such a feed gas (*6*).

Figure 3 is a schematic flow sheet for the process. It uses four parallel *A* beds and two parallel *B* beds in conjunction with a CO_2 compressor (P1) and a vacuum pump (P2). The *A* beds are packed with an adsorbent for selective removal of CO_2 and H_2O from CO, CH_4, N_2, and H_2, while the *B* beds are packed with one or more layers of adsorbent for selective removal of CO_2 from CO, CH_4, N_2, and H_2 and for removal of CO and CH_4 from N_2 and H_2. One *A* and one *B* bed are connected in series during the adsorption step, and then they undergo a completely different sequence of desorption and complementary steps as described below:

Cycle Steps for *A* Beds

The first five steps of the cycle for the *A* beds of Process C are identical to those for Process B (Steps *Aa–Ae*). Then the *A* bed is pressurized from P_I to P_A (Step *Af*) with N_2 from an external source instead of using a H_2-rich gas as in the case of Process B.

Cycle Steps for *B* Beds

The first two steps of the cycle for the *B* beds of Process C are also identical to those of Process B (Steps *Ba* and *Bb*). However, the effluent from the *B* beds during Step (*Ba*) of Process C is a mixture of N_2 and H_2 rather than pure H_2, which was the case for process B. The Step (*Bc*) of

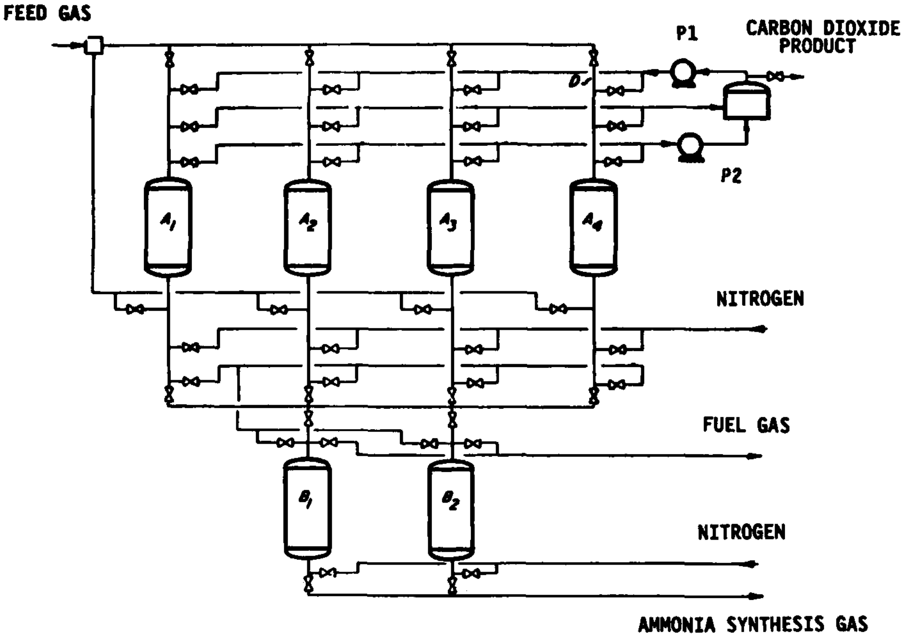

FIG. 3. Schematic flow diagram for PSA Process C.

Process B is eliminated, and Step (*Bd*) becomes the third step for Process C. Step (*Bg*) of Process B is also removed, and Steps (*Be*) and (*Bf*) become, respectively, the fourth and fifth steps for the *B* beds in Process C except that N_2 from an external source is used as the purge gas (Step *Be*) and pressurization gas (Step *Bg*) for the *B* beds instead of H_2 as in the case of Process B. Thus, Process C has a smaller number of steps for the *B* beds because the interactions between *A* and *B* beds (Steps *Af*, *Bg*) and those between *B* and *B* beds (Steps *Bc*, *Be*, *Bf*, and *Bg*) of Process B are eliminated. Consequently, Process C can be run continuously with the use of only four *A* beds and only two *B* beds.

Figure 4 shows a synchronized operational sequence for the steps of Process C. Again, each *B* bed goes through two complete cycles for each cycle of an *A* bed. This helps to reduce the adsorbent inventory of *B* beds.

Process Performance

The key features of Process C are the final pressurization of the *A* beds (Step *Af*) and low pressure purging (Step *Be*) and pressurization (Step

Bg) of the *B* beds by using an external source of N_2. They serve the following purposes:

(a) A certain amount of N_2 is introduced into the *A* and *B* beds before they start their adsorption steps (*Aa* and *Ba*). A part of this N_2 occupies the void space in the columns at pressure P_A, and the other part is adsorbed. Since the adsorbents used in these columns have adsorption selectivities in the order $H_2O > CO_2 > CO > CH_4 > N_2 > H_2$ or $H_2O > CO_2 > CH_4 > CO > N_2 > H_2$, the void and adsorbed N_2 are displaced by the feed CO_2, CO, and CH_4 during the adsorption step in these beds, thus producing a mixture of $N_2 + H_2$ as the effluent gas at nearly the feed gas pressure. Practically all of the N_2 present in the beds at the beginning of the adsorption step is expelled from the beds along with unadsorbed H_2 from the feed gas during the adsorption step. By controlling the feed gas pressure and the sizes of *A* and *B* beds, it is possible to adjust the molar ratio of N_2 and H_2 in the effluent gas from the *B* beds to 1:3 or any other desired value [2]. Thus, an ammonia synthesis gas can be directly produced during the adsorption step of Process C.

(b) The use of N_2 as a purge gas to clean the *B* beds instead of H_2 minimizes the H_2 loss from Process C. The purge step can be carried out at a positive pressure (say 5.0 psig) so that the effluent fuel gas does not have to be compressed for further use.

The overall performance of Process C is compared with those of Processes A and B in Table 1. It is seen that Process C is extremely efficient. It produces an ammonia synthesis gas with a H_2 recovery of about 95.0% from the feed reformer off-gas while producing a high purity CO_2 byproduct with high recovery. Approximately 75.0% of the external N_2 used in the process is recovered in the primary ammonia synthesis gas product. The fuel gas produced by Process C has a lower calorific value due to the presence of a large quantity of N_2 in that gas, but its total heating value is the same as that from Process B. Process C is, therefore, an ideal candidate for the production of urea from a reformer off-gas.

CONCLUSIONS

The pressure swing adsorption processes described demonstrate the diversity and flexibility of this technology in relation to bulk gas separation. Although fairly complex in design, they are capable of simultaneously producing two products of desired composition from a multicomponent feed gas containing bulk and dilute impurities. The high recoveries of the

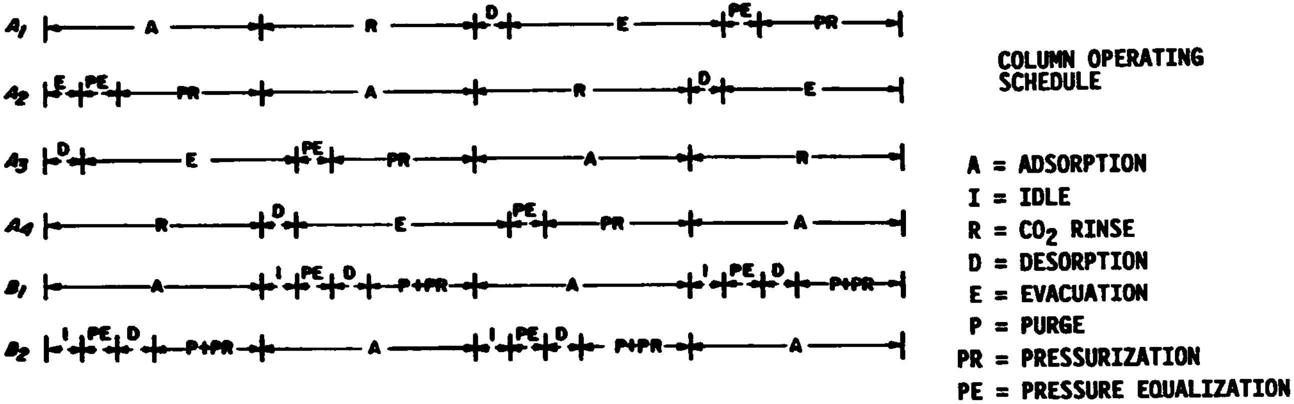

FIG. 4. Column operation schedule for PSA Process C.

desired components by these processes make them extremely valuable separations tools.

REFERENCES

1. *Polybed PSA Systems for Hydrogen Purification and Recovery*, Union Carbide Corporation, Houston, Texas.
2. S. Sircar, in *Adsorption: Science and Technology* (A. E. Rodrigues et al., eds.), Kluwer, The Netherlands, 1989, pp. 285–321.
3. S. Sircar and W. C. Kratz, *Sep. Sci. Technol.*, *23*(14 & 15), 2397 (1988).
4. S. Sircar, U.S. Patent 4,790,858 (1988).
5. S. Sircar, U.S. Patent 4,813,980 (1989).
6. A. Fuderer, U.S. Patent 4,375,363 (1983).

Received by editor October 31, 1989