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Simultaneous Production of Hydrogen and Carbon Dioxide from Steam Reformer Off-Gas by Pressure Swing Adsorption

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Abstract

Pressure swing adsorption (PSA) processes are used for the production of ultrapure hydrogen from a crude hydrogen stream containing H_2O, CO_2, CO, CH_4, and N_2 impurities which is produced by steam reformation of natural gas or naphtha. Two commercial PSA processes designed for this purpose are reviewed and a new commercial PSA process which simultaneously produces ultrapure hydrogen and high purity carbon dioxide products from the crude hydrogen with high recoveries of both components is described. Performance data for the new process are reported.

INTRODUCTION

Production of hydrogen by catalytic steam reforming of natural gas or naphtha is a common practice in the chemical industry (*1*). The reformed gas is subjected to a water-gas shift reaction to produce a crude hydrogen stream containing 75-80% H_2, 15-25% CO_2, 0.1-1% CO, 1-5% CH_4, and trace N_2 on a dry basis. The exact composition of this gas depends on many variables such as the steam-hydrocarbon ratio in the reformer, its operating pressure and temperature, types of catalysts used, the degree and conditions of the shift reaction, etc. The crude hydrogen stream which is typically available at a pressure of 150-350 psig is cooled to near

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ambient temperature and then purified to produce a very high purity (99.999%) hydrogen product.

The use of pressure swing adsorption (PSA) technology to remove the bulk (CO_2) and dilute (CO, CH_4, N_2, and H_2O) impurities from the crude H_2 stream by selective adsorption of the impurities on solid adsorbents such as zeolites and activated carbons has become the state-of-the-art method for hydrogen purification and many PSA process concepts for this separation have been patented (*2–8*). These processes are designed to produce a high purity hydrogen product stream and a reject stream containing all of the CO_2, CO, CH_4, N_2, and H_2O impurities in the feed gas along with unrecovered H_2. The reject stream is usually used as a fuel to the reformer. The PSA processes differ in the modes in which the process steps such as adsorption, desorption, pressure equalization, pressurization, etc. are carried out, the conditions (pressure, temperature, flow direction) of operation of these steps, the properties of the adsorbents, the number of adsorbent columns, and the types of machinery (compressors, vacuum pumps) and other hardware used. A key goal is to increase the product hydrogen recovery by the PSA process.

The early work in this field was done by the Union Carbide Corporation which developed the following two commercial PSA process cycles for the above-described separation (*2*, *3*).

PSA PROCESSES FOR PRODUCTION OF HYDROGEN FROM REFORMER OFF-GAS

The first PSA process consists of seven steps. Each adsorber undergoes each of these steps in a cyclic manner as follows.

(a) Adsorption Step. The feed gas is passed through an adsorber containing adsorbents for selective removal of the impurities from the crude H_2 stream at the highest pressure level of the cycle (P_A). The adsorber is pressurized to this pressure level prior to the start of the adsorption step. Very high purity hydrogen is produced at the effluent end of the adsorber. Part of this effluent is withdrawn as H_2 product gas, while the remainder is used to pressurize another adsorber undergoing Step (g) of the cycle.

(b) Cocurrent Depressurization Step I. The adsorption step is stopped when the impurity mass transfer zones (MTZ) have reached approximately the middle of the adsorber and then the column is depressurized by withdrawing gas through the H_2 product end of the adsorber (cocurrent). This effluent gas is high purity H_2 which is used to partially pressurize another adsorber which is undergoing Step (f) of the cycle. The pressure in the adsorber at the end of this step is P_1 ($<P_A$).

(c) Cocurrent Depressurization Step II. The adsorber is further depressurized to a pressure level of P_2 ($<P_1$) by withdrawing gas through the H_2 product end (cocurrent). The effluent gas, which is still good purity H_2, is used to purge another adsorber undergoing Step (e) of the cycle.

(d) Countercurrent Depressurization Step. The adsorber is depressurized to the lowest pressure level P_D ($<P_2$) of the PSA cycle, which is typically near atmospheric pressure, by withdrawing gas through the feed end (countercurrent). The effluent which contains the desorbed impurities from the adsorber forms a portion of the reject gas from the PSA process.

(e) Countercurrent Purge Step. A stream of good purity H_2 at pressure P_D is passed over the adsorbent by introducing the gas through the H_2 product end (countercurrent) to further desorb the adsorbed impurities from the bed. The effluent from the feed end constitutes the remaining portion of the reject gas from the process. The H_2 purge gas is obtained from a companion adsorber undergoing Step (c).

(f) Countercurrent Pressurization Step I. Following Step (e), the adsorber is pressurized to a pressure level of P_1 by introducing a high purity H_2 stream through the H_2 product end (countercurrent). The gas is obtained from another column undergoing Step (b).

(g) Countercurrent Pressurization Step II. Finally, the adsorber is brought back to the feed pressure level (P_A) by introducing a very high purity H_2 stream through the H_2 product end (countercurrent). This H_2 is produced by an adsorber in the adsorption Step (a).

(h). The adsorber is now ready to start a new cycle starting from Step (a).

The above process can be carried out using four (or more) adsorbent columns in parallel as shown by the schematic flow diagram in Fig. 1 (*2*). The use of four adsorbers allows continuous flow of feed and product H_2 gas. With a layer of an activated carbon at the feed end of the adsorber to

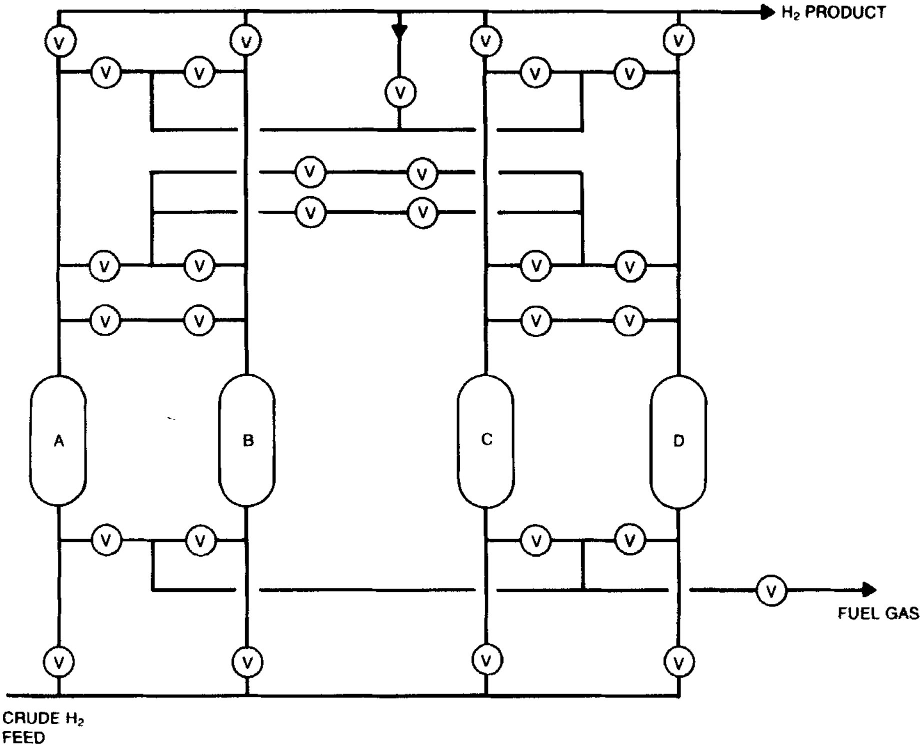

FIG. 1. Schematic of a four-column PSA system for production of only H_2 from the reformer off-gas.

remove H_2O and CO_2 impurities followed by a layer of 5A zeolite for removal of CO and CH_4, the process can produce a H_2 product containing 99.999% H_2 with a H_2 recovery of 76.2% (*2*) from a feed gas containing 77.1% H_2, 22.5% CO_2, 0.35% CO, and 0.013% CH_4 (dry basis) at 70°F. The feed gas pressure in this case is 195.3 psig and the lowest desorption pressure of the cycle is 0 psig. The reject gas contains 44.5% H_2, 54.6% CO_2, 0.85% CO, and 0.032% CH_4.

The second PSA cycle was developed to increase the H_2 recovery of the process (*3*). It introduced two more cocurrent depressurization steps (between Steps b and c) and two more countercurrent pressurization steps (between Steps e and f) in the cycle described above. The resulting 11-step cycle then consisted of:

(a) *Adsorption Step* identical to that of the first process.
(b) *Cocurrent Depressurization Step I* which serves the same purpose as that of the first process.
(c) *Cocurrent Depressurization Step II* where the adsorber pressure is reduced to a pressure level of P_2 ($<P_1$) and the hydrogen-rich effluent gas is used to countercurrently pressurize another adsorber.
(d) *Cocurrent Depressurization Step III* where the adsorber pressure is further reduced to P_3 ($<P_2$) and the effluent gas which is still H_2 rich is used to countercurrently pressurize another companion adsorber.
(e) *Cocurrent Depressurization Step IV* identical to Step (c) of the first process. The column pressure at the end of this step is P_4 ($<P_3$). The effluent gas is used to purge another adsorber countercurrently.
(f) *Countercurrent Depressurization Step* where the adsorber pressure is reduced from P_4 to P_D to produce a portion of the reject gas.
(g) *Countercurrent Purge Step* similar to Step (e) of the first process. The H_2 purge gas is obtained from an adsorber undergoing Step (e) above.
(h) *Countercurrent Pressurization Step I* where the adsorber is pressurized with good quality H_2 from a pressure level of P_D to P_3. The pressurization gas is obtained from an adsorber carrying out Step (d) above.
(i) *Countercurrent Pressurization Step II* which raises the adsorber pressure from P_3 to P_2 using the pressurization gas produced by an adsorber undergoing Step (c) above.
(j) *Countercurrent Pressurization Step III* in which the effluent from Step (b) above from another adsorber is introduced through the H_2 product end to raise the adsorber pressure from P_2 to P_1.
(k) *Countercurrent Pressurization Step IV* similar to Step (g) of the first process where the adsorber is pressurized to the feed gas pressure level (P_A) by using a part of the H_2-rich gas produced by another adsorber undergoing the adsorption Step (a) so that the adsorber can start a new cycle starting from Step (a).

As mentioned earlier, the impurity MTZ's are located in the middle of the adsorber at the end of the adsorption steps of both processes, leaving a relatively clean (impurity free) section in the adsorber near the H_2 product end. The void gas in the part of the adsorber retaining the impurities at the end of the adsorption step has a feed gaslike composition at the highest pressure level of the cycle and therefore it contains a significant amount of H_2. During the cocurrent depressurization steps, the void gas is expanded toward the H_2 product end, and the clean section of the bed adsorbs the impurities from the void gas to produce a good purity H_2 for pressurization and purging of other beds. Any desorbed impurities from the first half of the bed during these pressure reduction steps are also removed by the clean section of the bed. This reduces the void H_2 loss during the countercurrent desorption step. The adsorbers are designed so that the impurities do not significantly breakthrough the H_2 product end during these cocurrent depressurization steps. The elaborate depressurization–pressurization scheme of the second process utilizes this concept to maximize the H_2 recovery by the process.

Obviously, a multibed system is required to maintain continuous feed and product gas flows in the second process. Figure 2 shows a schematic flow diagram using 10 parallel beds for this purpose (*3*). This arrangement allows two of the adsorbers to be in the adsorption step of the cycle at any given time in the cycle while the others are executing Steps (b)–(k) of the cycle. This feature of the second process helps to reduce the total adsorbent inventory of the PSA system.

Using a layer of an activated carbon and a layer of 5A zeolite in the adsorbers like the first process, the second process can produce a 99.999% H_2 product with a H_2 recovery of 86.0% with a feed gas identical to that described in the example for the first process. Here the cycle is operated

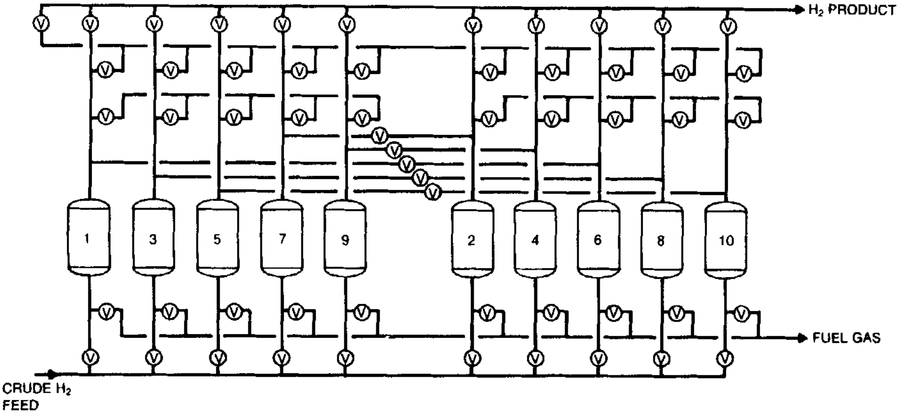

FIG. 2. Schematic of a ten-column PSA system for production of only H_2 from the reformer off-gas.

between an adsorption pressure of 290 psig and a final desorption pressure of 0 psig (*3*). The reject gas in this case contains 32.0% H_2, 66.8% CO_2, 1.0% CO, and 0.04% CH_4. The second process, therefore, offers a trade-off between the H_2 recovery and the capital cost of the PSA system.

Other variations of the second process where the effluent from Step (d) is used to purge another adsorber while the effluent from Step (e) is used for pressurization or adding another cocurrent depressurization–countercurrent pressurization step into the cycle have also been formulated (*3*).

PSA PROCESS FOR SIMULTANEOUS PRODUCTION OF HYDROGEN AND CARBON DIOXIDE FROM REFORMER OFF-GAS

The crude H_2 stream from the reformer contains carbon dioxide as a bulk impurity (15–25%). This CO_2 is wasted in the processes discussed above. Recovery of the CO_2 as a by-product by a PSA process without sacrificing the purity and recovery of the H_2 product can add significant value to the separation process. In addition, the production of a separate CO_2 product decreases the CO_2 content of the reject gas which increases its fuel value.

A PSA process for simultaneous production of high purity H_2 and CO_2 products with high recoveries of both gases has been developed by Air Products and Chemicals (*9*). Figure 3 shows a schematic flow sheet for this process. It consists of six parallel adsorbers (A beds) containing an adsorbent which can selectively adsorb CO_2 and H_2O from the feed gas and three parallel adsorbers (B beds) packed with adsorbents for selective adsorption of CO_2, CO, CH_4, and N_2 impurities from H_2. One A and one B bed are connected in series during the adsorption step of the cycle but they undergo two entirely different sequences of desorption and complementary steps in the process. These steps are described 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 is 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

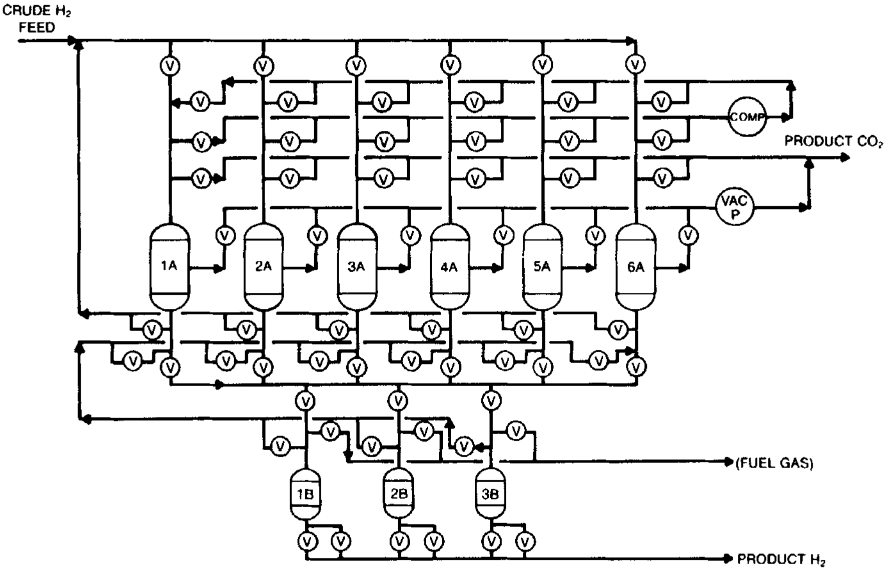

FIG. 3. Schematic of a nine-column PSA system for simultaneous production of H_2 and CO_2 from the reformer off-gas.

has slipped through the A bed. The adsorption step is continued until the CO_2 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, 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 gaslike 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 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), the remainder of this gas is withdrawn as part of the CO_2 by-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 using a vacuum pump. The effluent gas is high purity CO_2, part of which may be used to supply the CO_2 rinse gas in Step (Ab) while the remainder forms part of the CO_2 product gas.

(Ae) Countercurrent Pressurization Step I. After evacuation, the A bed is 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 passes 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 effluent. The bed is pressurized to the feed pressure level 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 purge another B bed (Step Be) as well as 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 impurities along with some H_2 which forms a part of the reject gas.

(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 another B bed undergoing Step (Ba). The effluent of this step forms the remaining portion of the reject gas.

(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 the latter part of 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 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.

The cyclic sequence of steps for the A and the B beds and the interaction between these beds can be better understood from Table 1 which describes the functions of all six A and three B beds of Fig. 3 during a complete cycle. The durations of each step of the cycle and the total cycle time of 24 min used in Table 1 are arbitrarily chosen. It may be seen from Table 1 that the B beds undergo two complete cycles (Steps Ba–Bg) while the A beds go through one complete cycle (Steps Aa–Af). Thus each B bed handles the feed gas from two A beds during a complete cycle of the A beds. This design significantly reduces the adsorbent inventory for the B beds.

TABLE 1
Process Step Sequence of A and B Beds during a Complete Cycle

Time (min)	Adsorbers 1A	2A	3A	4A	5A	6A	1B	2B	3B
0-1	Aa	—	Ae	Ad	Ac	Ab	Ba	Be	Bb
1-2	Aa	—	—	Ad	Ac	Ab	Ba	Bf	Bc
2-3	Aa	—	—	Ad	Ac	Ab	Ba	Bg	Bd
3-4	Aa	—	Af	Ad	Ac	Ab	Ba	Bg	Be
4-5	Ab	Aa	—	Ae	Ad	Ac	Bd	Ba	Be
5-6	Ab	Aa	—	—	Ad	Ac	Bc	Ba	Bf
6-7	Ab	Aa	—	—	Ad	Ac	Bd	Ba	Bg
7-8	Ab	Aa	—	Af	Ad	Ac	Be	Ba	Bg
8-9	Ac	Ab	Aa	—	Ae	Ad	Be	Bb	Ba
9-10	Ac	Ab	Aa	—	—	Ad	Bf	Bc	Ba
10-11	Ac	Ab	Aa	—	—	Ad	Bg	Bd	Ba
11-12	Ac	Ab	Aa	—	Af	Ad	Bg	Be	Ba
12-13	Ad	Ac	Ab	Aa	—	Ae	Ba	Be	Bb
13-14	Ad	Ac	Ab	Aa	—	—	Ba	Bf	Bc
14-15	Ad	Ac	Ab	Aa	—	—	Ba	Bg	Bd
15-16	Ad	Ac	Ab	Aa	—	Af	Ba	Bg	Be
16-17	Ae	Ad	Ac	Ab	Aa	—	Bb	Ba	Be
17-18	—	Ad	Ac	Ab	Aa	—	Bc	Ba	Bf
18-19	—	Ad	Ac	Ab	Aa	—	Bd	Ba	Bg
19-20	Af	Ad	Ac	Ab	Aa	—	Be	Ba	Bg
20-21	—	Ae	Ad	Ac	Ab	Aa	Be	Bb	Ba
21-22	—	—	Ad	Ac	Ab	Aa	Bf	Bc	Ba
22-23	—	—	Ad	Ac	Ab	Aa	Bg	Bd	Ba
23-24	—	Af	Ad	Ac	Ab	Aa	Bg	Be	Bd

PROCESS PERFORMANCE

The PSA cycle described above produces an ultrapure H_2 product at feed gas pressure and a high purity CO_2 by-product at near ambient pressure. It also produces a fuel stream of high Btu value. The H_2 and CO_2 product recoveries are also high (see test results). This is achieved by separating the adsorption beds for removal of the bulk and the dilute impurities from the feed gas after the adsorption step and then carrying out two entirely different sequences of operations for (a) the preservation of void H_2 from the adsorbers and (b) the regeneration of the adsorbents for reuse. The CO_2 rinse step in bed A displaces the void and coadsorbed H_2 left in the bed after the adsorption step with high-purity CO_2. The effluent gas contains all of the displaced H_2 which is recycled as feed gas, thus completely recovering the void H_2. The CO_2 rinse also saturates the

A beds with high purity CO_2 which is recovered in the subsequent depressurization and evacuation steps. These two steps also clean the adsorbent for re-use without any loss of H_2.

A part of the void and the coadsorbed H_2 from the B beds left over after the adsorption step is preserved by the two pressure equalization Steps (Bb) and (Bc) prior to the depressurization (Bd) and the H_2 purge Step (Bc) used for cleaning the bed. This minimizes the H_2 loss from the B beds. The high purity H_2 purge step and the final pressurization of the B beds with high purity H_2 provides extraordinary cleaning of the H_2 product end of that bed which allows production of ultrapure H_2 in the subsequent adsorption step. The removal of most of the CO_2 impurity in the A beds reduces the CO_2 content of the fuel gas which is produced during the regeneration of the B beds.

The A beds are fully utilized during the adsorption and the CO_2 rinse steps of the process. CO_2 is selectively adsorbed in this bed by displacing any preadsorbed CO, CH_4, N_2, and H_2. These displaced components move ahead (rollover effect) of the CO_2 mass transfer zone and they become more concentrated in the process. An isobaric type I column dynamics (*10, 11*) is established for CO_2 adsorption. Two pairs of mass and heat transfer zones are formed in the bed at the start of these steps. The front CO_2 MTZ moves more rapidly than the rear CO_2 MTZ which are separated by an expanding equilibrium section. During the adsorption step, the bed ahead of the front CO_2 MTZ contains a very complex concentration profile of CO_2, CO, CH_4, N_2, and H_2 created by the transfer of those impurities from the B bed during the first pressurization step and by the displacement (rollover) of these impurities from the adsorbed phase by selective adsorption of CO_2. The middle equilibrium section contains a gas having a composition very close to that of the feed gas. The temperature of this section, however, goes up to T_1^* due to accumulation of the heat of adsorption left behind by the moving front CO_2 MTZ. During the CO_2 rinse step, the bed ahead of the front CO_2 MTZ contains the displaced components, and the middle equilibrium section contains essentially pure CO_2. The temperature of this section reaches the highest temperature level (T_2^*) in the cycle. The process results in a high production capacity (amount of feed processed per unit amount of adsorbent) for the A beds. The A beds contain a large amount of residual CO_2 at the beginning of the pressurization steps at the cyclic steady-state operation of the process.

The operation of the B beds is much more complex due to back and forth transfer of the impurities with changing concentrations between the B and B and the B and A beds during the pressure equalization and the pressurization steps as well as due to rollover of dilute impurities from the A beds during the adsorption step. Consequently, the concentration of CO_2, CO, and CH_4 impurities entering the B beds during the adsorption step varies with time and their maximum concentrations are much greater than those in the feed gas.

Nevertheless, the feed end of the B beds retain the CO_2 impurities with some coadsorbed CO and CH_4 followed by a section where CO is preferentially adsorbed with some coadsorption of CH_4, N_2, and H_2. The B bed near the H_2 product end is used to retain the CH_4 and N_2 impurities with a considerable amount of coadsorbed H_2. This section is practically free of CO_2 and CO impurities (<1 ppm). The adsorption step in the B bed is stopped when the CH_4 or N_2 starts to break through the H_2 product end. Thus it is possible to produce a H_2 product by this process with very little CH_4 or N_2 in it (<10 ppm) and practically no carbon oxide impurities (<1 ppm) or to produce a hydrogen product with some CH_4 and N_2 impurities (e.g., 0.1–0.5%) but no CO or CO_2. This latter option increases the H_2 recovery by the process and reduces the size of the B beds.

This is a significant operational advantage of this process which permits a good control over the H_2 product purity. It can be utilized to produce a hydrogen stream free from CO and CO_2 impurities for hydrocracker application in petroleum refinery where a relatively high level of methane impurity can be tolerated.

PROCESS TEST DATA

A multibed pilot unit was used to study the performance of the PSA process for simultaneous production of CO_2 and H_2 products using a feed gas containing 75.4% H_2, 19.88% CO_2, 0.96% CO, and 3.73% CH_4 at 18°C. The feed gas pressure was varied between 200–300 psig. The A and B adsorbent beds were 2 in. in diameter and 156 in. long, and they were externally insulated. The beds were packed with a proprietary adsorbent for selective removal of CO_2, CO, CH_4, and N_2 from H_2. The adsorbent particles were 1/16 in. extrudates with a bulk density of 42–48 lb/ft^3. Each run was carried out until cyclic steady state was established which usually took 10–15 cycles of operation. The steady state was reached smoothly without any noticeable excursions in the product and the other effluent gas concentrations and pressures from the PSA system, and the process performance was extremely stable after that. The same steady state was achieved in 10–15 cycles irrespective of the initial column conditions. This proved that the apparently complex sequential steps of this process and the interactions between them do not have any adverse effect on the process performance during start-up and subsequent steady-state operation.

Figure 4 shows the temperature changes of the A bed during a complete cycle after cyclic steady state is reached. The data show a typical central line column temperature as a function of time. The fractional duration of each step of the process is also given in the figure. The temperature is 7°C at the start of the first pressurization Step (Ae) and it reaches 11°C at the end of that step. The temperature rises to 17°C at the end of the second pressurization Step (Af). A sharp temperature rise to 41°C (T_1^*) takes place when the CO_2 MTZ reaches the point of temperature measurement during the adsorption Step (Aa) and a second sharp rise in temperature to 49°C (T_2^*) occurs when the CO_2 MTZ of the

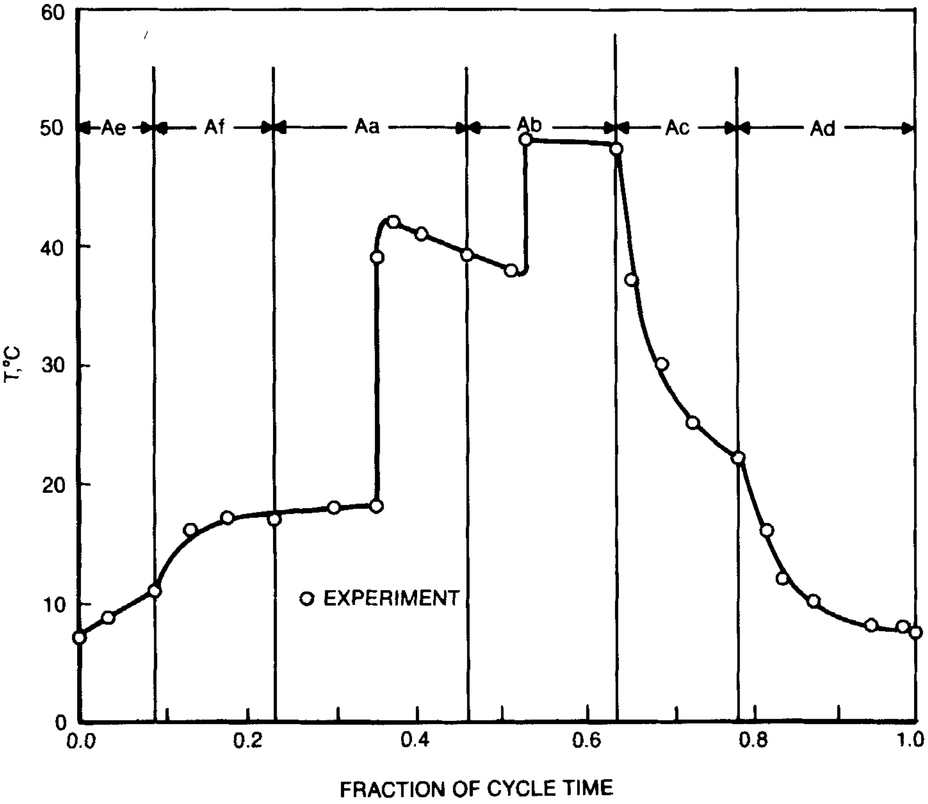

FIG. 4. Column temperature changes in the A beds during a complete cycle.

CO_2 rinse Step (Ab) reaches that point in the column. During the depressurization Step (Ac) the temperature goes down to 22°C and then it is further reduced to 7°C at the end of the evacuation Step (Ad).

Figure 5 shows the variation of the impurity concentration with time in the feed gas entering the B bed during the adsorption step of the process, and Figure 6 shows the gas phase mole fractions of the impurities as a function of the distance in the B bed from the feed end at the end of the adsorption step. The complex concentration–time profiles of the impurities entering the B beds during the adsorption step are caused by the transfer of the impurities from the B bed to the A bed during pressurization (Step Ae) of the A bed using desorbed and void gases from the B bed (Step Bb) as well as by the "rollover" effect in the A bed produced by the displacement of adsorbed CO and CH_4 by CO_2 during the adsorption step. At the cyclic steady state, the CO and CH_4 concentrations of the desorbed gases from the B bed (Step Bb) are much higher than those in the fresh feed to the PSA system. These impurities are readsorbed near the effluent end of the A beds during the pressurization step, and they are eluted out of the A beds by H_2 produced during the initial portion of the adsorption step. Thus the concentrations of CO and CH_4 in the effluent gas from the A beds start at a high level and then decrease as shown by Fig. 5. The subsequent rise in the concentration levels of these impurities in the effluent gas in the latter part of the adsorption step is caused by the "rollover" effect in the A beds. The CO_2 and CO impurities are essentially retained in the first 31 and 62% of the bed, respectively, while the CH_4 impurity zone is elongated. The maximum concentration of these impurities in the B bed at the cyclic steady state of operation of the process are much higher than those in the feed gas mixture.

Table 2 summarizes the overall process performance and reports the amounts and compositions of some of the major process streams. The amounts are given as the quantity of the gas per unit amount of fresh feed gas to the PSA system. The data of Figs. 4 and 5 correspond to Run (b) of Table 2.

It may be seen from Table 2 that the process can produce ultrapure H_2 (99.999+%) with a high H_2 recovery from the feed gas (86–87%) simultaneously with a CO_2 by product containing 99.4% CO_2 with a recovery of 90+%. The fuel gas stream produced by the process is very rich in H_2 and CH_4, containing only 8–10% CO_2. The fuel gas, therefore, has a very good Btu value. The CO and CH_4 concentrations of the fuel gas are about six times larger than those in the feed gas. In contrast, the fuel gas from the processes described earlier contain a large (55–67%) amount of CO_2 and the CO and CH_4 concentrations are enriched by a

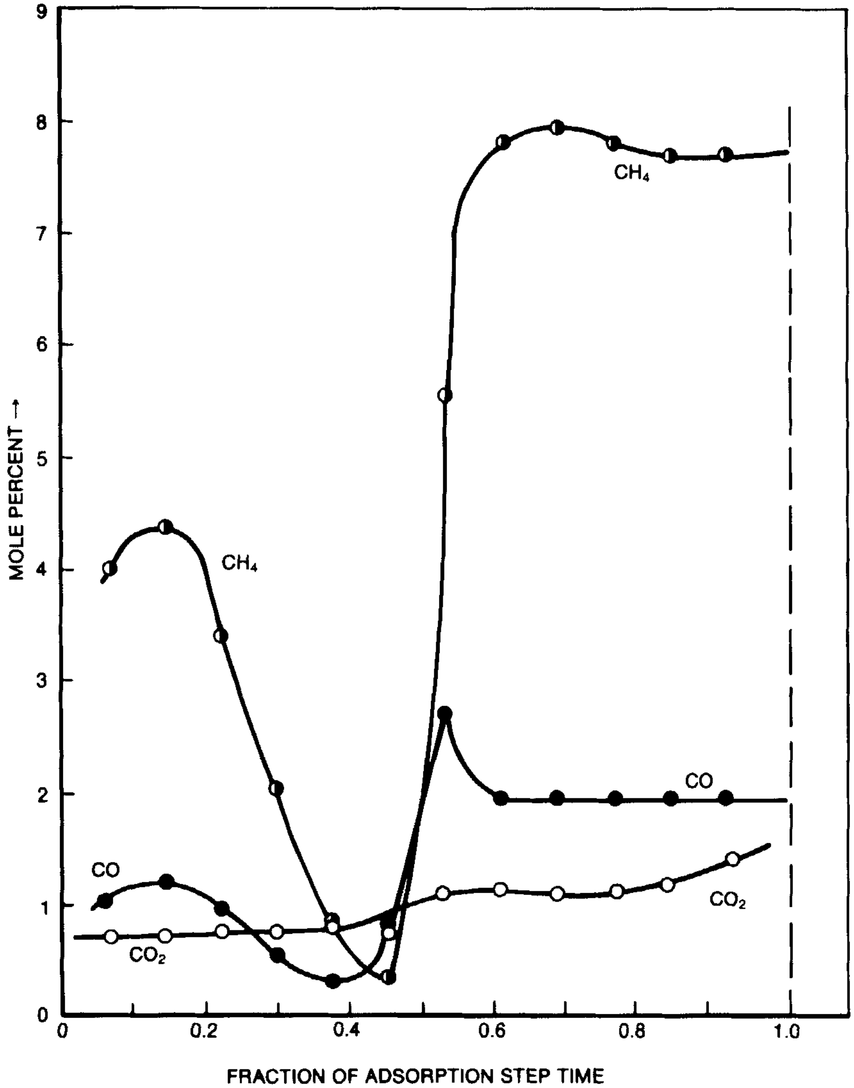

FIG. 5. Variation of the impurity concentration in the feed gas to B bed during the adsorption step.

TABLE 2
Performance of the PSA Process for Simultaneous Production of H_2 and CO_2

	Feed[a]	Relative amounts of gases				H_2 product			CO_2 product			Fuel gas				
													Mole%			
Run	P (psig)	CO_2 rinse	A Bed desorption	A Bed evacuation	H_2 purge to B bed	Amount	% H_2	Recovery (%)	Amount	% CO_2	Recovery (%)	Amount	CO_2	CO	CH_4	H_2
(a)	200	0.252	0.275	0.160	0.078	0.645	99.999+	85.9	0.183	99.4	90.1	0.180	9.5	6.0	22.5	61.9
(b)	250	0.259	0.295	0.152	0.061	0.657	99.999+	87.1	0.188	99.4	94.0	0.172	8.1	5.6	20.8	65.4
(c)	300	0.283	0.310	0.144	0.050	0.656	99.999+	86.7	0.171	99.4	86.9	0.165	10.7	6.3	23.6	59.3
(d)	250	0.259	0.294	0.154	0.048	0.672	99.962	89.0	0.189	99.3	94.5	0.157	8.6	5.8	21.6	63.8

[a] Feed gas contains 75.4% H_2, 19.9% CO_2, 0.96% CO, and 3.73% CH_4.

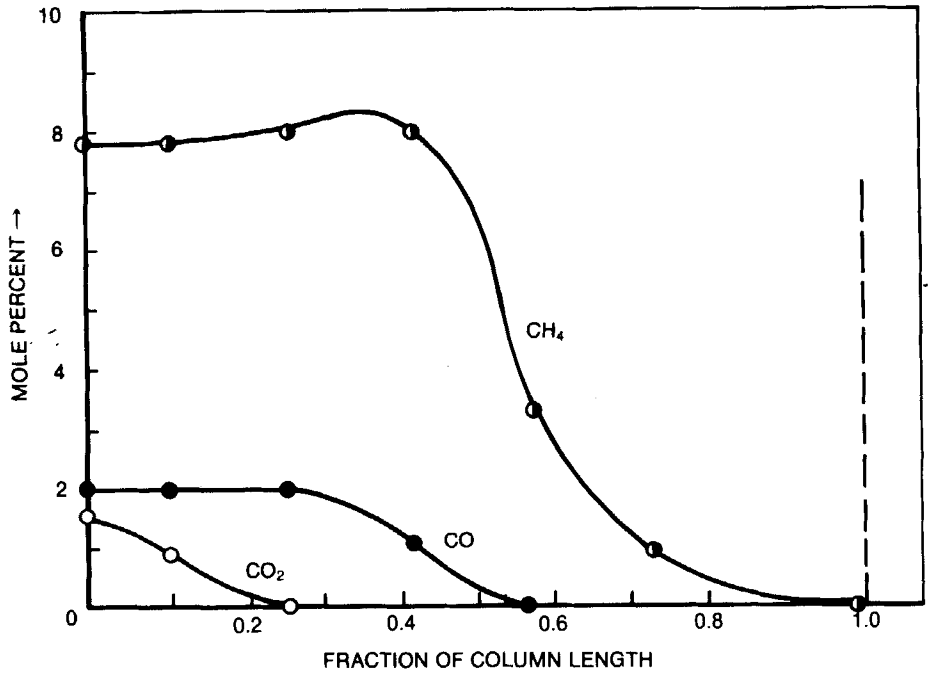

FIG. 6. Gas-phase impurity mole fractions in the B beds at the end of the adsorption step.

factor of 2–3 only. This results in a very poor quality fuel gas for these processes.

The H_2 recovery can be increased (Run d) by 2% if the product purity is reduced from 99.999+% (Run b) to 99.96+% (only CH_4 impurity). Thus the present process can have a significant advantage for certain H_2 purification applications mentioned above. The performance of the process (higher H_2 recovery, smaller adsorbent inventory) can be further improved by employing a better adsorbent in the CH_4 adsorption section of the B beds.

A practical advantage of this process was found to be its flexibility in handling feed gases of varying composition and pressure without sacrificing the purities and the recoveries of the major products. It could be achieved by varying the times of the individual steps in the cycle and the feed gas flow rate.

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