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

Separation of Methane and Carbon Dioxide Gas Mixtures by Pressure Swing Adsorption

Shivaji Sircar[a]
[a] Air Products and Chemicals, Inc., Allentown, Pennsylvania

To cite this Article Sircar, Shivaji(1988) 'Separation of Methane and Carbon Dioxide Gas Mixtures by Pressure Swing Adsorption', Separation Science and Technology, 23: 6, 519 — 529
To link to this Article: DOI: 10.1080/01496398808057650
URL: http://dx.doi.org/10.1080/01496398808057650

SEPARATION SCIENCE AND TECHNOLOGY, 23(6 & 7), pp. 519-529, 1988

Separation of Methane and Carbon Dioxide Gas Mixtures by Pressure Swing Adsorption

SHIVAJI SIRCAR

AIR PRODUCTS AND CHEMICALS, INC.
ALLENTOWN, PENNSYLVANIA 18105

Abstract

Two pressure swing adsorption processes for separation of methane and carbon dioxide gas mixtures are described. One process simultaneously produces a high purity CH_4 and a high purity CO_2 product with high recoveries of both components from the feed gas. The other process only produces a high purity CH_4 product with high recovery. Test data for these processes are reported and their relative advantages are discussed.

Separation of bulk gas mixtures containing methane and carbon dixoide is an important problem in the chemical industry. Many natural gas reservoirs contain up to 50% CO_2 as impurity. The effluent gas from an oil well undergoing CO_2 flooding for enhanced oil recovery may contain 20–80% CO_2 and CH_4. A typical municipal or industrial landfill gas consists of 40–60% CO_2 and CH_4. It may be necessary to separate the CH_4 and the CO_2 from these gases in order to improve their fuel value and to recover and reuse the CO_2.

Different separation methods such as physical or chemical absorption of CO_2 in a solvent, selective permeation of CO_2 through a polymeric membrane, selective adsorption of CO_2 on a solid adsorbent, etc. may be used to achieve this goal. The purpose of this paper is to describe two pressure swing adsorption (PSA) processes which can carry out the required separation very efficiently.

PSA PROCESS PRINCIPLES

The principle of separation used by the PSA technology is selective adsorption of one or more components of the feed gas mixture on a solid adsorbent so that an adsorbed phase having a composition different from that of the feed gas is formed when it is contacted with the solid. This produces a gas stream enriched in the less selectively adsorbed species of the feed gas. The adsorbed components are then desorbed by reducing their superincumbent partial pressures to produce a gas stream enriched in the more selectively adsorbed component of the feed gas. The desorption process also cleans the adsorbent for reuse. Consequently, a practical PSA process consists of a cyclic sequence of various adsorption and desorption steps along with other complementary steps. The adsorption is usually carried out by contacting the feed gas with an adsorbent in a packed fixed bed or by flowing the gas over the adsorbent bed at the highest pressure level of the cycle. The desorption is generally achieved by lowering the pressure of the bed or by flowing a gas stream enriched in the less selectively adsorbed species of the feed gas through the bed or by a combination of these methods. Complementary steps like pressure equalization, where a part of the void gas from one adsorbent bed is directly transferred to another bed for preservation of the valuable components in the void gas, and pressurization, whereby the adsorbent bed is brought back from its lowest pressure level in the cycle to the highest pressure level, are also practiced in various combinations.

Usually these steps are carried out using two or more adsorbent beds so that when one or more beds are undergoing the adsorption steps, the other beds are carrying out the desorption and the complementary steps of the process in order to get ready for a new adsorption step. Every bed cyclically goes through each step of the process. Thus, each bed operates in a cyclic steady-state manner even though any particular step in the cycle is an unsteady-state process. A typical total cycle time for the PSA process is between one to several minutes. The durations of the individual steps may be equal or not, but a continuous feed and product gas flow can be achieved by the integrated performance of the multibed system. It is also possible to maintain a continuous product gas flow by using gas storage tanks and a lesser number of adsorption beds. The choice is dictated by the economics of the process.

ADSORBENT FOR CO_2-CH_4 SEPARATION

All inorganic adsorbents (zeolites, aluminas, silica gels) and organic adsorbents (activated carbons) selectively adsorb CO_2 over CH_4 because

of its larger molecular weight and because CO_2 has a permanent quadrupole moment (4.3×10^{-26} e.s.u. cm^2) while CH_4 is nonpolar. The adsorption capacities of these gases, their heats of adsorption, and the selectivity of adsorption of CO_2 over CH_4 as functions of gas pressure, temperature, and composition, however, can be significantly different for different adsorbents. The preferred adsorbent should offer high working adsorption capacity for CO_2 (difference between the amounts of CO_2 adsorbed at the end of the adsorption step and at the end of the desorption steps), high selectivity of adsorption for CO_2 over CH_4, and low heat of adsorption for CO_2. It should also provide relatively fast kinetics of ad(de)sorption for both CO_2 and CH_4.

PSA PROCESS FOR SIMULTANEOUS PRODUCTION OF CO_2 AND CH_4

The following PSA process for separation of CO_2 and CH_4 mixtures was developed and commercialized by Air Products and Chemicals, Inc. (*1*). It is designed to simultaneously produce a stream of high purity CH_4 (~99.0%) and a stream of high purity CO_2 (~99.0%) from a CO_2-CH_4 feed gas mixture. The recoveries of both components are also very high (~99.0%). The process consists of the following cyclic steps.

(a) Adsorption Step

The feed CO_2-CH_4 gas mixture is passed through a packed bed containing the CO_2 selective adsorbent at the highest pressure level of the PSA cycle. The bed has been previously pressurized to the feed gas pressure level with a CH_4-rich gas. The effluent from the bed constitutes a CH_4-rich gas, a part of which is withdrawn as the CH_4 product gas. The remaining gas is used for the bed pressurization step described later. Adsorption is continued until the effluent gas reaches its maximum tolerable CO_2 concentration level.

(b) Carbon Dioxide Rinse Step

At the end of the adsorption step, the bed is rinsed with a stream of high purity CO_2 at about the feed gas pressure in the same direction as feed gas flow (cocurrent). The effluent from the bed during this step has a feed gas-like composition which is recycled as feed to another bed by

mixing it with the fresh feed stream. The step is continued until the bed is essentially saturated with high purity CO_2.

(c) Depressurization Step

The CO_2 saturated bed is then depressurized from the feed pressure level to near atmospheric pressure level by withdrawing gas from the feed end of the bed in a direction opposite to that of feed gas flow (countercurrent). The desorbed gas consists of high purity CO_2, a part of which is recompressed to the feed pressure level and used as the CO_2 rinse gas to another bed. The remainder of the gas is withdrawn as part of the CO_2 product gas. A CO_2 compressor is used for this purpose.

(d) Evacuation Step

At the end of Step (c), the bed is evacuated through the feed end (countercurrent) to the lowest desorption pressure level of the cycle using a vacuum pump. The desorbed gas is high purity CO_2, a part of which may be used as the CO_2 rinse gas in Step (b). The balance forms the remaining part of the CO_2 product gas.

(e) Pressurization Step

The bed is finally pressurized to the feed pressure level by introducing a part of the CH_4-rich gas produced during Step (a). The gas is introduced into the bed through the CH_4 product end (countercurrent), and it is available from a companion bed undergoing Step (a).

The bed is now ready to undergo a new cycle starting from Step (a).

One mode of operation of this five-step process is to use five adsorbent beds in parallel, each undergoing one step of the process at any given time. Figure 1 shows a schematic flow diagram for this embodiment. This configuration allows continuous feed gas flow and product gas withdrawal as well as continuous operation of the rotating machines. CH_4 and CO_2 product surge tanks (S_1 and S_2) and a mixing tank (S_3) to mix the effluent of Step (b) with fresh feed gas may or may not be necessary for smooth operation of the process. The CH_4 product gas is produced essentially at the feed gas pressure, and the CO_2 product gas is produced at near atmospheric pressure by this process.

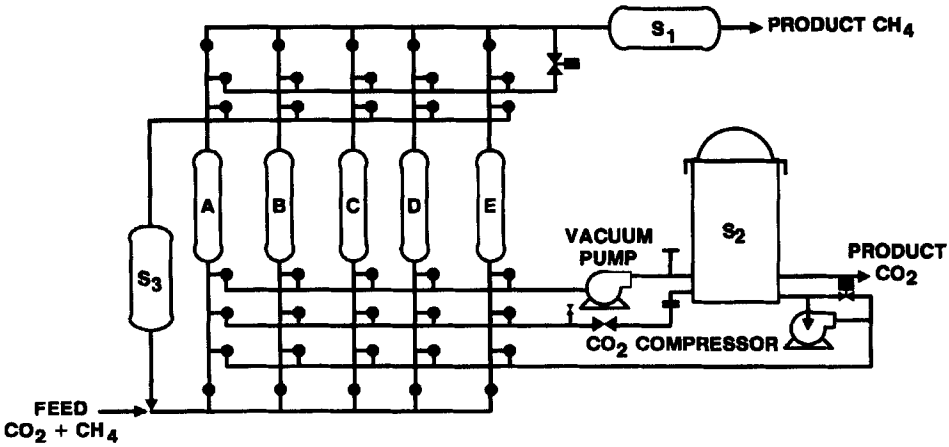

FIG. 1. Schematic flow diagram for the PSA process for the separation of CO_2-CH_4 mixtures.

PROCESS PERFORMANCE

The process is designed for very efficient use of the adsorbent. During the adsorption step, which is carried out under an isobaric condition, a type I column dynamics is established within the bed (*2*, *3*). Two pairs of mass and heat transfer zones are formed within the bed which are separated by an expanding equilibrium section. The front pair of transfer zones moves much faster than the rear pair. The bed ahead of the front mass transfer zone (MTZ) remains saturated with the CH_4-rich pressurization gas while the bed behind the rear MTZ is equilibrated with the feed gas. The section between the two zones is equilibrated with a gas having a composition very close to that of the feed gas but its temperature is elevated (T_1^*) due to the accumulation of the heat of adsorption in this section. The heat is generated in the front MTZ but it is left behind as the zone moves. During the CO_2 rinse step, another isobaric type I column dynamics is established. The bed ahead of the front MTZ, in this case, is saturated with the feed gas at T_1^* and the bed behind the rear MTZ is equilibrated with pure CO_2. The middle equilibrium section contains essentially pure CO_2 but its temperature goes up further to T_2^*. Since the adsorption and the CO_2 rinse steps are continued until the leading edges of the corresponding front MTZs are about to break through the CH_4 product end of the bed, and the lengths of these MTZs are relatively small compared to the bed length due to fast kinetics of adsorption, the bed is utilized to its full capacity for adsorption of CO_2 from the feed gas

mixture and the CO_2 rinse gas during these steps. This results in large specific production capacity (amount of gas processed per unit amount of the adsorbent) for this process. The CO_2 rinse essentially displaces the void and the coadsorbed CH_4 from the bed left behind at the end of the adsorption step by good purity CO_2. This is important because it increases the CO_2 product purity and the overall CH_4 and CO_2 recovery by the process.

The process was tested using a 96-in. long bed which was externally insulated. A 42.5% CO_2 + 57.5% CH_4 gas mixture was used as feed. A proprietary zeolite was used as the adsorbent. The feed gas pressure was varied between 5.8 and 12.5 atm and the feed temperature was 21–22°C. The final evacuation pressure was between 50 and 200 torr. The adsorption step was controlled in such a way that a CH_4 product containing 98.8–99.0% CH_4 was obtained. The CO_2 rinse step was controlled to obtain a CO_2 product containing 99.0% CO_2. The test data were gathered after a cyclic steady state was attained in each run, which usually took 5–7 cycles of operation.

Figure 2 shows a typical steady-state bed temperature profile during a complete cycle. The central line column temperature at the middle of the adsorbent column is plotted as a function of time (Run b, Table 1). The

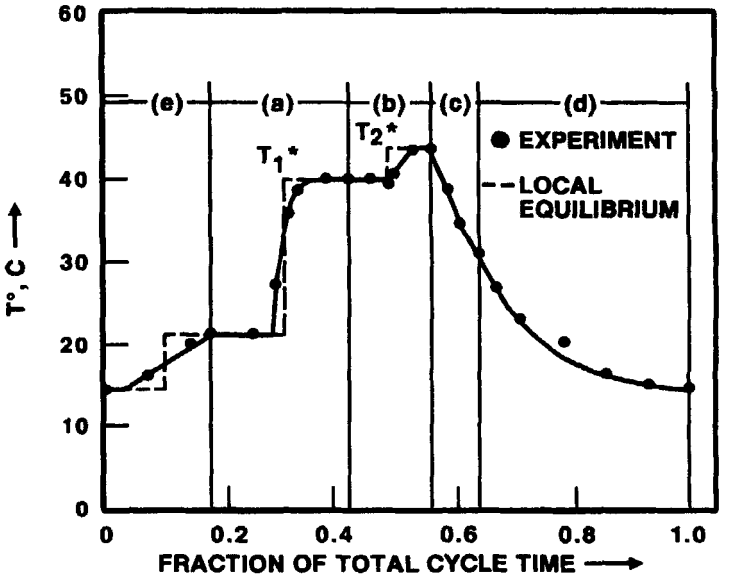

FIG. 2. Adsorber midpoint column temperature change during Steps (a)–(e) of the PSA process.

fractional cycle times for each step of the process are indicated in the figure. The midpoint column temperature starts at 15°C and goes up to 22°C during the pressurization step. The temperature rises to 41°C (T_1^*) when the front MTZ of the adsorption step arrives at the column midpoint. The temperature further rises to 45°C (T_2^*) when the front MTZ of the CO_2 rinse step reaches the midpoint. The temperature then falls to 33°C during the depressurization step and finally cools down to 15°C at the end of the evacuation step when a new cycle begins. The dashed lines in Fig. 2 show the temperature profile in the column which would be exhibited if the mass and heat transfer resistances were negligible (local equilibrium conditions).

Table 1 summarizes the overall performance of the process which gives the purity and the amount of each major stream of the process. The amount of gas is reported as millipound moles per pound of adsorbent per cycle. The table shows that the process provides a very efficient method for separating the CO_2–CH_4 mixture. A very high recovery of both components of the mixture at high purity can be achieved.

It may also be seen from Table 1 that the overall CH_4 and CO_2 production capacities of the process are not significantly affected by the change in the feed gas pressure in the range studied. Although the absolute CO_2 capacity of the adsorber during the adsorption step increases with increasing partial pressure of CO_2 in the feed gas, the amount of void and coadsorbed CH_4 in the adsorber also increases with increasing feed gas pressure. This, in turn, increases the feedlike effluent from the adsorber during the CO_2 rinse step which is recycled as feed; thus the amount of fresh feed to the adsorber does not change appreciably with increasing feed gas pressure. In fact, the amount of fresh feed decreases if the feed gas pressure is increased substantially. The CO_2 rinse gas quantity increases with increasing feed gas pressure because it has to displace larger amounts of CH_4 from the bed and because of larger CO_2 capacity at higher CO_2 rinse gas pressure. The depressurization gas quantity increases with increasing feed and CO_2 rinse gas pressures, but the evacuation gas quantity is not affected by them as expected.

ENERGY OF SEPARATION

The energy of separation for the above-described process is supplied through the feed and CO_2 rinse gas compressors and the vacuum pump. The energy consumed by the vacuum pump is approximately proportional to the rate of actual volumetric displacement (V, ft^3/min) of the

TABLE
Performance of the CO_2-CH_4 PSA Separation

	Fresh feed			CO_2 rinse		Depressurization	
Run	P (atm)	% CH_4	Amount	P (atm)	Amount	% CO_2	Amount
a	5.8	57.5	2.08	5.8	0.80	98.9	0.73
b	7.1	57.5	2.16	7.1	0.83	98.5	0.83
c	12.5	57.5	1.96	12.5	1.30	98.6	1.22
d[a]	7.1	57.5	2.62	7.1	0.91	99.4	0.87

[a]Process with inert gas purge step using 1.35 mmol/lb of adsorbent N_2 purge.
[b]55.0% CO_2, 44.9% N_2, 0.1% CH_4.

pump (*4*). For example, the brake horsepower of a roots or lobular vacuum pump is equal to $0.0285V^{1.043}$. V can be calculated from the evacuation characteristics of the adsorbent by the following mass balance across the pump:

$$\frac{VP}{RT} = W\frac{dQ}{dt} \tag{1}$$

where Q (lb mol/lb) is the total amount of gas evacuated (desorbed) per unit amount of the adsorbent in time t (min) and P (atm) is the adsorber pressure at that time. (dQ/dt) is the instantaneous rate of evacuation at time t when the gas pressure at the pump inlet and the adsorber is P. W (lb) is the total amount of adsorbent in the bed. R is the gas constant, and T is the gas temperature at the pump inlet. Equation (1) assumes that V does not vary with P, and that the pressure drops in the adsorber and the gas headers are negligible.

Equation (1) can be integrated to get

$$V = W\frac{RT}{t_E}\int_1^{P_D}\frac{dQ}{P} = W\frac{RT}{t_E}I \tag{2}$$

where t_E is the total evacuation time for the PSA cycle in which the bed pressure changes from 1 atm to the final evacuation pressure of P_D (atm). Equation (2) shows that for a given adsorber size, P_D, and t_E, V is proportional to the integral I of Eq. (2) which can be evaluated from the desorption characteristics (Q vs P) of the system.

For example, Curve (a) in Fig. 3 shows the desorption characteristics of

1
Processes (amounts are in mlb mol/lb adsorbent)

Evacuation		CH_4 product			CO_2 product		
% CO_2	Amount	% CH_4	Recovery	Amount	% CO_2	Recovery	Amount
99.5	0.95	98.8	99.7	1.21	99.0	97.8	0.87
99.3	0.94	98.8	99.3	1.25	99.0	98.1	0.91
99.0	0.95	99.0	99.3	1.13	99.0	98.6	0.83
55.0[b]	0.43	99.0	99.2	1.51	—	—	—

CO_2 from the zeolite plotted as $1/P$ vs Q. The area under this curve between $P_D \leqslant P \leqslant 1$ is equal to the integral I. The figure shows that a large amount of CO_2 is desorbed at the lower values of P because it is very strongly adsorbed on the zeolite. Consequently, the energy needed for the evacuation step of this process is a considerable part of the total energy of separation. The value of I for Curve (a) of Fig. 3 is 1.04 mlb mol/lb of adsorbent/atm for a P_D of 200 torr.

PSA PROCESS FOR PRODUCTION OF CH_4 ONLY

An alternative PSA cycle can be designed for separation of CO_2–CH_4 mixtures which can reduce the evacuation energy of the above-described process significantly without sacrificing the CH_4 product purity and recovery (*1*). The process, however, does not produce a CO_2 by-product and it does require a source of dry inert gas (e.g., nitrogen).

The PSA cycle, in this case, consists of Steps (a)-(c) of the first process. Thereafter, (d) the bed is purged with an inert gas countercurrent to the direction of feed at near ambient pressure in order to desorb most of the remaining CO_2 from the bed after depressurization Step (c). The inert gas is introduced into the bed through the CH_4 product end. The effluent gas from this step consists of CO_2 contaminated with the inert gas, which is wasted. The bed is then (e) evacuated countercurrently through the feed end to desorb the inert gas and the remaining CO_2, which is wasted. Finally (f) the bed is countercurrently repressurized to the feed gas pressure with the CH_4-rich product as in Step (e) of the first process so that a new cycle can start.

This six-step cycle can be implemented using six adsorbent beds in parallel and a flow diagram similar to that of Fig. 1. However, a lesser

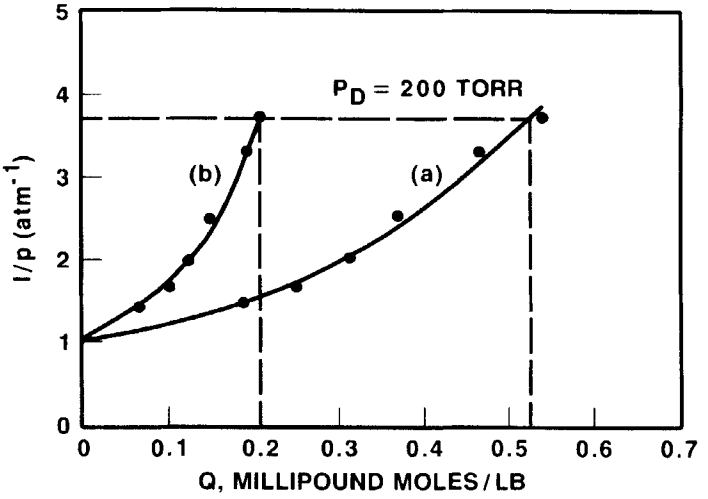

FIG. 3. Desorption characteristics from the zeolite during the evacuation step: (a) first process, (b) second process.

number of beds can be employed by properly designing the individual cycle times for the steps and using gas storage tanks.

Run d of Table 1 shows the performance of this process using operating conditions comparable to those for the first process (Run b). The amount of inert purge gas (N_2) used was 1.35 mlb mol/lb of the adsorbent. It may be seen that the inert gas purge step increases the working adsorption capacity of the bed for CO_2 by providing a cleaner bed at the start of the adsorption step. This is reflected by about a 20% increase in the CH_4 production capacity of the process while maintaining the high CH_4 product purity and recovery. A large amount of residual CO_2 remains in the bed at the cyclic steady state of the first process. The extent of CO_2 removed by the inert gas purge step of the second process depends on the quantity of purge gas used.

Figure 3(b) shows the desorption characteristics of the bed after the inert gas purge. For a P_D of 200 torr, the total quantity evacuated is only 41% of that for the first process. The desorption curve, in this case, is drastically different from that of the first process due to weak adsorption of N_2 on the zeolite. The integral I for Curve 3(b) has a value of only 0.41 mlb mol/lb/atm. This indicates that the second process has a potential of reducing the vacuum pump size and energy by 39.5% compared to the first process. It may be seen from Table 1 that the inert gas purge also reduces the CO_2 rinse quantity per unit amount of CH_4 product, which translates into a smaller CO_2 compressor and energy.

All of these advantages of the second process must be weighed against the availability and cost of the inert gas and the absence of CO_2 product in that process. A higher capital investment may also be required for a six-bed system, so this process offers a trade-off between capital and energy costs.

The processes described in this paper can be used to separate other binary gas mixtures of industrial importance (CO_2/H_2, CO/H_2, CH_4/N_2, N_2/H_2, etc.) provided the appropriate adsorbents for these separations can be found.

REFERENCES

1. S. Sircar and J. W. Zondlo, U.S. Patent 4,077,779 (1978).
2. S. Sircar and R. Kumar, *Ind. Eng. Chem., Process Des. Dev., 22,* 271 (1983).
3. C. Y. Pan and D. Basmadjian, *Chem. Eng. Sci., 25,* 1653 (1970).
4. G. A. Huff, *Chem. Eng.,* p. 83 (1976).

Received by editor July 20, 1987