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Separation of a Binary Gas Mixture by Pressure Swing Adsorption: Comparison of Different PSA Cycles

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Abstract. Gas separation of a binary gas mixture by various pressure swing adsorption (PSA) cycles was studied by a numerical simulation in order to provide a guidance in selecting PSA cycles. PSA cycles considered in this study are 3, 4-step cycles for production of only one component and a cycle with pressure equalization for production of a light component. 4 and 5-step cycles for simultaneous production of both components of a binary gas mixture are also considered. Separation of a CH_4/CO_2 gas mixture with zeolite 5A was chosen as a case study. Performances of cycles were examined and compared in view of purity, recovery and productivity. Their relative advantages were discussed. Inclusion of a purging step to a 3-step cycle for production of only one component improves a cycle performance. Further performance improvement of a cycle for production of a light component can be achieved by employing pressure equalization. Sircar's 4-step cycle with a recycle of effluent shows the best performance in view of purity and recovery among cycles for simultaneous production of both components.

Keywords: processes and applications—bulk separation, simulation, pressure swing adsorption

1 Introduction

Pressure swing adsorption (PSA) has been used widely in gas separation for its simplicity and a low energy consumption. Since the first introduction of a basic 4-step PSA cycle by Skarstrom (1960), modified and new cycles have been proposed to improve a performance of separation or to separate a binary gas mixture simultaneously. The basic 4-step cycle has been most intensively studied theoretically and experimentally for production of a light component (less preferentially adsorbed component) from a binary gas mixture by equilibrium-based separation (Shendalman and Michell, 1972; Chihara and Suzuki, 1983; Knaebel and Hill, 1985; Raghavan and Ruthven, 1985; Hassan et al., 1985; Raghavan, 1986), or for production of a heavy component (more preferentially adsorbed component) by kinetic separation (Shin and Knaebel, 1987, 1988; Hassan et al., 1986). A simple 3-step cycle excluding a purge step of the basic 4-step was also examined (Fernandez and Kenney, 1983; Cheng and Hill, 1983, 1985; Lu et al., 1993). A PSA cycle with pressure equalization (PE) was studied for an increase of component recovery (Hassan et al., 1987; Farooq and Ruthven, 1991). Cocurrent depressurization is included in the basic 4-step cycle in order to obtain purified both components of a binary mixture (Yang and Doong, 1985, 1986, 1987). Kapoor and Yang (1989) investigated a 4-step cycle including cocurrent depressurization and evacuation steps instead of high pressure feed and purge steps. They also examined a 5-step cycle incorporating a high pressure feed step into their 4-step cycle. A cycle including a heavy-component rinse step instead of a cocurrent blowdown was proposed by Sircar (1988) for a simultaneous production of a high purity of light and heavy components.

Since all those prior works focused mainly on an investigation of effects of operating parameters in one or two selected cycles, they are helpful for understanding the selected cycles. However, they do not provide a guidance in selecting an appropriate cycle for separating a gas mixture in a given situation. Selection of a suitable cycle requires separation performances of all possible PSA cycles. Therefore, the present work is concerned with comparing performances of PSA cycles for separating a binary gas mixture on an equilibrium basis, thereby providing a guidance in selecting an appropriate cycle. Cycles for production of only one component and both components shown in literatures are considered. Their separation performances are determined by a mathematical simulation. The system considered here is a separation of CH_4/CO_2 gas

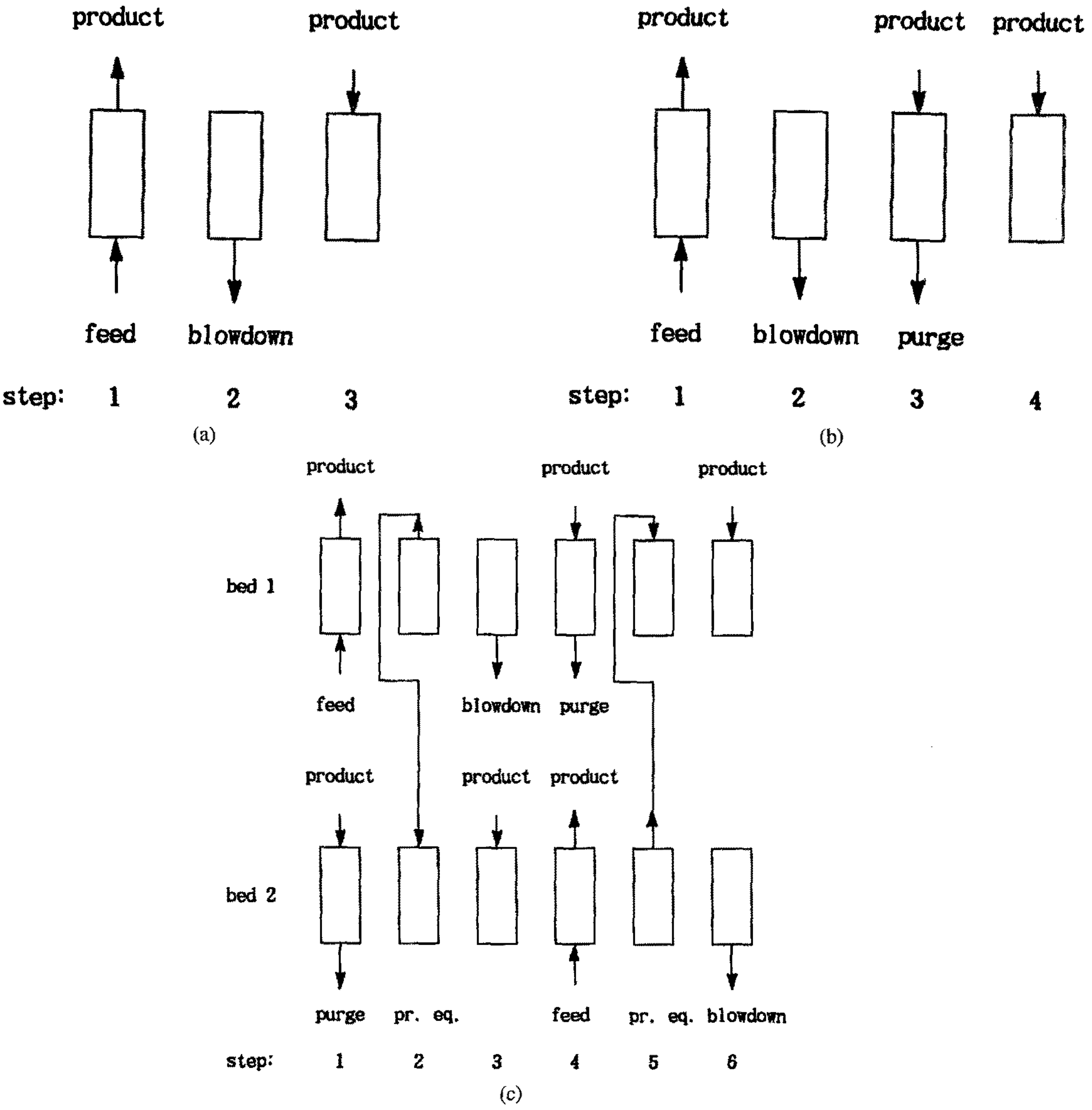


Fig. 1. Cycles for light-component production: (a) 3-step (b) 4-step (c) two-bed cycle with PE steps.

mixture with 5A zeolite. An equilibrium cell model is used in simulating PSA cycles for its simplicity. Cycle performance is examined in terms of product purity, component recovery, and productivity.

2 Theory

2.1 Process Description

2.1.1 Cycles for Production of Only One Component. The process considered here utilizes one column packed with an adsorbent. PSA cycles for production of light or heavy components are shown in Figs. 1 and 2 respectively. The processes shown in Figs. 1, 2, and 3 in the following section are single-bed processes even though they require normally at least two beds in actual operations. The reason of considering a single-bed process is to reduce a computation time and complexity required in the simulation. Since each bed of a multi-bed PSA process shows an identical performance during cyclic steady-state, a simultaneous simulation of all beds is not necessary. The 4-step cycle for light-component production in Fig. 1(b) is a modified Skarstrom's cycle, where a bed is pressurized with a product rather than a feed. The 3-step cycle in Fig. 1(a) is the one without a purge step of the 4-step

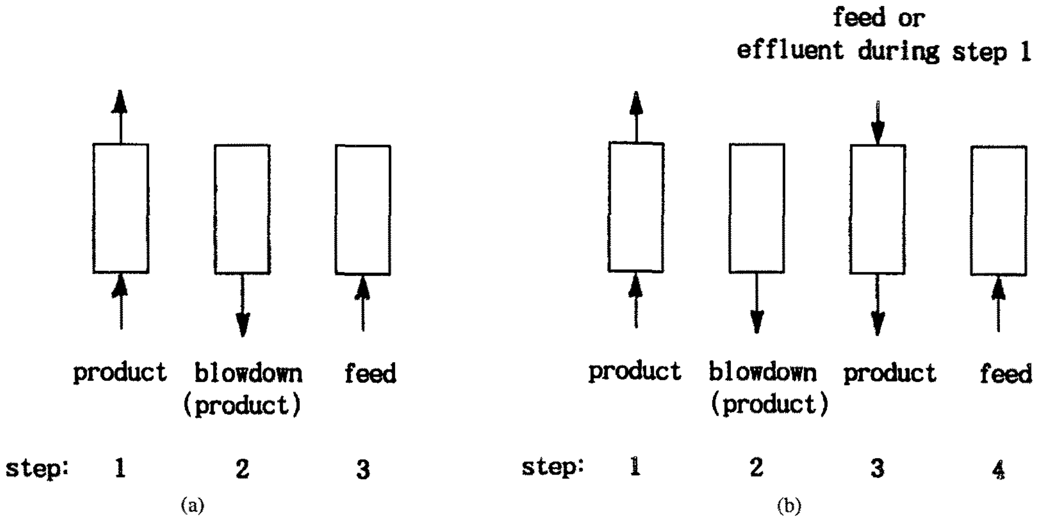


Fig. 2. Cycles for heavy-component production: (a) 3-step (b) 4-step.

cycle. In a two-bed cycle with PE steps of Fig. 1(c), pressure equalization occurs by connecting the product end of one bed to that of the other. In the first step of a 3-step cycle for heavy-component production of Fig. 2(a), a high pressure product of a heavy component is continuously supplied to a bed through the feed end in order to saturate a bed with a heavy component, which is referred to as a heavy-component rinse step. In the second step, a bed undergoes depressurization or blowdown countercurrently through the feed end to a low pressure to obtain a product rich in a heavy component. In the third step, a bed is repressurized cocurrently to a high pressure with a feed. In the 4-step cycle of Fig. 2(b), a countercurrent purging step with a feed is inserted into a 3-step cycle for heavy-component production in order to increase a heavy-component recovery by obtaining a gas stream rich in a heavy component remained within a bed after a countercurrent blowdown. Alternatively, purging with the effluent from a bed during a heavy-component rinse step instead of a feed is also considered.

2.1.2 *Cycles for Simultaneous Production of Light and Heavy Components.*

Cycles for simultaneous production of light and heavy components are shown in Fig. 3. The effluent during a countercurrent blowdown step in the cycles of Figs. 1(a) and (b) for light-component production is a little rich in a heavy component. By adding a cocurrent depressurization step to an intermediate pressure or a heavy-component rinse step at a high pressure to the cycles of Figs. 1(a) and (b), a heavy-component purity of the effluent during a countercurrent blowdown can be increased. Thus, both purified products of light and heavy components can be obtained. The cycle with a heavy-component rinse step shown in Fig. 3(a) was proposed by Sircar (1988) for simultaneous separation of a CH_4/CO_2 gas mixture. The 5-step cycle with a cocurrent blowdown shown in Fig. 3(b) was studied by Yang and Doong (1985, 1986, 1987). Alternatively, simultaneous production of both components can be achieved by modifying the 4-step cycle for heavy-component production. The effluent during a heavy-component rinse step in the 4-step cycle for heavy-component production of Fig. 2(b) is rich in a light component to some degree. The effluent purity can be increased by supplying a product rich in a light component instead of a feed during a purge step as shown in Fig. 3(c). The products and effluents from a bed are assumed to be well-mixed. An average concentration is used during the purge and repressurization steps. Pressures are assumed to change linearly during blowdown and pressurization steps and to remain constant during all other steps. On the other hand, for a cycle with PE steps a pressure is not assumed. Its time-derivative is obtained from influent or effluent velocities from a bed (Shin, 1995).

2.2 *Mathematical Model for a Single Bed*

The model is based on the following assumptions:

1. An adsorption bed is isothermal.
2. Gas is ideal.
3. The pressure drop through an adsorption bed is negligible.

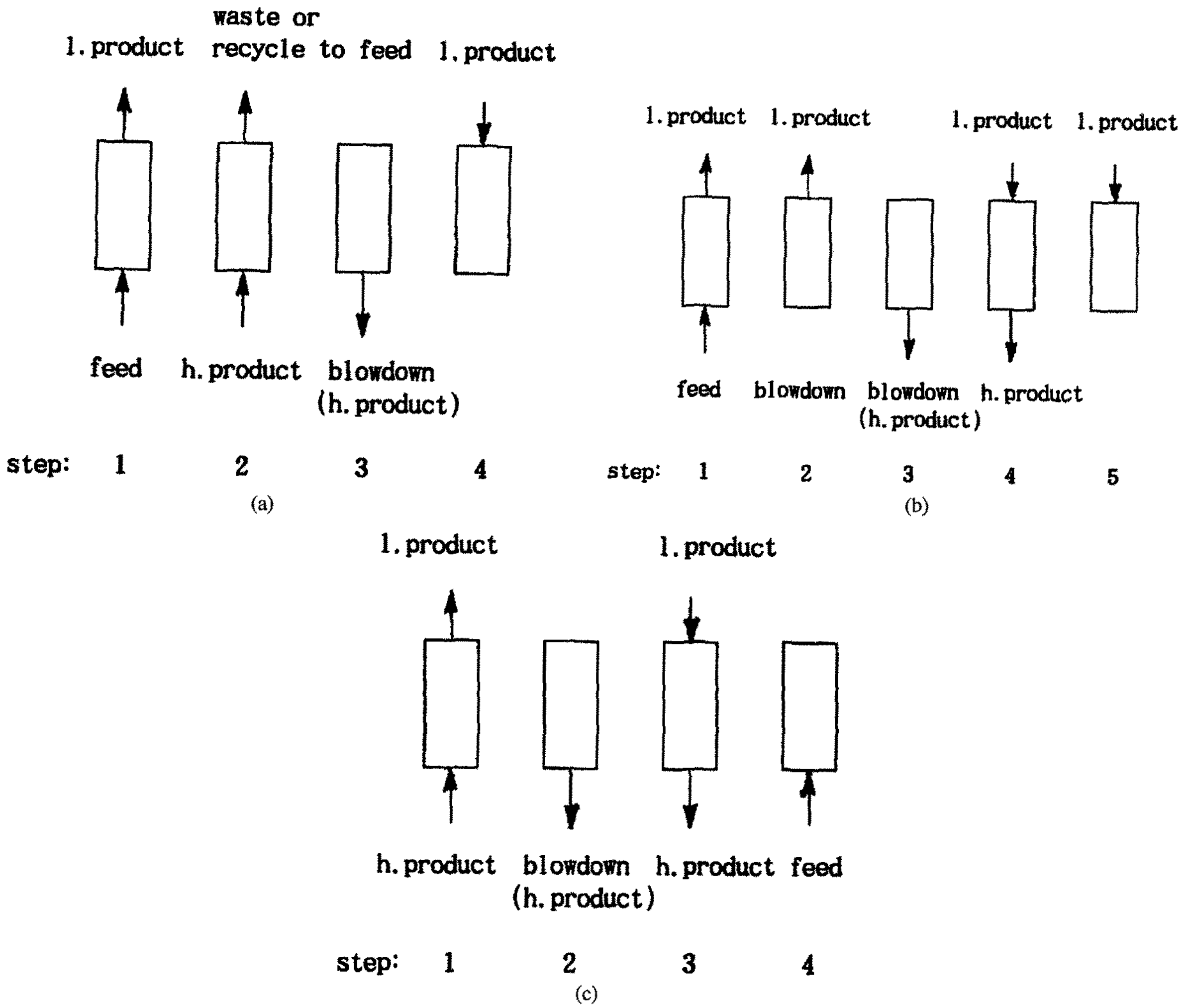


Fig. 3. Cycles for simultaneous production of light and heavy components: (a) Sircar's 4-step (b) 5-step (c) 4-step.

4. Adsorption of gases follows Langmuir type isotherm.
5. An adsorption bed is considered to consist of N well-mixed cells, in which equilibrium is always maintained between a gas and an adsorbent.

While the cell model was proposed by Chen and Hill (1983) for a linear isotherm, nonlinearity of an isotherm is included in this model. A cell number starts from the cell at $z = 0$. Subscript i is placed on the effluent from the ith cell. For the influents to the first and Nth cells, subscripts 0 and $N + 1$ are placed respectively. Even though the simple equilibrium cell model may not depict actual PSA processes accurately, it has an advantage over more elaborate models of not requiring many adsorbent and bed characteristics in advance. Thus, a quantitative comparison among different PSA cycles can be made roughly before elaborate experiments.

Under the above assumptions, the material balances for light (A) and heavy (B) components of a binary gas mixture within the ith cell for steps with a cocurrent gas flow are given by:

$$\frac{dC_{A,i}}{dt}+\frac{\rho}{\varepsilon}\frac{dn_{A,i}}{dt}=\frac{1}{\Delta z}[U_{i-1}C_{A,i-1}-U_iC_{A,i}] \tag{1}$$

$$\frac{dC_{B,i}}{dt}+\frac{\rho}{\varepsilon}\frac{dn_{B,i}}{dt}=\frac{1}{\Delta z}[U_{i-1}C_{B,i-1}-U_iC_{B,i}] \tag{2}$$

$dn_{A,i}/dt$ and $dn_{B,i}/dt$ can be expressed as follows by a chain rule:

$$\frac{dn_{A,i}}{dt}=\frac{\partial n_{A,i}}{\partial C_{A,i}}\frac{dC_{A,i}}{dt}+\frac{\partial n_{A,i}}{\partial C_{B,i}}\frac{dC_{B,i}}{dt} \tag{3}$$

$$\frac{dn_{B,i}}{dt}=\frac{\partial n_{B,i}}{\partial C_{A,i}}\frac{dC_{A,i}}{dt}+\frac{\partial n_{B,i}}{\partial C_{B,i}}\frac{dC_{B,i}}{dt} \tag{4}$$

Insertion of Eqs. (3) and (4) into Eqs. (1) and (2) gives:

$$\frac{dC_{A,i}}{dt} = \frac{1}{D_i \Delta z} \times \left[(U_{i-1}C_{A,i-1} - U_i C_{A,i})\left(1 + \frac{\rho}{\varepsilon}\frac{\partial n_{B,i}}{\partial C_{B,i}}\right) - (U_{i-1}C_{B,i-1} - U_i C_{B,i})\frac{\rho}{\varepsilon}\frac{\partial n_{A,i}}{\partial C_{B,i}} \right] \quad (5)$$

$$\frac{dC_{B,i}}{dt} = \frac{1}{D_i \Delta z} \times \left[(U_{i-1}C_{B,i-1} - U_i C_{B,i})\left(1 + \frac{\rho}{\varepsilon}\frac{\partial n_{A,i}}{\partial C_{A,i}}\right) - (U_{i-1}C_{A,i-1} - U_i C_{A,i})\frac{\rho}{\varepsilon}\frac{\partial n_{B,i}}{\partial C_{A,i}} \right] \quad (6)$$

where D_i is defined as follows:

$$D_i = \left(1 + \frac{\rho}{\varepsilon}\frac{\partial n_{A,i}}{\partial C_{A,i}}\right)\left(1 + \frac{\rho}{\varepsilon}\frac{\partial n_{B,i}}{\partial C_{B,i}}\right) - \frac{\rho^2}{\varepsilon^2}\frac{\partial n_{A,i}}{\partial C_{B,i}}\frac{\partial n_{B,i}}{\partial C_{A,i}} \quad (7)$$

After an addition of Eqs. (5) and (6), application of an ideal gas law results in the following Eq. (8). U_i can be obtained from U_{i-1} by using Eq. (8).

$$U_i\left[C_{A,i}\left(1 + \frac{\rho}{\varepsilon}\frac{\partial n_{B,i}}{\partial C_{B,i}} - \frac{\rho}{\varepsilon}\frac{\partial n_{B,i}}{\partial C_{A,i}}\right) + C_{B,i}\left(1 + \frac{\rho}{\varepsilon}\frac{\partial n_{A,i}}{\partial C_{A,i}} - \frac{\rho}{\varepsilon}\frac{\partial n_{A,i}}{\partial C_{B,i}}\right)\right] = U_{i-1}\left[C_{A,i-1}\left(1 + \frac{\rho}{\varepsilon}\frac{\partial n_{B,i}}{\partial C_{B,i}} - \frac{\rho}{\varepsilon}\frac{\partial n_{B,i}}{\partial C_{A,i}}\right) + C_{B,i-1}\left(1 + \frac{\rho}{\varepsilon}\frac{\partial n_{A,i}}{\partial C_{A,i}} - \frac{\rho}{\varepsilon}\frac{\partial n_{A,i}}{\partial C_{B,i}}\right)\right] - \frac{D_i \Delta z}{RT}\frac{dP}{dt} \quad (8)$$

Similarly, for steps with a countercurrent gas flow $dC_{A,i}/dt$ and $dC_{B,i}/dt$ can be summarized as:

$$\frac{dC_{A,i}}{dt} = \frac{1}{D_i \Delta z} \times \left[(U_{i+1}C_{A,i+1} - U_i C_{A,i})\left(1 + \frac{\rho}{\varepsilon}\frac{\partial n_{B,i}}{\partial C_{B,i}}\right) - (U_{i+1}C_{B,i+1} - U_i C_{B,i})\frac{\rho}{\varepsilon}\frac{\partial n_{A,i}}{\partial C_{B,i}} \right] \quad (9)$$

$$\frac{dC_{B,i}}{dt} = \frac{1}{D_i \Delta z} \times \left[(U_{i+1}C_{B,i+1} - U_i C_{B,i})\left(1 + \frac{\rho}{\varepsilon}\frac{\partial n_{A,i}}{\partial C_{A,i}}\right) - (U_{i+1}C_{A,i+1} - U_i C_{A,i})\frac{\rho}{\varepsilon}\frac{\partial n_{B,i}}{\partial C_{A,i}} \right] \quad (10)$$

The equation corresponding to Eq. (8) can be expressed as:

$$U_{i+1}\left[C_{A,i+1}\left(1 + \frac{\rho}{\varepsilon}\frac{\partial n_{B,i}}{\partial C_{B,i}} - \frac{\rho}{\varepsilon}\frac{\partial n_{B,i}}{\partial C_{A,i}}\right) + C_{B,i+1}\left(1 + \frac{\rho}{\varepsilon}\frac{\partial n_{A,i}}{\partial C_{A,i}} - \frac{\rho}{\varepsilon}\frac{\partial n_{A,i}}{\partial C_{B,i}}\right)\right] = U_i\left[C_{A,i}\left(1 + \frac{\rho}{\varepsilon}\frac{\partial n_{B,i}}{\partial C_{B,i}} - \frac{\rho}{\varepsilon}\frac{\partial n_{B,i}}{\partial C_{A,i}}\right) + C_{B,i}\left(1 + \frac{\rho}{\varepsilon}\frac{\partial n_{A,i}}{\partial C_{A,i}} - \frac{\rho}{\varepsilon}\frac{\partial n_{A,i}}{\partial C_{B,i}}\right)\right] + \frac{D_i \Delta z}{RT}\frac{dP}{dt} \quad (11)$$

Stipulated boundary conditions for each step are obtained from the operating policy.

For a high pressure feed step:

$$C_{A,0} = C_{A,\text{feed}} \quad (12)$$

$$U_0 = U_H \quad (13)$$

For a countercurrent blowdown step:

$$U_{N+1} = 0f \quad (14)$$

For a cocurrent blowdown step:

$$U_0 = 0 \quad (15)$$

For a purge step:

$C_{A,N+1} = C_{A,\text{product}}$ (when purging with product) (16)

$C_{A,N+1} = C_{A,\text{feed}}$ (when purging with feed) (17)

$$U_{N+1} = U_p \quad (18)$$

For a countercurrent pressurization step:

$$C_{A,N+1} = C_{A,\text{product}} \quad (19)$$

$$U_1 = 0 \quad (20)$$

For a cocurrent pressurization step:

$$C_{A,0} = C_{A,\text{feed}} \quad (21)$$

$$U_N = 0 \quad (22)$$

For a heavy-component rinse step:

$$C_{A,0} = C_{B,\text{product}} \quad (23)$$

$$U_0 = U_R \quad (24)$$

Initial conditions:

At $t = 0$, $C_{A,i} = C_{A,\text{feed}}$ $(i = 1, 2, \ldots, N)$ (25)

$U_i = 0$ $(i = 1, 2, \ldots, N)$ (26)

Langmuir type isotherm is given as ($j = A$ or B):

$$n_j = \frac{n_{js}B_j P_j}{1 + B_j P_j} \quad (27)$$

The use of uncoupled Langmuir isotherms can be justified by the work by Miller et al. (1987). They have shown that the mixed gas and pure component isotherms for a mixture of oxygen and nitrogen in zeolite 5A do not deviate significantly below partial pressures of 1.0 bar at 25°C. Even though the gas mixture in this study is different from that in the Miller's work, it is inferred that the interaction between pure components is not significant at subatmospheric pressures considered in this study. Concentrations within cells and effluent velocities from cells are obtained by using Eqs. (5) to (27). The time-derivative of pressure is calculated from the assumed history of pressure versus time. On the other hand, the simulation of two-bed PSA cycle with PE is performed differently. The two-bed cycle is modified in the form of an one-bed cycle by an introduction of a hypothetical storage tank. Also, the time-derivative of pressure for pressure-changing steps is calculated from the specified influent or effluent velocities from a bed. Detailed procedures are given by Shin (1995). Gear's method is used to solve the ordinary differential equations. 150 cells were thought to be enough for obtaining a reasonably accurate solution under the condition of this study. Cyclic steady state is assumed to reach when the absolute difference of product mole fraction between two neighboring cycles is less than 2×10^{-4}.

3 Results and Discussion

The system studied here is a separation of 50/50 vol% CH_4/CO_2 gas mixture with 5A zeolite. The characteristics of a packed bed and an adsorbent are given in Table 1. CO_2 is more preferentially adsorbed component than CH_4 on 5A zeolite. All PSA cycles are operated below atmospheric pressure, viz. between 0.266 and 1.01 bar. The subatmospheric operation is chosen for the ease of regeneration because isotherms of components are quite favorable. A component recovery is defined as the ratio of an amount of component in a net product to that introduced to a bed as a fresh feed. A productivity is defined as the amount of net product per a unit time and a unit amount of an adsorbent.

Table 1. Characteristics of a packed bed and an adsorbent.

Bed:	Diameter: 0.83 m Length: 2.0 m Bed void fraction: 0.4
Adsorbent*:	bulk density: 0.77×10^3 kg/m^3 $n_{CH_4,s} = 2.604$ mol/kg of adsorbent $B_{CH_4} = 0.2538$ bar^{-1} $n_{CO_2,s} = 4.659$ mol/kg of adsorbent $B_{CO_2} = 1.346$ bar^{-1}

*From data of Chen et al. (1990).

3.1 Cycles for Production of Only One Component

The separation performances by 3, 4-step cycles and a cycle with PE for production of only CH_4 are shown together for comparison in Fig. 4. The purity and amount of product vs. recovery plot of a 3-step cycle is

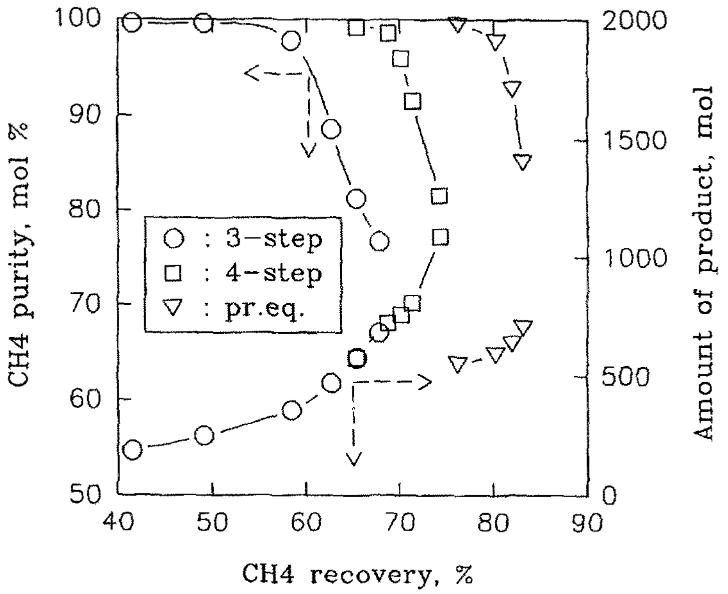


Fig. 4. Comparison of performance by a 3-step cycle with that by a 4-step cycle and a cycle with PE steps for CH_4 production.

determined by varying an amount of feed, which is the only adjustable variable for a fixed operation pressure range. On the other hand, the amounts of feed and product for purging are two adjustable variables for the fixed pressure range in a 4-step cycle and a cycle with PE. By varying those two variables, the loci of maximum recovery at a given purity and its corresponding amount of product per one cycle are determined. Even though a productivity is a more commonly used parameter than an amount of product when comparing among PSA cycles, an amount of product is used in expressing the results. In a 3-step cycle for production of a light component, the cycle performance in view of purity, recovery and amount of product will be identical for a fixed operation pressure range regardless of step durations as long as an amount of feed to a bed is same, which is determined by the combination of a feed step duration and a feed velocity. Different choice of step durations under a same feed amount results in a different productivity, but in a same amount of product. Thus, performance expressed in an amount of product rather than a productivity is more general in this separation even though more calculation is required in order to obtain a productivity from an amount of product.

Figure 4 shows that at a same CH_4 purity the recovery is about 10% higher for a 4-step than a 3-step cycle. Since a bed is rich in a heavy component at the end of a blowdown step of a 3-step cycle, it becomes clean by introducing a light-component product at a product end. Even though a part of product is consumed for purging a bed, more product is produced for a 4-step cycle. As a result, recovery increases. A productivity depends on an amount of product and a duration of one cycle. A duration is shorter in a 3-step cycle than a 4-step while an amount of product is much larger in a 4-step cycle as shown in Fig. 4. A duration of a purge step is equal to or less than that of a high pressure feed step (Shendalman and Michell, 1972; Yang and Doong, 1985; Hassan et al., 1986). Since the extent of an increase in productivity due to more product in a 4-step cycle surpasses that of a decrease in productivity due to a longer duration of one cycle, a productivity expects to be higher in a 4-step cycle. A cycle with PE gives 10% higher recovery with almost a same amount of product at a same purity than a 4-step cycle. Even though a duration is longer in a cycle with PE due to two additional PE steps, the longer duration does not decrease a productivity significantly due to a short duration of PE step. For example, two seconds of pressure equalization is employed in the work by Hassan et al. (1987).

The separation performance by a 3-step cycle for production of only CO_2 is shown in Fig. 5. The results show that CO_2 purity decreases gradually as CO_2 recovery increases. This trend is somewhat different from that in a cycle for production of CH_4. Since a product rich in CO_2 is obtained during a countercurrent

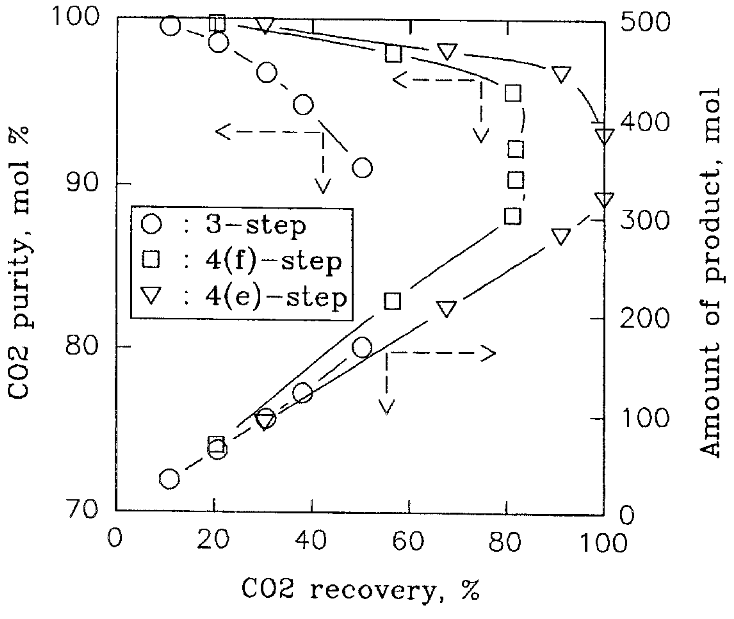


Fig. 5. Comparison of performance by a 3-step cycle with that by a 4-step cycle for CO_2 production. 4(f): feed-purging. 4(e): effluent-purging.

blowdown step where concentration simple-wave is formed, a purity of CO_2 product decreases smoothly. In contrast, since a product rich in CH_4 is obtained during a high pressure feed step where concentration shock-wave is formed, a purity of CH_4 product remains nearly constant until a breakthrough of feed begins.

After a countercurrent blowdown step for CO_2 production, a bed is still rich in CO_2. Therefore, CO_2 recovery can be increased greatly without a significant decrease in purity by introducing a feed at the product end of a bed and taking the CO_2-rich effluent as a product. The results of a 4-step cycle including the feed-purging are given in Fig. 5. The maximum recovery locus is determined in the same way as made in a production of only CH_4. The comparison of performances by 3 and 4-step cycles reveals that an addition of the feed-purging step to a 3-step cycle results in a significant increase in CO_2 recovery. However, as the amount of feed-purging increases, impurer effluent is produced during the feed-purging step. As a result, CO_2 purity decreases drastically with only a negligible increase in recovery. A higher productivity is expected in a 4-step cycle due to a much larger increase in an amount of product despite a longer duration of one cycle than in a 3-step cycle. In order to increase a recovery further by reducing an amount of feed introduced to a bed, the effluent during a CO_2-rinse step is used in a purge step instead of a feed. Its results are shown in Fig. 5. The effluent-purging gives a higher recovery than the feed-purging with a nearly same productivity. Especially, a complete recovery of CO_2 can be achieved.

3.2 *Cycles for Simultaneous Production of Light and Heavy Components*

The 4-step cycle (Fig. 3(a)) proposed by Sircar (1988) for simultaneous production of CH_4 and CO_2 is studied for a comparison with other cycles. Three cases of Sircar's cycle are considered in this study. The first one is without a recycle of the effluent during a CO_2-rinse step to a feed stream. The second is an insertion of a countercurrent CH_4-purging step after countercurrent blowdown. The last one is a recycle of the effluent. The typical results for the case without a recycle are shown in Figs. 6(a) and (b). They indicate that as CH_4 recovery increases, CH_4 purity and CO_2 recovery decreases while CO_2 purity remains nearly constant. The trend between CH_4 purity and recovery is same as that in only CH_4 production. The reason of a nearly constant CO_2 purity is that there is no noticeable change in concentration profiles within a bed at the end of CO_2 rinse step for a change in the amount of a feed input as long as the amount of CO_2 rinse remains constant. As the amount of a feed decreases, which results in a decrease in CH_4 recovery, the amount of CO_2 fed to a bed decreases. However, the amount of effluent during a blowdown step is nearly constant at a constant amount of CO_2 rinse. Therefore, CO_2 recovery increases for a decrease in CH_4 recovery. Even though Sircar's cycle without a recycle can produce a high purity of CH_4 and CO_2 streams simultaneously, it gives lower component recoveries compared with the previous cycles for only one-component production. Since a bed is highly rich in CO_2 at the end of a blowdown step, insertion of a countercurrent CH_4-purging step after blowdown can increase CO_2 recovery as in the 4-step cycle for only CO_2 production and make a bed clean for CH_4 production. A CH_4-rich product is used for purging a bed in order to produce a high purity of CH_4 product simultaneously. The results for an inclusion of the CH_4-purging step are presented in Fig. 6(a) together with those by Sircar's cycle without a recycle. Clearly, CH_4 and CO_2 recoveries increase for a given purity of CH_4 at the expense of a small decrease in CO_2 purity. The small decrease in CO_2 purity is inevitable because the average CO_2 purity of effluent during the CH_4-purging step is inherently lower than that during a countercurrent blowdown step. In order to examine Sircar's cycle without a recycle and its modified 5-step cycles in view of productivity, amounts of products as a function of product purity are presented in Fig. 6(b). A CH_4 product in the 5-step cycle can be obtained more than twice as that in Sircar's cycle at a region of high CH_4 purity; however, an increase in an amount of CO_2 product accompanys a small decrease in CO_2 purity. Thus, product recoveries and productivities can be increased with a small decrease in CO_2 purity by adding a CH_4-purging step to Sircar's cycle without a recycle. The other way of increasing recoveries of components is to recycle the effluent during a CO_2-rinse step to a feed stream, which has a feed gas-like composition at a normal operation condition. This idea is already mentioned by Sircar (1988). The typical results are given in Table 2. Recycling the effluent increases recoveries of both components significantly by reducing an amount of feed. Moreover, ultra high purity of components with complete recoveries can be obtained theoretically by increasing an amount of CO_2 rinse; however, productivities decrease drastically.

Sircar's cycle with a recycle gives very high component recoveries because it produces no waste stream. Another two cycles without a waste stream are

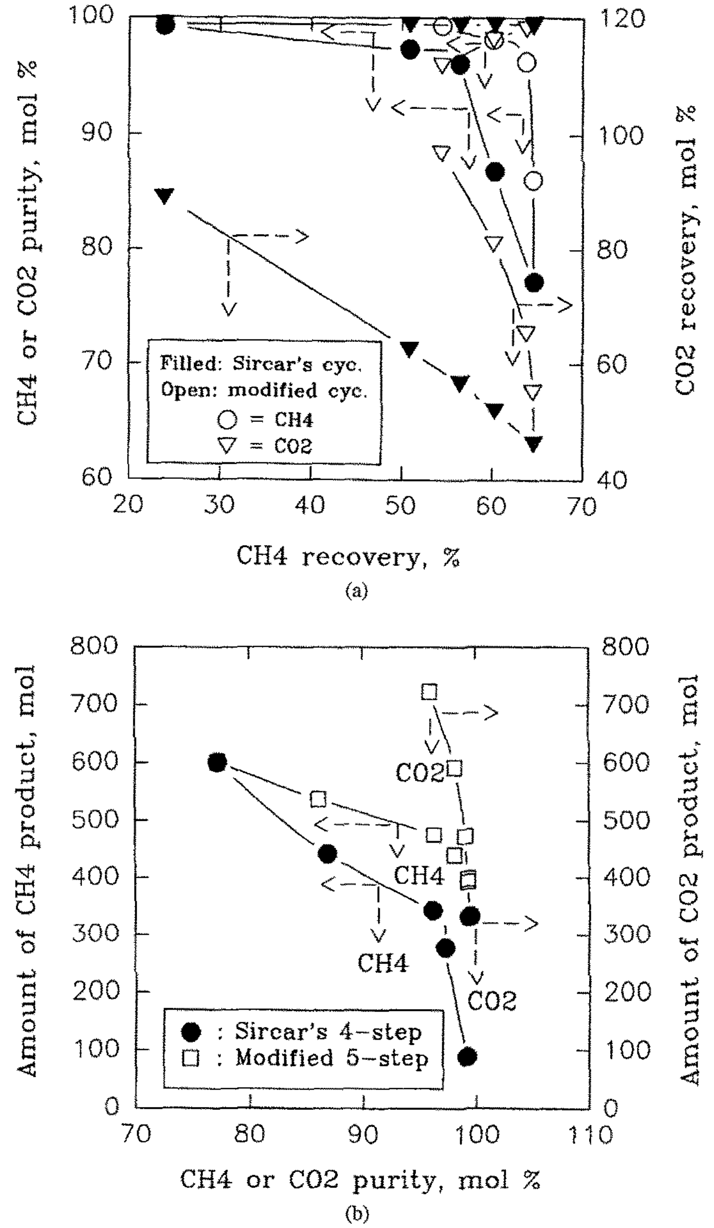


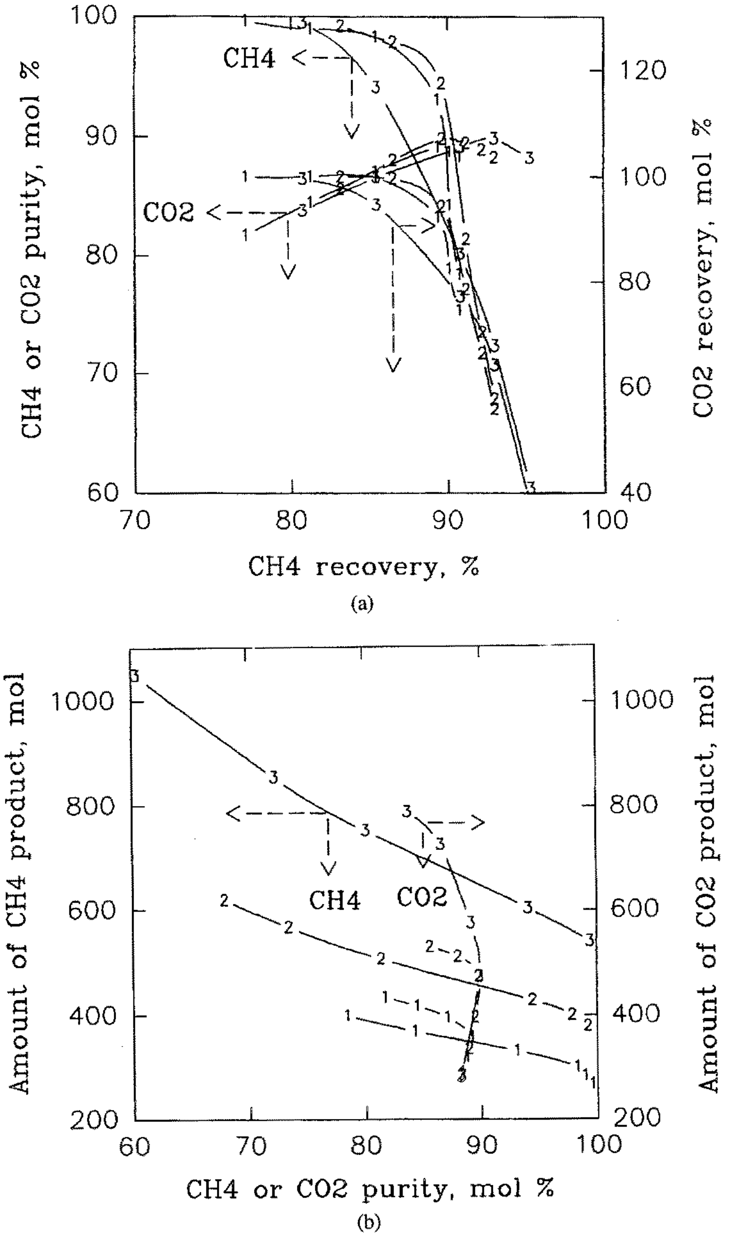
Fig. 6. Comparison of performance by Sircar's 4-step cycle without a recycle (Fig. 3(a)) with that by its modified cycle including a CH_4-purging step in view of (a) purity and recovery (b) amount of product. Amount of CO_2 rinse in both cycles = 902.8 mol; amount of feed in the modified cycle = 1434 mol.

considered in this study. One is a 5-step cycle (Fig. 3(b)) with a cocurrent blowdown. The effluents during high pressure feed and cocurrent blowdown steps are taken as a CH_4-rich product. Those during countercurrent blowdown and purge steps are taken as a CO_2-rich product. The simulation results are shown in Fig. 7(a). They reveal that the 5-step cycle can produce a high purity of CH_4 product with a higher CH_4 recovery than Sircar's cycle without a recycle and its modified cycles, but less than Sircar's cycle with a recycle. A higher CH_4 productivity is also expected due to more CH_4 product as shown in Fig. 7(b) and a short duration of cocurrent blowdown (Yang and Doong, 1985). However, a high purity of CO_2 product can not be produced.

Table 2. Typical results of Sircar's cycle with a recycle of the effluent during a CO_2-rinse step.

CH_4 purity (%)	CH_4 recovery (%)	CO_2 purity (%)	CO_2 recovery (%)	Amount of CH_4 product per one cycle (mol)	Amount of CH_4 product per one cycle (mol)
(1)95.89	99.22	99.12	96.79	353.7	351.6
(2)99.14	99.65	100.0	100.0	115.3	116.3

Amount of fresh feed (mol): 1) = 678.6; 2) = 226.5.
Amount of CO_2 rinse (mol): 1) = 902.8; 2) = 1115.



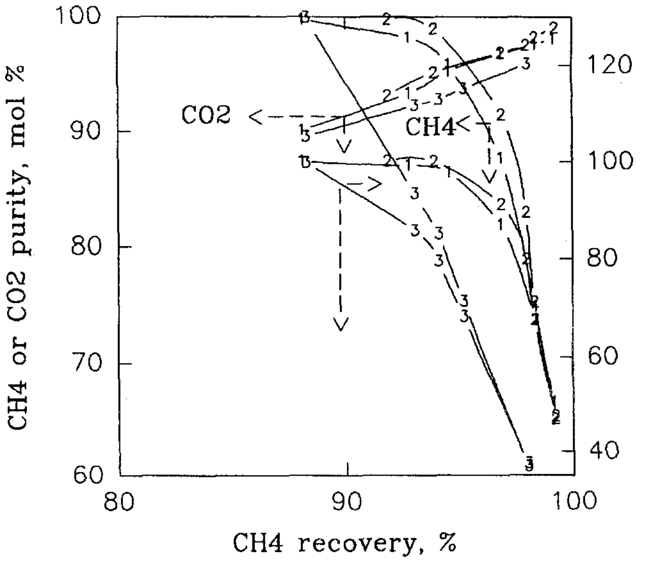
(a)

(b)

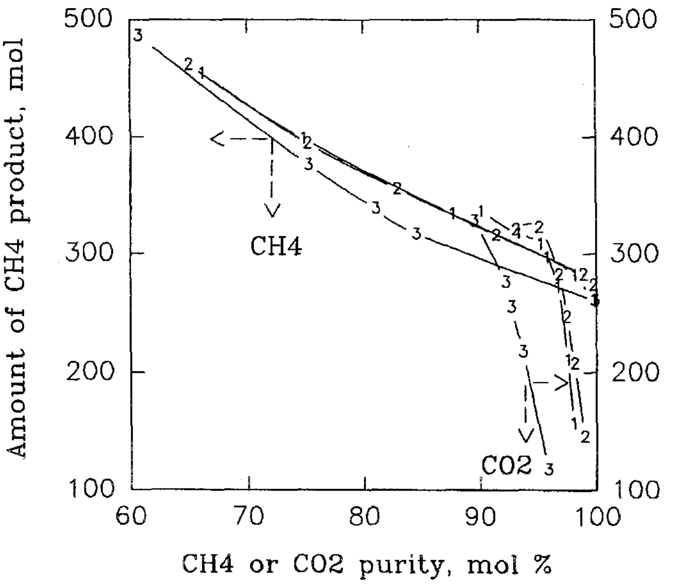
Fig. 7. Performance by a 5-step cycle (Fig. 3(b)) in view of (a) purity and recovery (b) amount of product. Cocurrent blowdown pressure is 0.4 bar. Amount of feed(mol): 1 = 609.4; 2 = 902.8; 3 = 1328.

The reason of a relatively low purity of CO_2 product is that a CO_2 product is taken as the effluents during countercurrent blowdown and purge steps, not passing through a CO_2-enriching step, viz. a CO_2-rinse step at a high pressure. In addition to include a CO_2-rinse step for a high purity of CO_2 product, several facts should be considered to produce both components of a binary gas mixture simultaneously. One is that the effluent during a CO_2-rinse step is also a purified product for attaining a high CH_4 recovery. Others are that CH_4-enriching and feed-supplying steps are included in a cycle.

The other cycle without a waste stream considering all those facts is proposed and shown in Fig. 3(c). Its results are presented in Figs. 8(a) and (b). One noticeable point in Figs. 8(a) and (b) is that an excessive



(a)



(b)

Fig. 8. Performance by a 4-step cycle (Fig. 3(c)) in view of (a) purity and recovery (b) amount of product. Amount of CO_2 rinse(mol): 1 = 1168; 2 = 1381; 3 = 1593.

CO_2 rinse decrease CH_4 recovery, CO_2 purity and recovery at the given CH_4 purity. Comparison of the newly proposed 4-step cycle with a 5-step cycle (Fig. 3(b)) reveals a better performance by the 4-step cycle in view of recovery and purity, e.g. a higher CH_4 recovery and CO_2 purity with almost a same order of CO_2 recovery at a given CH_4 purity. However, productivities are lower in the proposed 4-step cycle due to much less product. The simultaneous production of as high purity of CH_4 and CO_2 products as in Sircar's cycle is impossible because trade-off between CH_4 and CO_2 purity is observed. The small decrease in component purities for the proposed 4-step is compensated by a significantly large increase in component recoveries. Nevertheless, the resulting recoveries are less than those by Sircar's cycle with a recycle.

4 Conclusion

The following guidelines are obtained through a simulation study of PSA cycles for separation of a binary gas mixture. When only a light component is produced, inclusion of countercurrent purging with a product improves a cycle performance. Further improvement is achieved by employing a cycle with pressure equalization. Likewise, inclusion of countercurrent purging gives a better performance when only a heavy component is produced. Purging with the effluent during a heavy-component rinse step rather than a feed shows a better performance.

Sircar's cycle without a recycle can produce a high purity of products with relatively low recoveries and productivities. Addition of a light-component purging step to Sircar's cycle with no recycle results in higher recoveries and productivities with a small decrease in purity of a heavy component. Recycling the effluent during a heavy-component rinse step to a feed stream gives a very high purity of products with almost complete recoveries. The 5-step cycle with cocurrent blowdown has an advantage of high recoveries and productivities; however, it can not produce a high purity of heavy-component product. The newly proposed 4-step cycle is able to obtain relatively high purities of products with very high recoveries, while its productivities are lower than those by the 5-step cycle and a high purity of products with complete recoveries as by Sircar's cycle with a recycle can not be obtained.

Nomenclature

B = Langmuir adsorption constant, bar^{-1}.
C = concentration of sorbate in gas phase, mol/m^3.
D = defined by Eq. (7).
n = amount of sorbate in solid phase, mol/kg.
n_s = monolayer amount adsorbed, mol/kg.
P = pressure, bar.
R = gas constant, J/mol K.
T = temperature, K.
t = time, s.
U = effluent gas velocity, m/s.
Δz = height of one cell, m.

Greek letters

ρ = bulk density of a bed, kg/m^3.
ε = bed void fraction.

Subscripts

A = CH_4
B = CO_2
H = high pressure feed step
P = purge step
R = heavy-component rinse step
i = cell number ($i = 1$ to N)

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