

Process intensification in PSA processes for upgrading synthetic landfill and lean natural gases

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Abstract Process intensification aims at reducing the size of equipment by orders of magnitude and is actively perused in separation processes. Its feasibility in Pressure Swing Adsorption (PSA) processes has been explored. A 4-bed PSA and a 3-bed PSA, which emulate the moving bed processes, and duplex PSA and a modified duplex PSA have been selected for the exploratory studies. Simulation studies on the separation of a mixture of CH₄–CO₂ over 5A zeolite were carried out to compare the performance of these processes. An index has been proposed to quantify the process intensification. The 3-bed PSA and the modified duplex PSA exhibited superior performance compared to the other two for a purity of 99.9 mol% of both the products. However, the performances of the processes other than duplex were comparable when purities were set at 95 mol%. In 3-bed PSA a modest process intensification of four times reduction in size and two times reduction in energy requirement appears to be feasible if benchmarked against the PSA based on the variant of the Skarstrom cycle.

Keywords Process intensification · PSA · Duplex PSA · Synthetic landfill gas · Natural gas

Notations

b Langmuir parameter (m³/mol)
 c Concentration in gas phase (mol/m³)
 C_A Cost of adsorbent (thousand US \$/kg of adsorbent)

C_{AA} Annual cost of adsorbent (thousand US \$/y·(mol/s))
 C_{AC} Annual capital cost of adsorber (thousand US \$/y·(mol/s))
 C_{AE} Annual cost of energy (thousand US \$/y·(mol/s))
 C_{AR} Annual running cost (thousand US \$/y·(mol/s))
 C_E Energy cost (thousand US \$/kWh)
 C_{LO} Cost of component loss (thousand US \$/y·(mol/s))
 d_p Particle diameter (mm)
 D Diameter of bed (mm)
 D_{LO} Dispersion coefficient (m²/s)
 D_M Molecular diffusivity (m²/s)
 E Energy (kJ/mol-feed)
 f Friction factor
 g_c Gravitational constant (m/s²)
 I_{PI}, I'_{PI} Index for process intensification (thousand US \$/y·(mol/s))
 k_i Linear driving force constant (s⁻¹)
 L Bed length (m)
 L_e Equivalent length of the valve (m)
 n Number of moles
 N Number of components
 P Pressure (bar)
 \mathcal{P} Productivity of CH₄ (LSTP/h·kg of adsorbent)
 P_H Adsorption pressure (bar)
 P_I Intermediate desorption pressure (bar)
 P_L Desorption pressure (bar)
 P_1, P_2 Pressures used in (9) (bar)
 q Amount adsorbed in solid phase (mol/m³)
 q^e Amount adsorbed in solid phase at equilibrium with gas phase (mol/m³)
 q_s Saturation constant (mol/m³)
 Q_T Total amount adsorbed in solid phase (mol/m³)
 R Universal Gas constant (bar·m³/mol·K)

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R_E, R_R	Extract, Raffinate reflux ratio
T	Operating temperature (K)
t	Time (s)
t_f	Feed step time (s)
t_{Ib}	Intermediate blowdown time (s)
t_{fb}	Final blowdown time (s)
v_f	Superficial velocity (m/s)
x	Mole fraction in gas phase
x_f	Mole fraction of CO ₂ in feed
X	Mole fraction of CO ₂ in gas phase
Y	Mole fraction of CO ₂ in solid phase
z	Axial position in a adsorption bed (m)

Greek symbols

ε_B	Bed voidage
μ	Viscosity of gas (kg/m·s)
γ	Atomicity of gas
ρ_b	Bulk density of bed (kg/m ³)
ρ_g	Density of gas (kg/m ³)

Subscripts

i	Component i
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1 Introduction

Process intensification is a design philosophy in chemical engineering that has received much attention in recent years. It aims at innovations that reduce the plant size and energy consumption by orders of magnitude for a given production objective (Stankiewicz and Moulijn 2000, 2002; Reay et al. 2008). One of the ways of achieving process intensification (PI) is by the integration of reaction and separation processes. Reviews on combining reaction with different separation processes including adsorption are available (Kulprathipanja 2002). Another way of achieving PI is by enhancing the reaction rate, or heat- and mass-transfer rates. Extensive studies have been reported on the use of rotating packed beds (also known as HIGEE) for absorption and distillation (Rao et al. 2004). Pressure Swing Adsorption (PSA) units are bulky and their size reduction is desirable. Rota and Wankat (1990) have established scaling rules to quantify the effect of different parameters on PI in PSA. Xebec Inc. (Babicki and Hall 2003) is offering a PSA technology with structured adsorbents which permits rapid cycling to realize the size reduction in PSA units. The development of adsorbents to enhance selectivity, the use of structured adsorbents like monoliths which facilitate rapid cycling to enhance productivity, devising cycles to get both products of high purity, replacement of pressure swing with thermal swing would qualify as the attempts for PI in adsorption.

The moving-bed adsorber, being a countercurrent contactor of gas and solids, offers the highest possible driving force for mass transfer and hence the highest productivity.

Further, it employs raffinate and extract refluxes similar to distillation which lead to ‘perfect separation’ of a binary mixture (Treybal 1981). Depending on the nature of adsorption equilibria of binary gas mixtures, the adsorptive separation processes may be classified as *distillation-like* processes and *absorption-like* processes (Rao et al. 2005). To realize the advantages of moving-bed adsorber, Sivakumar (2007) proposed a 4-bed PSA for distillation-like processes and a 3-bed PSA for absorption-like processes which emulate the moving-bed processes in fixed beds. These have been referred to, hereafter, as *4-bed PSA* and *3-bed PSA*. Sircar et al. (1988) proposed PSA cycles for the separation of the CH₄–CO₂ mixture which employ 4-beds as well as 3-beds. The cycles proposed by Sivakumar (2007) and Sircar et al. (1988) are similar but differ in the implementation of blowdown. The latter used countercurrent blowdown whereas the former used co-current blowdown.

A mass-transfer zone (MTZ) forms in one of the beds of 3-bed PSA and two beds of 4-bed PSA which limits the mass transfer rate as the gas and solids are in equilibrium on either side of the zone. Further, these processes require almost complete regeneration of adsorbent by the application of deep vacuum to obtain products of high purity.

Hirose (1991) and Leavitt (1992) independently proposed a novel two-bed PSA which yields both products of high purity without the need for deep vacuum. The former named it as dual-reflux PSA and the latter as duplex PSA. We refer to it as *duplex-PSA*. Sivakumar (2007) showed that the duplex PSA superficially resembles the 4-bed and 3-bed PSA but differs entirely in its mechanism of separation. The mass-transfer zone extends over the entire bed and the overall driving force can be set much higher than those feasible with the 4-bed and 3-bed PSA. These features are expected to lead to PI. Kumar et al. (2006) proposed a modification to the duplex PSA to improve productivity and product purities and called it as *modified duplex PSA*.

The up-gradation of landfill and lean natural gases require removal of carbon dioxide to enhance their calorific values. Skid-mounted mobile PSA units are desirable for up-grading landfill gas for relocation at different sites. Compact units are also essential for natural gas upgrade on offshore platforms where the available space and weight are at a premium. Therefore, synthetic landfill gas has been selected for studies on PI in PSA processes. The objective of the present study is to quantify the process intensification attainable using the 4-bed, 3-bed, duplex and modified duplex PSA cycles for synthetic landfill gas.

2 Previous work

Several studies have been reported on the separation of CO₂–CH₄ and a few with nitrogen as an additional component. Table 1 presents the relevant details. Either the

Table 1 Compilation of the performances of the CH₄–CO₂ separation reported in literature

Reference	E/S ^a	Number of Beds/steps	Adsorbent	Pressure (bar)	Bed parameters		Steps in PSA cycle ^b	Cycle time (s)	Feed mole fraction CO ₂ /CH ₄ /N ₂	Purity CH ₄ (mol%)	Recovery CH ₄ (%)	\mathcal{P} (LSTP/h·kg of CH ₄)
				P_H/P_L	L (m)	D (mm)						
Equilibrium separation												
Sircar (1988)	E	5/5	–	12.66/0.07	2.44	–	AD, CoPuH, CnD, CnB, CnPR	–	0.575/0.425/–	99.0	99.3	–
Sircar et al. (1988)	E	4/4	13X	5.76/0.125	–	–	AD, CnD, CnB, CnPR	–	0.57/0.43/0.0	98.6	97.7	–
Kapoor and Yang (1989)	E	1/4	5A	4.06/0.340	0.61	41.0	AD, CoD, CnB, PRPL	600	0.50/0.50/–	95.8	88.4	42.9
Cavenati et al. (2006a)	S	1/4	13X	5.00/0.100	0.83	21.0	AD, CnB, CnPuR, CnPR	645	0.2/0.6/0.2	78.6	80.3	247.5
Delgado et al. (2006)	S	4/4	Silicalite	1.00/0.100	0.20	40.0	AD, CnB, CnPuR, FP	90	0.38/0.62/–	98.9	47.9	215.6
	E	1/3	Sepiolite	1.20/0.013	0.19	16.0	AD, CnB, FP	100	0.50/0.50/–	98.1	52.0	189.0
								150	0.34/0.66/–	97.7	38.1	36.4
								175	0.56/0.44/–	96.5	33.6	13.9
Kinetic separation												
Kapoor and Yang (1989)	E	1/4	CMS3K	3.77/0.300	0.61	41.0	FP, CoD, CnD, CnB	120	0.50/0.50/–	93.3	93.4	67.7
Jayaraman et al. (2002)	S	4/4	CMS 3A	4.00/0.200	0.60	40.0	AD, CnB, CnPuR, FP	140	0.50/0.50/–	96.8	76.7	232.4
			BF-CMS	3.72/0.340			FP, CoD, CnD, CnB	240		91.9	65.7	45.5
Cavenati et al. (2005a)	E	1/4	13X + CMS	1.20/0.100	0.8	16.0	AD, CnB, CnPuR, FP	195	0.2/0.7/0.1	92.5	54.5	121.0
Cavenati et al. (2005b)	E	1/4	CMS 3K	3.20/0.100	0.83	21.0	AD, CnB, CnPuR, FP	340	0.45/0.55/–	97.1	79.4	56.4
	S			4.00/0.100						97.9	68.1	48.4
	E			3.20/0.100			AD, CnB, CnPuR, CnPR	400		97.4	77.0	69.4
	S			7.00/0.100						98.7	63.9	57.6
Kim et al. (2006)	E	2/6	CMS 3A	4.00/–	1.00	35.0	AD, PE, CnB, CnPuR, PE, FP	480	0.50/0.50/–	95.8	71.2	64.6
Cavenati et al. (2006b)	E	1/4	13X + CMS 3K	2.50/0.100	0.80	16.0	AD, CnB, CnPuR, CnPR	240	0.2/0.6/0.2	88.8	66.2	95.3
Grande and Rodrigues (2007)	S	2/5	13X + CMS	8.00/0.100	4.67	933.4	AD, CoD, CnB, CnPuR, CnPR	400	0.45/0.55/–	98.0	80.3	167.9

^aE—Experimental, S—Simulation

^bAbbreviations: AD—adsorption, CnB—counter current blowdown, CoB—cocurrent blowdown, CnD—countercurrent depressurization, CoD—cocurrent depressurization, CoPuH—cocurrent purge with heavy component, CnPR—counter-current pressurization with raffinate, CnPuR—counter current purge with raffinate, FP—pressurization with feed, PE—pressure equalization, PRPL—pressurization with pure light component

equilibrium-based or kinetic-based separation was employed. In former type of separation, 13X zeolite was employed whereas carbon molecular sieve was used in the latter. In recent studies (Cavenati et al. 2005a, 2006b; Grande and Rodrigues 2007), both types of separation are utilized by employing layered beds with different adsorbents. Besides the adsorption step, either countercurrent or co-current blowdown step was used. Pressurization with either feed or raffinate was employed though the latter is preferable for equilibrium-based separation whereas the former for kinetic-based separation. The objective of most of those studies was to obtain one product rich in CH_4 . The CH_4 recoveries were in the range of 34 to 93%.

2.1 Adsorption phase equilibria

The nature of adsorption equilibria plays an important role in devising PSA cycle. Let us confine to the binary mixtures. As mentioned earlier the PSA processes are classified as *absorption-like* and *distillation-like* processes. In the former only one component is adsorbed, the phase equilibria is similar to absorption equilibria. Perfect clean-up, that is, pure light component as the raffinate is feasible. In the latter, competing adsorption of the components prevails, the phase equilibria is akin to vapor-liquid equilibria. The use of extract and raffinate refluxes, which resembles liquid and vapor refluxes in distillation, yields ‘perfect separation’.

Figure 1 shows the X - Y diagram and the Q_T - Y diagram (similar to enthalpy-concentration diagram) for the CO_2 - CH_4 -5A zeolite system at different pressures. The required data were generated from the extended Langmuir equation with the constants obtained from the pure component data. Note that the extended Langmuir equations cannot account for the effect of pressure on the X - Y data. Though this system exhibits competing adsorption, the amount of CH_4 adsorbed is four times less compared to the amount of CO_2 adsorbed at 2 bar as shown in Fig. 1. Hence, the characteristic of this separation is closer to the absorption like processes mentioned earlier. Therefore, the suitability of both the 4-bed and 3-bed PSA cycles has been explored in

this work. We may mention here that the 4-bed, duplex and modified duplex PSAs are not suitable for the kinetic-based separations as the ‘raffinate reflux’ (pressurization with raffinate) is detrimental for the separation.

3 Description of PSA processes

3.1 4-bed/3-bed PSA

A brief outline of the 4-bed and 3-bed PSA processes emulating moving-bed adsorber is presented below. To highlight the role of refluxes in these PSA processes, we treated them from a view point different from that commonly found in the literature.

4-bed PSA: Fig. 2 shows a schematic diagram of the 4-bed PSA emulating moving-bed adsorber. As the name implies it has four beds. Each bed undergoes all the steps of the cycle, namely, stripping (adsorption), enriching, blowdown and pressurization. The MTZs in stripping and enriching beds can be viewed as similar to the stripping and enriching sections in a distillation column where counter exchange of the components between phases take place. The regeneration of adsorbent by blowdown is similar to the function of condenser and saturation of adsorbent by pressurization with raffinate is similar to the function of reboiler in distillation.

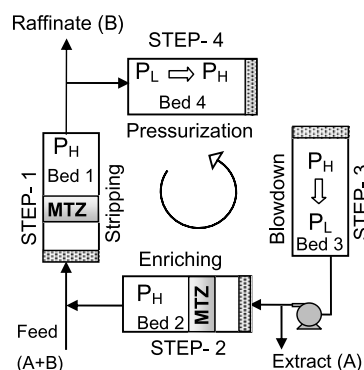
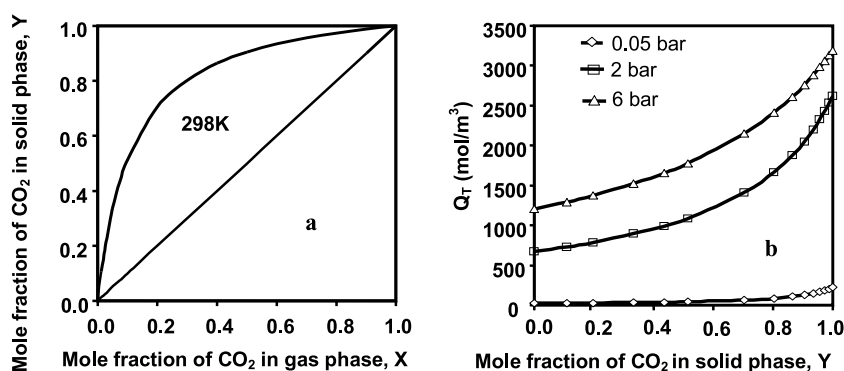


Fig. 2 Schematic diagram of 4-bed PSA with both refluxes

Fig. 1 CO_2 - CH_4 -5A zeolite system (a) X - Y diagram (b) Q_T - Y diagram



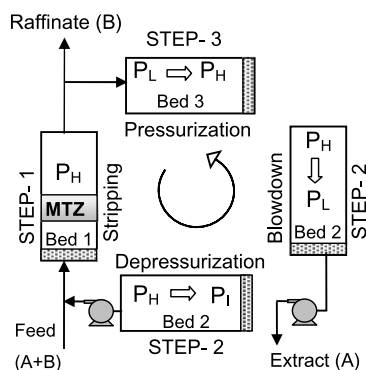


Fig. 3 Schematic diagram of 3-bed PSA without enriching reflux

The beds are visualized as if they switch positions at the end of the steps. The central arrow shows the direction of switching of the beds, which is in the opposite direction to that of flow of streams. One end of a bed is hatched to identify the ends of the bed. Let us follow Bed-1 as it undergoes the four steps. The feed along with the effluent from enriching bed flows into the stripping bed. A MTZ forms and moves through the bed. A part of the raffinate is drawn as product and the rest is used for pressurization. At the end of the step, Bed-1 is switched to the position of enriching bed. The enriching MTZ forms and moves through the bed as the extract reflux flows into the bed. In the next step, the bed is subjected to blowdown for regeneration. A part of the extract drawn is refluxed and the rest is collected as product. In the final step, the bed is subjected to countercurrent pressurization to saturate it with the raffinate. This adsorbate is the raffinate ‘reflux’ to the moving MTZ in the stripping section. Alternately, the bed can be purged at a low pressure for some time before the pressurization step. The resulting effluent can be compressed and recycled with feed. Thus, each bed goes through the four steps.

3-bed PSA: Fig. 3 shows the 3-bed PSA emulating moving bed adsorber. The process is similar to the 4-bed process except for the missing enriching step. This cycle has three steps. In the stripping step, the MTZ forms and moves through the bed. When it is about to break through the bed, the step is terminated. The light component is present only in the voids if the single component adsorption prevails. The light component held in the voids is drawn out by fast depressurization to enrich the bed with heavy component. This is done in the beginning of the step and the resulting effluent is compressed and recycled with feed. In the remaining step time, the blowdown is carried out to withdraw the extract product and regenerate the adsorbent. In the third step, the bed is pressurized with the raffinate to ensure that the feed does not gush through the bed to the other end and contaminate the raffinate with heavy component. Note that the sum of the step times for depressurization and blowdown is set to be equal to the step time of stripping or pressurization. It

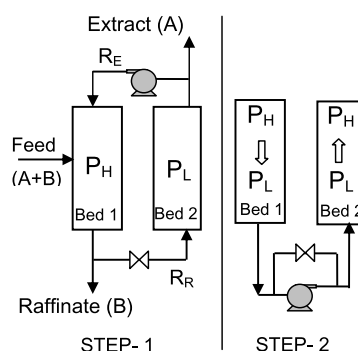


Fig. 4 Schematic of duplex PSA

may be mentioned here that the raffinate present in the bed after pressurization is not a reflux as in distillation as it does not play a role in mass exchange between the phases.

3.2 Duplex and modified duplex PSA

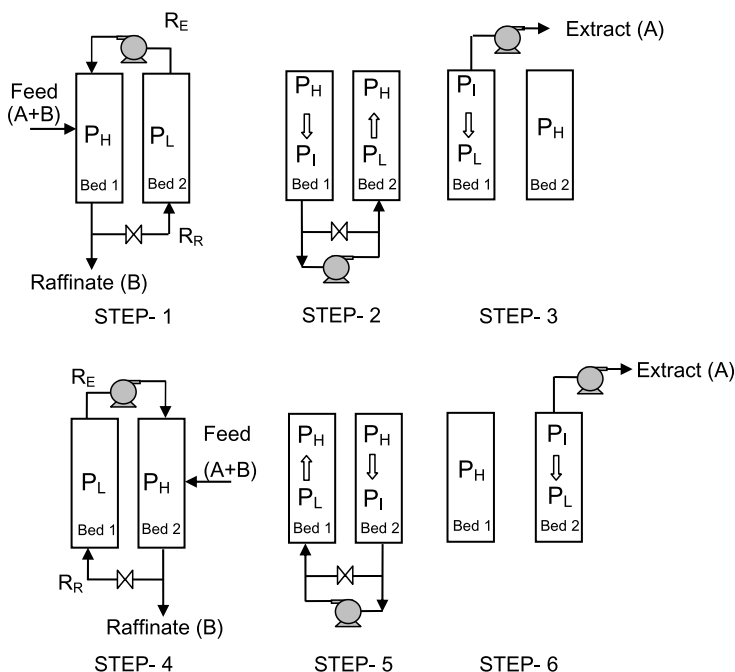
Figure 4 shows the half cycle of the original duplex PSA. It has two beds and operates in a cycle consisting of four steps. In Step-1, Bed-1 is at high pressure P_H , while Bed-2 is at low pressure, P_L . The feed is introduced into Bed-1 at an intermediate point along its length, as in distillation. A part of the raffinate, drawn from Bed-1, is recycled to Bed-2 and the rest is collected as the raffinate product. Likewise, a part of the extract drawn from Bed-2, undergoing purge step, is recycled to Bed-1 and the rest is drawn as extract product. In Step-2, Bed-1 and -2 are connected either at the top or bottom ends of the beds and the pressure in Bed-1 is set to P_L and in Bed-2 to P_H by transferring the gas; which we refer to as pressure-resetting step. Thus in step 2, Bed-1 undergoes blowdown while Bed-2 is pressurized. Step-1 and step-2 need not be of the same duration. Step-3 and Step-4 of the cycle (not shown) are the mirror image of the Step-1 and Step-2, with the roles of the beds reversed.

Figure 5 shows six steps of the modified duplex PSA cycle. It is nearly the same as duplex PSA except for the following. Here, the effluent from the bed undergoing purge step is completely recycled to the other bed and the required amount of extract is withdrawn in a final countercurrent blowdown step. During this step, the bed pressure decreases from intermediate pressure, P_I , to final evacuation pressure, P_L .

4 Mathematical model

The mathematical model developed for these processes by Sivakumar (2007) has been adapted here. A brief outline of the model is presented here. The assumptions made in the modelling are: (a) the gas obeys the ideal-gas law, (b) the process is isothermal, (c) the gas mixing in the bed is

Fig. 5 Steps in Modified duplex PSA



represented by a dispersed-plug flow model, (d) the inter-phase mass transfer is represented by the linear driving force (LDF) model and (e) the adsorption equilibrium follows the extended Langmuir isotherm model.

The process model for a bed undergoing any of the steps, mentioned in the above section, is given by:

Total pressure

$$\frac{\partial P}{\partial t} = KP \frac{\partial^2 P}{\partial z^2} + K \left(\frac{\partial P}{\partial z} \right)^2 - \frac{(1 - \varepsilon_B)}{\varepsilon_B} RT \sum_{i=1}^N \frac{\partial q_i}{\partial t} \quad (1)$$

Mass balance of species 'i' in the gas phase

$$\begin{aligned} \frac{\partial c_i}{\partial t} = & \frac{D_{L0}}{P} \frac{\partial x_i}{\partial z^2} + K \left(\frac{\partial P}{\partial z} \right) \left(\frac{\partial c_i}{\partial z} \right) \\ & + \frac{(1 - \varepsilon_B)}{\varepsilon_B} \frac{RT}{P} \left(x_i \sum_{i=1}^N \frac{\partial q_i}{\partial t} - \frac{\partial q_i}{\partial t} \right), \quad i = 1, 2 \quad (2) \end{aligned}$$

where

$$K = - \frac{d_p^2 \varepsilon_B^2}{150 \mu (1 - \varepsilon_B)^2} \quad (3)$$

and, the mass balance for the *i*-th species in the solid phase

$$\frac{\partial q_i}{\partial t} = k_i (q_i^e - q_i), \quad i = 1, 2 \quad (4)$$

Equations (1)–(4) are solved with the appropriate boundary conditions for each step. The parameters used in the model are estimated as follows:

The equilibrium solid-phase concentration is obtained from the extended Langmuir equation

$$q_i^e = \frac{q_{s,i} b_i c_i}{1 + \sum_{i=1}^N b_i c_i} \quad (5)$$

The axial dispersion coefficient has been estimated from the correlation (Huang and Chou 1997)

$$D_{L0} = 0.75 D_M + \frac{0.5 d_p v_f}{1 + 9.5 \left(\frac{D_M}{d_p v_f} \right)} \quad (6)$$

The velocities in the blowdown and pressurization steps were adjusted using the valve equation (based on a simple pipe flow and equivalent length of a valve) as

$$\frac{\Delta P}{\rho_g} = \frac{4 f L_e v_f^2}{2 D g_c} \quad (7)$$

On rearranging, we get

$$v_f = k C \Delta P^{0.5} \quad (8)$$

where, *C* is proportionality constant and *k* accounts for fractional opening of valve, which is adjusted using the regula-falsi method to attain the required pressure in a given step time in the blowdown and pressurization steps. In other steps, the velocity of streams were computed from the total number of moles fed in a given step time.

The energy requirement was calculated considering that feed and products are at the same pressure. The theoretical

energy required for change of the pressure from P_1 to P_2 of a stream was calculated from

$$W = \frac{n\gamma RT}{\gamma - 1} \left[\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \quad (9)$$

where, n is the total number of moles. If the pressures are varying during the step, work done is calculated by numerical integration. Total energy in cycle is found by summing up of the energy required in different steps.

5 Process intensification index

One of the ways to quantify the PI for adsorptive separation, besides volume reduction or productivity, is the cost of the separation. However, its rigorous evaluation is difficult. We propose a simple index to account for the productivity, \mathcal{P} , and the energy requirement, E . We have used the production rate of one *mole* of extract or raffinate per *second* as the basis for the yearly cost calculations. Productivity, \mathcal{P} has been expressed in terms of extract or raffinate product rate as *LSTP per hour* per kg adsorbent, and E , energy required for producing raffinate or extract, as kWh/(mol/s).

Let the cost of adsorbent be C_A per kg and its life span be t_{LS} in *years*. The annual cost of adsorbent, C_{AA} , is

$$C_{AA} = (3600 \times 22.4)C_A/(\mathcal{P}t_{LS}) \quad (10)$$

The annual Capital cost of adsorber, C_{AC} , is

$$C_{AC} = W_C C_{AA} \quad (11)$$

where, W_C is weighting factor (to account for vessels, valves and piping).

The annual cost of energy required for producing raffinate at the rate of one mol/s, C_{AE} , is

$$C_{AE} = (365 \times 24)EC_E \quad (12)$$

where, C_E is the cost of electrical energy per kWh. The annual running cost, C_{AR} is

$$C_{AR} = W_R C_{AE} \quad (13)$$

and a weighting factor, W_R , (to account for the annual cost of pumps and compressors). We may obtain an index for process intensification, which is a sort of total annual cost for producing raffinate product at the rate of one mol/s, I_{PI}

$$I_{PI} = C_{AC} + C_{AR} \quad (14)$$

The unit of I_{PI} are expressed as *thousand* US \$ per mol/s of CH_4 per *year*. In many a PSA processes, the recovery of the desired component is considerably low and varies from process to process. In these cases, the loss of the component could be accounted for in I_{PI} as additional cost of the loss per *year*, C_{L_0} , as

$$I'_{PI} = C_{AC} + C_{AR} + C_{L_0} \quad (15)$$

6 Simulation

The details of the method of simulation are given elsewhere (Sivakumar 2007). A brief outline is presented here. The parameters used in the simulations are presented in Table 2. In all cases, the extract and raffinate product rates were set as from the overall mass balance equations as to obtain the perfect separation or equal purity of both products. The recovery rates of the components can be calculated from the overall component mass balances. We have carried out simulations to examine the feasibility of perfect separation and the I_{PI} for product purities of 99, 97.5 and 95 mol%.

To compute the bed profiles, the bed length was divided into number of grids. It was varied from 53 to 209 grids as required to limit the numerical errors and ensure convergence. The spatial discretization was done using the central-difference scheme to convert the set of partial differential equation to a system of ordinary differential equations. These are stiff equations and were integrated using

Table 2 Parameters used in simulation

Feed composition (base case)	45 mol% CO_2 55 mol% CH_4	Saturation constant for CO_2 , q_{s,CO_2} ^a (mol/m ³)	3587.4
Adsorbent	5A Zeolite	Saturation constant for CH_4 , q_{s,CH_4} ^a (mol/m ³)	2005.1
Particle diameter, d_p (mm)	1.5	LDF constant for CO_2 , k_{CO_2} ^b (s ⁻¹)	0.1
Bed length, L (m)	1	LDF constant for CH_4 , k_{CH_4} ^b (s ⁻¹)	0.2
Bed diameter, D (mm)	25	Operating temperature, T (K)	298
Langmuir constant for CO_2 , b_{CO_2} ^a (m ³ /mol)	3.29E-02	Bed voidage, ε_B	0.4
Langmuir constant for CH_4 , b_{CH_4} ^a (m ³ /mol)	0.62E-02	Bulk density, ρ_b (kg/m ³)	770

^aChen et al. (1990)

^bPark et al. (2000)

DDASPG subroutine of IMSL library of FORTRAN 4.0 that uses the Petzold-Gear method. For a faster convergence smaller number of grids was used. However, for purities more than 97.5 mol%, more number of grids were required to ensure the convergence.

The calculations were initiated with the blowdown step considering that the bed was saturated with feed at adsorption pressure. The average effluent composition, velocity and pressure profiles were calculated. The profiles at the end of step were set as the initial profiles for the next step. The calculations for subsequent cycles were performed using the profiles in steps of previous cycle and repeated till the cyclic steady state was reached. Its attainment was ascertained when the average product composition difference was within $\pm 0.5\%$ of their previous cycle.

In the case of 4-bed PSA, first the operating pressures (P_H and P_L) were fixed then several simulation runs were performed with different step times and feed rates to obtain the desired purity of products.

In simulation of 3-bed PSA, the step times, and feed rate were adjusted, along with P_I for a given P_H to obtain the set target purities. The P_L was found from the amount of extract product withdrawn from the bed. Step time for feed and pressurization were of equal duration whereas the sum of step times of depressurization and blowdown was set equal to the step time for feed.

The duplex PSA required adjustment of feed location, feed rate and R_R (ratio of recycle and raffinate product) to yield the desired product purities for a given operating pressure and step time. In modified duplex PSA, in addition to the adjustable parameters of duplex PSA, P_I was also tuned to obtain the target purities. Like in 3-bed PSA, P_L was adjusted to obtain the desired extract amount. The computer code adapted here was validated by previous workers (Kumar et al. 2006; Sivakumar 2007). For the desired purity of 97.5 and 95 mol%, the cyclic steady state was obtained in about 30–50 cycles; but, we have used 50 cycles in simulation of all the processes. However, purity of 99 mol% and above required about 100 cycles to attain steady state. The CPU time for 50 cycles was about 3600 s on Intel (R) machine with 3.16 GHz.

7 Results and discussion

Several simulation runs have been carried out for the four processes to obtain I_{PI} for 99, 97.5 and 95 mol% purity of both products. Further, we have explored the possibility of perfect separation in each process. The simulations were carried out as detailed in Sect. 6. The parameters like raffinate or extract recycle, step times and feed rate were adjusted to obtain the desired product compositions. Table 3 presents the salient results. Several features may be noted:

1. As mentioned earlier, the purities of both products should have been the same. However, they differed slightly due to the numerical errors in the simulation.
2. Consider the first four rows in Table 3. They show that near perfect separation is possible with 4-bed PSA, the original and modified duplex PSA. Even the 3-bed yielded near perfect separation. Sircar et al. (1988) proposed both 4-bed and 3-bed cycles for the separation of the CH_4 – CO_2 mixture and demonstrated experimentally that the purities of 98 mol% are feasible. These cycles are same as the ones used here except for the implementation of blow down in 4-bed PSA. They used countercurrent blowdown whereas co-current one is used in this work. The direction of flow in blowdown would not matter for the products of high purities, considered in this work.
3. Leavitt (1992) claimed to have got perfect separation with duplex PSA for fractionation of air. The feasibility of perfect separation so far has been demonstrated for co-adsorption (non-competing) with linear isotherms using the equilibrium theory (Ebner and Ritter 2004; Kearns and Webley 2006). However, the theoretical and experimental studies on CO_2 – N_2 separation indicate that product purities are within 95 mol% (Hirose 1991; Sivakumar 2007). Table 3 shows that it is possible to get perfect separation with duplex PSA for competing adsorption with nonlinear isotherms using a moderate vacuum. However, the energy requirement is very high.
4. The productivities increased and energy requirements decreased rather steeply on lowering product purities for the 4-bed and duplex PSA whereas their variation for the 3-bed and modified duplex PSA was moderate. Even the performance of duplex PSA improved significantly for purities of 95 mol%.
5. The productivities of the 3-bed PSA are higher, energy requirements are lower and I_{PI} are smaller than the other three processes. Perhaps, the weaker adsorption of CH_4 compared to CO_2 adsorption has contributed to rather surprisingly good performance of the 3-bed PSA. However, it may not be the case for systems in which the adsorbed amounts of pure light and heavy components (distillation-like processes) are nearly equal.
6. Though the 3-bed process is superior to the modified duplex PSA, it requires deep vacuum for regeneration. On the other hand, the latter can be operated at a moderate vacuum if we compromise with high productivity. This may have practical significance if the leakage of air into the beds is not acceptable.
7. It must be pointed out that the highest throughputs for given purities were found by trial and error. Suitable optimization technique needs to be used to determine the best operating conditions. The weighting factors were set to unity in this study. A realistic evaluation including thermal effects may alter the economics of the process.

7.1 Composition profiles in beds

To gain insight into the processes, we have examined the composition profiles of bed in the important steps of the cycles. Figures 6–9 present the portraits of the profiles for the processes.

In 4-bed PSA, for the near perfect separation, the reflux ratio was close to the total reflux and most of the separation took place in the enriching section. The stripping section was relatively inactive. As the purities declined, the stripping section became active. Consider the variation of profiles with time at the exit end of the stripping bed for 95 mol% purity. They indicate that higher purities are pos-

Table 3 Comparison of performance of PSA processes for $x_f = 0.45$, and $P_H = 2$ bar

Run #	Process	R_E or R_R^a	P_I/P_L (bar)	$t_f/t_{Ib}/t_{fb}$ (s)	Purity CH_4/CO_2 (mol%)	\mathcal{P} (LSTP/h·kg of CH_4)	E (kJ/mol·feed)	$C_{AC}/C_{AR}/I_{PI}$ ($10^3 \times \text{US } \$/\text{y} \cdot (\text{mol/s of } \text{CH}_4 \text{ product})$)
Near perfect separation								
1	4-Bed PSA	67.69	-0.01	each step 160	100.0/99.7	4.1	353.7	24.6/131.5/156.1
2	3-Bed PSA	1.69	0.11/0.03	80/40/40	99.5/99.9	111.0	18.9	0.9/5.7/6.6
3	Duplex ^b	1.81	-0.44	200/-/150	99.9/99.9	1.3	108.2	77.5/33.5/111.1
4	MDPSA ^c	0.70	0.20/0.16	150/80/20	100.0/99.9	20.5	24.8	4.9/7.9/12.8
≈ 99 mol% purity								
5	4-Bed PSA	2.01	-0.05	each step 160	99.0/98.6	98.1	10.0	1.0/3.3/4.3
6	3-Bed PSA	1.52	0.20/0.08	80/40/40	99.1/98.8	119.3	9.1	0.8/3.1/3.9
7	Duplex	1.91	-0.45	200/-/150	99.1/98.8	1.6	85.5	61.5/27.4/88.9
8	MDPSA	0.70	0.20/0.08	120/60/20	99.1/99.0	63.7	23.9	1.6/7.7/9.3
≈ 97.5 mol% purity								
9	4-Bed PSA	1.51	-0.05	each step 90	97.7/97.5	199.6	9.4	0.5/3.0/3.6
10	3-Bed PSA	0.67	0.40/0.09	80/40/40	97.6/97.6	258.2	5.3	0.4/1.7/2.1
11	Duplex	1.00	-0.45	200/-/150	97.6/97.4	4.3	17.1	23.4/5.6/29.0
12	MDPSA	0.05	0.30/0.05	70/50/50	97.8/97.8	166.8	8.1	0.6/2.6/3.2
≈ 95 mol% purity								
13	4-Bed PSA	0.73	-0.05	each step 90	95.0/94.9	274.2	6.5	0.4/2.1/2.5
14	3-Bed PSA	0.48	0.65/0.08	80/40/40	95.7/95.0	364.1	4.6	0.3/1.5/1.8
15	Duplex	0.60	-0.45	200/-/150	95.0/95.1	10.6	8.1	9.5/2.7/12.2
16	MDPSA	0.03	0.60/0.06	70/50/40	95.3/95.1	250.7	6.2	0.4/2.1/2.5

^a R_E in case of 4-bed and R_R for the other processes

^b Duplex PSA

^c Modified duplex PSA

Fig. 6 Gas-phase profiles in 4-bed: stripping step (top) and enriching step (bottom) of runs 1, 5, 9 and 13 reported in Table 3; profiles from left to right are for 99.9, 99, 97.5 and 95 mol%

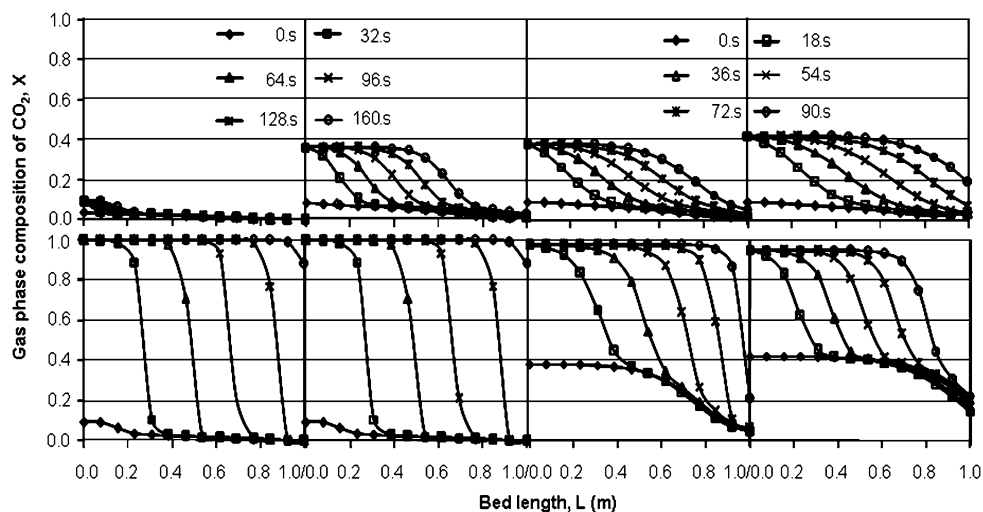


Fig. 7 (a) Gas-phase profiles in 3-bed: stripping step (*top*) and depressurization step (*bottom*) of runs 2, 6, 10, and 14 reported in Table 3; profiles from left to right are for 99.9, 99, 97.5 and 95 mol%. (b) Solid-phase profiles in 3-bed: stripping step (*top*) and depressurization step (*bottom*) of runs 2, 6, 10, and 14 reported in Table 3; profiles from left to right are for 99.9, 99, 97.5 and 95 mol%

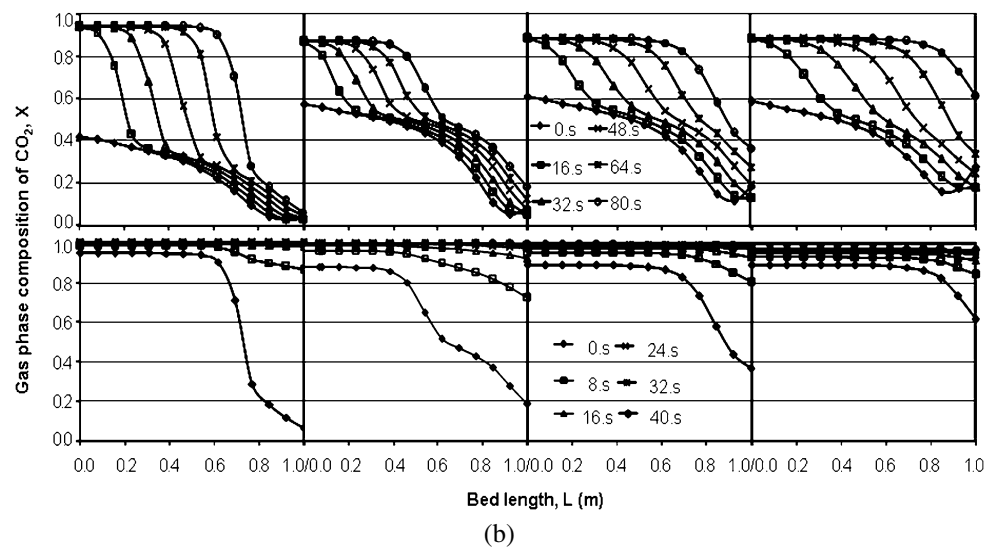
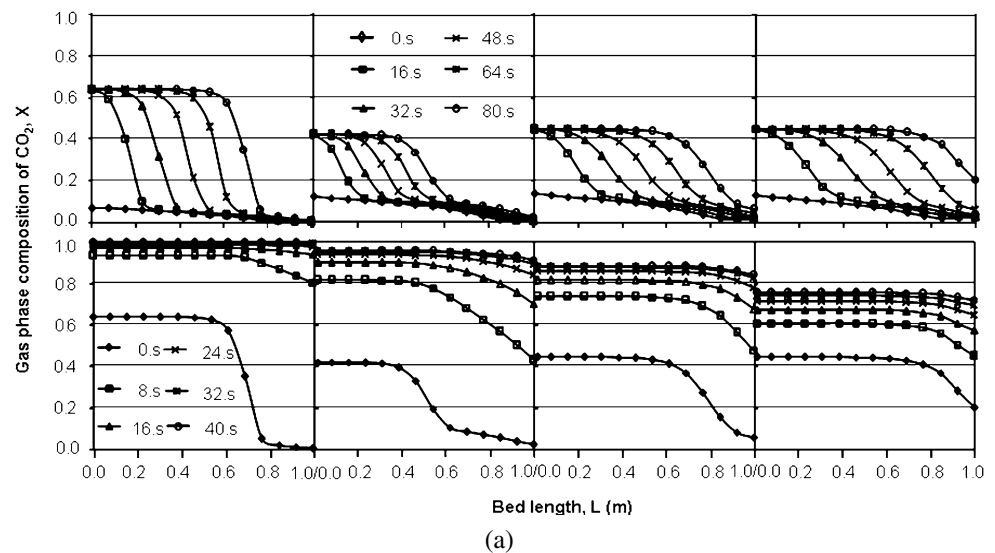
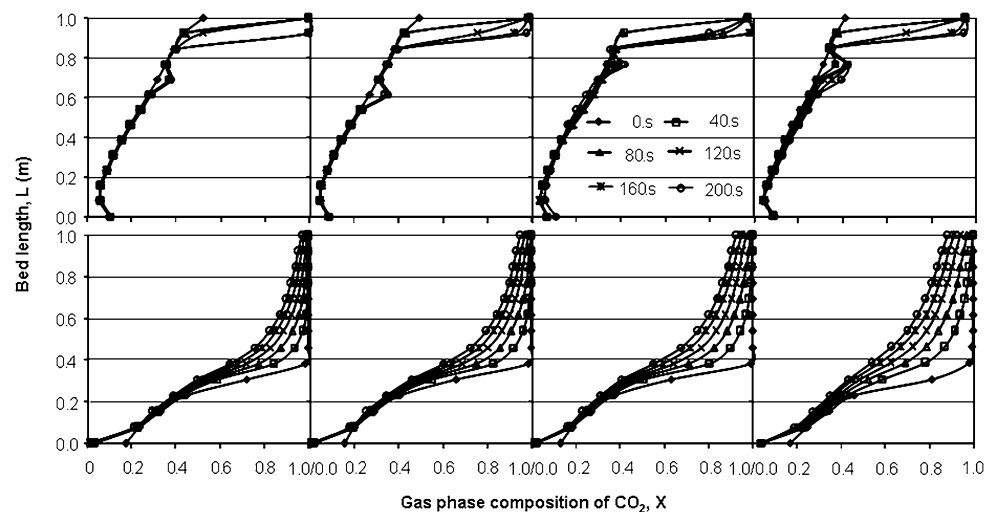


Fig. 8 Gas-phase profiles in duplex PSA: stripping step (*top*) and purge step (*bottom*) of runs 3, 7, 11 and 15 reported in Table 3; profiles from left to right are for 99.9, 99, 97.5 and 95 mol%



sible if the raffinate is drawn in the beginning of the step. Alternately, the throughput can be increased if the purity is held constant. Issac et al. (2009) showed that such a mode of withdrawal can lead to modest process intensification.

Figures 7a and 7b present gas phase and solid phase profiles for 3-bed PSA. The initial profile of gas phase in stripping step shows that the gas phase is lean in CO₂ and is almost zero at the raffinate exit end, which led to near pure CH₄. The corresponding solid-phase profiles show the MTZ is spread over the entire bed at the beginning and gradually its trailing end reached the equilibrium. This provided large driving force and hence led to process intensification compared to the other processes. The solid-phase profiles in depressurization bed show that the bed was free from CH₄ at 40 s step time. This yielded high purity extract product.

Fig. 9 Gas-phase profiles in modified duplex PSA: stripping step (top) and purge step (bottom) of runs 4, 8, 12, and 16, reported in Table 3; profiles from left to right are for 99.9, 99, 97.5 and 95 mol%

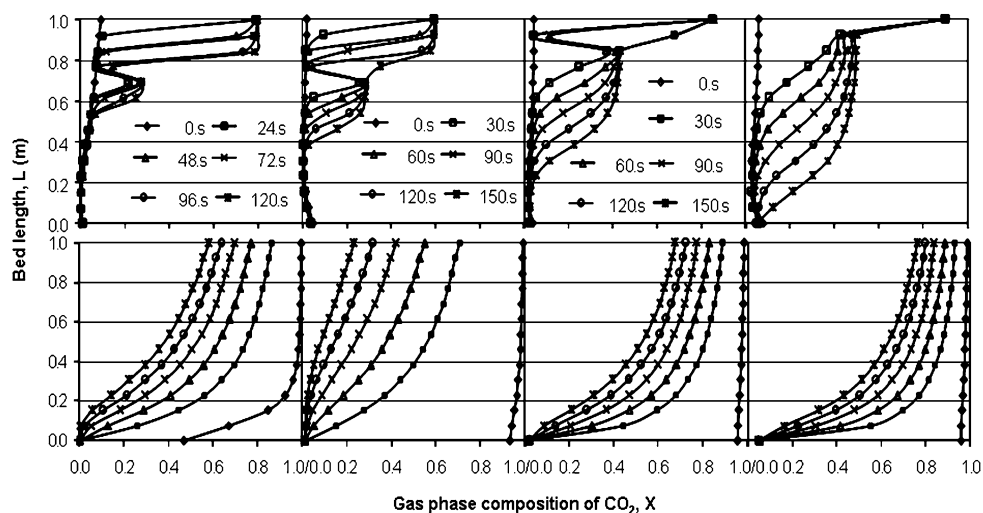


Table 4 Effect of feed composition on performance of PSA processes

Run #	CH ₄ mole fraction in feed	R_E or R_R	P_I/P_L (bar)	$t_f/t_{1b}/t_{fb}$ (s)	Purity CH ₄ /CO ₂ (mol%)	\mathcal{P} (LSTP/h·kg) of CH ₄	E (kJ/mol·feed)	$C_{AC}/C_{AR}/I_{PI}$ ($10^3 \times$ US \$/y·(mol/s of CH ₄ product))
4-Bed PSA								
17	0.20	0.08	-/0.08	Each step 90	95.4/95.0	70.9	6.2	1.4/6.5/7.9
18	0.55	0.73	-/0.05	Each step 90	95.0/94.9	274.2	6.5	0.4/2.1/2.5
19	0.80	4.66	-/0.08	Each step 100	95.4/95.2	284.7	6.9	0.4/1.5/1.9
3-Bed PSA								
20	0.20	1.68	1.70/0.18	80/20/60	95.7/95.0	87.9	4.3	1.1/4.7/5.9
21	0.55	0.48	0.60/0.08	80/40/40	95.7/95.0	364.1	4.6	0.3/1.5/1.8
22	0.80	0.32	0.25/0.09	100/50/50	95.0/95.1	435.8	2.9	0.2/0.7/0.9
Modified duplex PSA								
23	0.20	0.05	1.00/0.07	40/30/40	95.3/95.3	85.3	9.9	1.2/10.8/12.0
24	0.55	0.03	0.60/0.06	70/50/40	95.3/95.1	250.7	6.2	0.4/2.1/2.5
26	0.80	0.05	0.23/0.07	70/50/40	95.2/95.0	404.3	5.1	0.2/1.1/1.4

Figure 8 shows the gas-phase profiles for the feed and purge steps of duplex PSA. During the feed step, most of the bed is inactive, and the driving force is small. Hence, the productivity was poor. On the other hand, the bed in the purge step is relatively active.

Figure 9 shows the profiles for the modified duplex PSA. The beds in both feed and purge steps are active. The MTZ has spread over the entire beds. Therefore, the productivity was comparable to 3-bed PSA.

7.2 Effect of feed composition

Table 4 presents the effect of feed composition on productivity, energy requirement and I_{PI} . The productivity increased with increase of CH₄ mole fraction in the feed, as the rate of CO₂ to be stripped decreased for the three PSA processes.

As consequence, the annual capital cost decreased. The energy requirement remained nearly constant in the case of 4-bed PSA whereas it decreased with increase in mole fraction of CH_4 in the feed for the other processes. The I_{PI} , which is a measure of total annual cost, decreased significantly for the three processes with increase in CH_4 mole fraction in the feed.

7.3 Comparison with other cycles

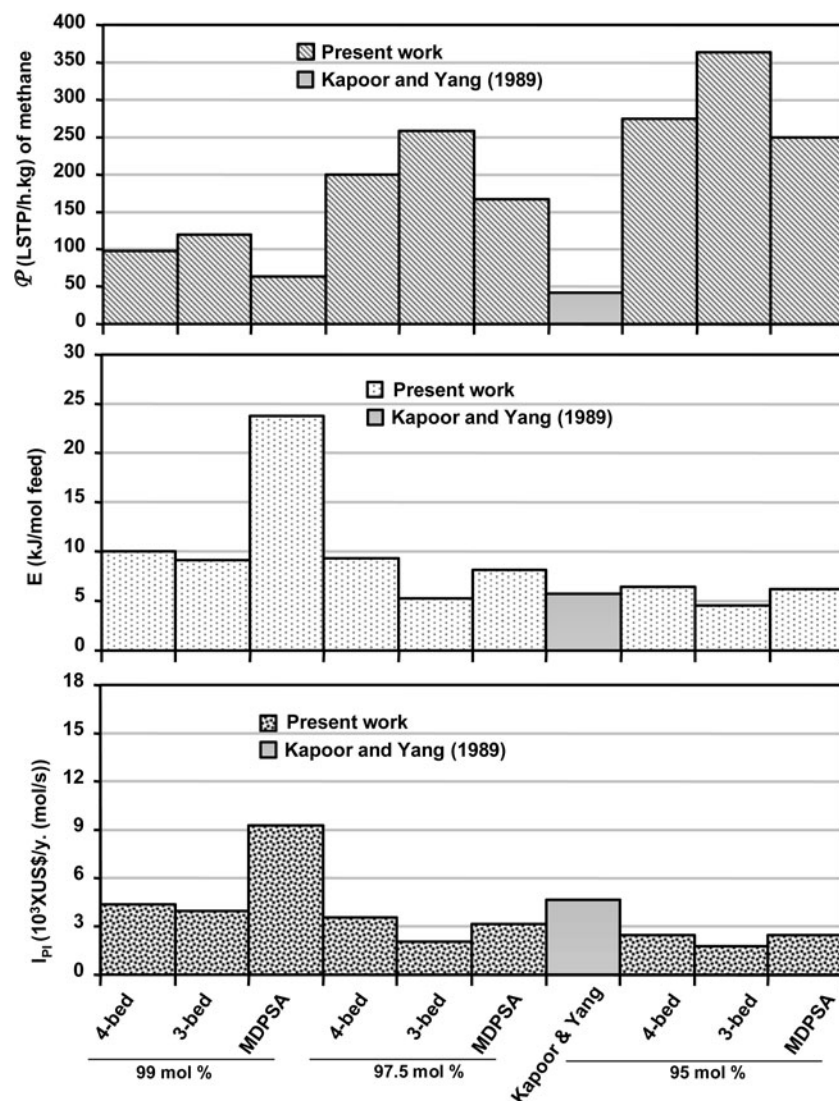
The experimental data reported by Sircar et al. (1988) shows that purities in excess of 98 mol% are possible. Unfortunately, the required data are not available to compute the I_{PI} for comparison. Though the purity of CH_4 is nearly the same in most cases, its recoveries were low. We have selected the Kapoor and Yang (1989) data for comparison since the purity and recovery of CH_4 are close to those obtained in this work. Figure 10 presents the comparison of the

performances. For the 3-bed PSA, productivity is higher, the energy requirements and I_{PI} are lower by two times compared to the data reported for the other cycles.

8 Conclusions

The performances of 4-bed and 3-bed PSA and duplex and modified duplex PSA have been studied to explore the process intensification that can be achieved with the variation of product purities. In addition, an index to quantify the process intensification was proposed. It accounts for the productivity, energy requirement and recovery of the desired component. The separation of $\text{CH}_4\text{--CO}_2$ mixture, which represents a synthetic landfill gas, over 5A zeolite, was selected for the case study. It is shown that, almost perfect separation was feasible in all these processes. However, the performances of 3-bed and modified duplex PSA were found

Fig. 10 Comparison of performance of 4-bed, 3-bed and MDPSA (modified duplex PSA) reported in Table 3 with data of Kapoor and Yang reported in Table 1



to be superior over the other two for the product purities of 99.9, 97.5 and 95.0 mol%. The performance improved with decrease in the purities and increase in the mole fraction of light component in feed. The quantitative results suggest that a four-fold reduction in equipment size and two-fold reduction in energy consumption are feasible with the 3-bed PSA compared to the PSA based on variants of the Skarstrom cycle.

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