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Heuristics for synthesis and design of pressure-swing adsorption processes

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Abstract Simulation based synthesis and design of adsorptive enrichment of CO from tail gas having 51 % CO are presented. The adsorption breakthrough curve simulation using this feed gas composition, helped to provide a starting guess of the adsorption step duration in a pressure-swing adsorption cycle for meeting the purity and recovery targets. Use of smaller bed dimensions facilitated the simulation of many cycles. These simulations helped to decide the operating pressure range, operating temperature, constituent steps of the cycle, their sequence, direction of pressurization of the bed, number of beds in the cycle and the composition of the streams to be used for pressurization and/or rinse and/or purge steps. Only an optimally designed pressure-vacuum-swing adsorption cycle achieves the stiff separation targets of getting an extract having 80 % pure CO at 80 % recovery in a single-stage with an adsorbent that uses physical adsorption and offers CO/CH_4 sorption selectivity of just 2.44. Additional simulations are done wherein the bed sizes and velocities are increased to predict the performance of a large-scale unit. These require deciding only the durations of the steps that are finalized from the small-scale unit simulations. These durations were kept fixed and the bed dimensions were varied till the separation targets are obtained for the particular feed rate. The scale-up criteria was matching residence times in the bed. A strategy for treating a feed gas having only 30 % CO is also discussed and a novel concept of cascaded PSA is evaluated using simulations. Some heuristics are evolved from the studies.

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Abbreviations

AC	Activated carbon
CPU	Central processing unit
CSS	Cyclic steady state
DE	Depressurization to extract step
DR	Depressurization to raffinate/rinse-out
FA	Feed adsorption step
L	Total bed height, m
LD	Linz and Donawitz
NCMPH	Normal cubic metres per hour (at 1.013 bara and 303 K)
NLPM	Normal litres per minute (at 1.013 bara and 303 K)
P	Instantaneous absolute pressure at a bed location, bara or Pa absolute
P^{ADS}	Adsorption pressure, bara (1 bara = 10^5 Pa absolute) or Pa absolute
P^{DES}	Desorption pressure, bara or Pa absolute
PF	Pressurization with feed step
PR	Pressurization with raffinate step
PSA	Pressure-swing adsorption
PU	Purge step
PVSA	Pressure-vacuum-swing adsorption
Q^F	Volumetric flow rate of feed gas averaged over the duration of FA step, NLPM (small capacity) or NCMPH (large capacity)
Q^{RI}	Volumetric flow rate of rinse-in stream averaged over the duration of RI step, NLPM or NCMPH
RI	Rinse step
SMB	Simulated moving bed
t	Time or temporal coordinate, s or minutes (1 minute = 60 s)

t^*	Time for achieving the maximum permissible mixed cup content of desired product in the raffinate
t_b	adsorption breakthrough time, s
TSA	Temperature-swing adsorption
u	Instantaneous linear superficial velocity of the fluid at a bed location, m/s
VSA	Vacuum-swing adsorption
y_{CO}	Instantaneous mole fraction of CO in fluid phase stream at a bed location, unit-less
z	Distance or spatial coordinate, m

1 Introduction

Adsorptive separation processes such as pressure-swing/pressure-vacuum swing/vacuum-swing adsorption (PSA/PVSA/VSA) are widely used for separation or purification of gaseous mixtures. It is difficult to arrive at an optimum cycle for such processes on the basis of first principles as it requires consideration of many factors, several of which are inter-linked (Knaebel 2008). The process is of discrete-continuous nature and could have to coexist between an upstream unit (supplying feed) and downstream units (utilizing raffinate and extract). Like any process design problem, all PSA based separation process synthesis and design problems are under-defined and open-ended (Douglas 1988). Rules of thumb or heuristics help to reduce the options available for achieving the separation performance targets at the stage of preliminary evaluation (Douglas 1988). In this work, useful heuristic rules have been inferred from a commercially important case study with a challenging separation task. Extensive simulations were carried out to extract a systematic procedure for synthesis and design. The outcome is evolutionary in nature and should be of help in quick screening of various alternatives.

Attempts to generate some guidelines for design of adsorptive separation systems have been reported. Selection matrix has been developed for selecting the type of adsorption process among PSA, temperature-swing adsorption (TSA), simulated moving bed (SMB), chromatography and inert-purge depending upon phase of the feed mixture, content of adsorbate in the feed and ease of separation of inert or displacement agent (Perry and Green 1997). Rules of thumb on various aspects of adsorption of organic chemicals on Carbon adsorbents have been documented by US Army Corps of Engineers to serve as a design guide (2001). Specifically for PSA, guidelines have been established for selecting the number of beds in a cycle depending on the pressure ratio, number of pressure equalization steps and feed gas flow rate for the application of high purity H_2 production (Stocker et al. 1998).

A breakthrough curve serves as an important source in extracting the system parameters (kinetic and thermodynamic). It actually has all the information that one would like to have to carry out simulation-based design of a PSA process. Simple heuristics can be used along with it to arrive at a basic PSA cycle and bed sizes for a desired performance as explained in this work. This serves as a starting guess for simulation based design and the simulation route can arrive at the final design swiftly. Extensive simulations for varied process embodiments carried out by the authors have thrown up several guidelines for process synthesis and design (Mhaskar 2012; Mhaskar and Moharir 2011; Peter et al. 2010).

Most reported applications of PSA are where the raffinate is the desired product. The important steps in such a PSA cycle are as follows: Pressurization by feed (PF) or counter-currently by raffinate (PR), Adsorption of feed to produce raffinate (FA), Counter-current depressurization to produce extract (DE), Co-current depressurization to raffinate (DR) and Counter-current Purge (PU). In rare cases where extract is the desired product, PU step is replaced by Co-current Rinse (RI) step. The steps of PU or RI are used to ensure purity of the desired product while the step of PR is mainly an energy saving steps. In the present work, we have extensively studied a PSA where extract is the desired product.

Some important observations regarding the various applications of PSA technology have been reported and variations in PSA cycle configuration in terms of component steps have been commented upon in other work (Mhaskar 2012). Factors like the nature of upstream unit, operating conditions of upstream unit, desired product, content of the desired product in the feed gas, condensation behavior of each component of the feed mixture, required purity of the desired product, operating conditions required for downstream applications of the two product streams and adsorption behavior of other components of the feed gas play a role in the design of a PSA process.

Explicit study on heuristics based design of PSA has been reported (Jain et al. 2003). In that work, nine rules have been developed by way of model based case studies on five binary mixtures. All these five systems belonged to a type of PSA termed as raffinate PSA in this work. It means that the desired product was the weakest adsorbate and ends up in raffinate stream during FA step. In this work, the enrichment of CO in a tail gas in mixture with CH_4, N_2 etc. is selected as a challenging separation task. The composition of the feed gas, temperature, pressure, flow rate and the separation objectives are given in Table 1. The adsorbent is only marginally selective towards CO (with CO/CH_4 selectivity of 2.44) unlike in most known PSA applications where the selectivity ratios of 8 or above are offered by the adsorbent. Minimum CO purity and recovery targets of 80 % each were also difficult to reach unless the cycle was properly designed. The PSA addressing this task is a typical case where strongly adsorbed component is the desired product and ends up in an extract stream during DE step to be termed as extract PSA type. This type is unconventional considering the number of PSA applications studied so far and the CO recovery case is unconventional in the sense that the equilibrium selectivity values are less than 3.

2 Background of CO recovery from tail gas

In the present work, the enrichment of CO in a tail gas was used to carry out extensive simulation studies to try and extract some useful heuristic rules for simulation-based synthesis and design of PSA processes. There could be many sources of a tail gas containing CO and CH_4 as main components. CO is a highly toxic and flammable component that also acts as a poison for the catalyst used in NH_3 synthesis reactor. It is removed in the liquid N_2 washing section before entry to the reactor, and becomes a major component in the tail gas from this section. The tail gas feed in the present case had this origin. The capture of CO emissions from the tail gas by use of processes like PSA is desirable for pollution abatement and the captured CO has many commercial uses such as a fuel gas, making many organic chemicals and Phosgene, purification of Nickel, etc. (Douglas 1988; Wikipedia 2011).

There is a limited choice of adsorbents for this adsorptive separation. Physical adsorption based materials have been developed that are selective for CO or for CH_4 (Dutta and Patil 1995; Iossifova et al. 2006; Lopes et al. 2009; Predescu et al. 1996; Sethia et al. 2010). A two-stage PSA process operated with feed gas from the steel industry wherein the first stage was packed with CH_4 selective material and the raffinate from this stage was fed to a another stage packed with CO selective material (Dutta and Patil 1995; Wiessner 1988). Material that chemically adsorbs CO has been used in pilot scale as well as commercial PSA units for CO capture from sources like gases from Steel plants and Ammonia plants (Chen et al. 2008; Dutta and Patil 1995; Kasuya and Tsuji 1991; Miyajima et al. 2005; Xie et al. 1996; Yi et al. 2004; Zhu et al. 1991). Performance comparison of cycles based on physical adsorption and cycles based on chemical adsorption has been done (Yi et al. 2004). Depending on the choice of the adsorbent and its selectivity, the PSA process could become a raffinate PSA or an extract PSA. By using an adsorbent selective for CH_4, this system can be made to belong to the category of raffinate PSA separation where CO will come out in the raffinate at high pressures. By using an adsorbent selective for CO, this system can be made to belong to the category of extract PSA separation. Design of extract PSA systems has not been intensively considered unlike raffinate PSA systems. This work provides the framework for the development of the design of PSA based CO recovery from Ammonia Plant Tail gas as an illustrative case of extract PSA.

3 Simulation studies

3.1 Decision-making in PSA process synthesis and design

PSA cycle development in the present work attempts to use the simulation studies based on the generic simulation model for PSA/VSA/PVSA developed by the authors (Mhaskar et al. 2012). The model is used to come up with a cycle based on a single adsorbent material that physically adsorbs the components in a single-stage and meets very challenging dual performance criteria of minimum 80 % pure CO product at 80 % recovery for a typical tail gas composition in a fertilizer plant.

PSA process synthesis and design for a desired separation task and given feed stream specifications and flow rate involves decision-making or selection regarding the following parameters:

(1) Appropriate adsorbent material or materials
(2) Number of stages (single-stage/cascade)
(3) Bed dimensions (inner diameter and height of adsorbent material layer)
(4) Temperature
(5) Adsorption pressure, desorption pressure and purge/rinse pressure (PSA/PVSA/VSA)
(6) Constituent steps of the PSA cycle (extract/raffinate as desired product), their sequence and duration of each step
(7) Appropriate choice of streams (the stream composition) to be used for pressurization, rinsing and purge steps respectively.
(8) Appropriate flow direction of stream used for pressurization relative to the feed gas flow direction (counter-current/co-current).

Parameters (1) and (3)–(8) have to be decided for designing a single-stage or a constituent stage of a cascaded unit. A bed in a stage can be packed with layers of more than one adsorbent material. So in a layered bed, the order of packing the adsorbent materials and the height of each adsorbent material layer also have to be decided. A cascaded unit may or may not have the same adsorbent material in its constituent stages. For a cascaded unit, additional decisions have to be made about the feed stream to the next stage, need to recycle a stream to the previous stage and the stream to be recycled back to the previous stage.

These decisions are made based on process performance criteria such as the purity and recovery of the desired product. These are defined in Eqs. (1) to (8) for CO recovery case. Economics may also govern the choice. That aspect is not explicitly covered in this work.

$$\%\ \text{CO Purity} = 100\frac{\text{Moles of CO out in DE step}}{\text{Total moles out in DE step}} \tag{1}$$

Table 1 Specification of feed gas and separation objective

Average composition of the feed gas	51 % CO + 21 % CH_4+ 11 % N_2 + 4 % H_2 + 13 % (Ar + other inerts)
Feed gas pressure (bara)	1.013
Feed gas temperature (bara)	303.15 K
Feed gas flow rate (NCMPH)	1200
Minimum required purity of CO product (%)	80
Minimum required recovery of CO (%)	80

(1) For rinsing with part of extract

$$\begin{aligned} X = {} & \text{Moles of CO out in DE step} \\ & - \text{Moles of CO used in RI step} \end{aligned} \tag{2}$$

When pressurizing with feed before adsorption:

$$\begin{aligned} Y = {} & \text{Moles of CO used in PF step} \\ & + \text{Moles of CO used in FA step} \end{aligned} \tag{3}$$

When pressurizing counter-currently with raffinate fraction before adsorption:

$$Y = \text{Moles of CO used in FA step} \tag{4}$$

If the application is for a tail gas in a fertilizer complex as was the case in this work, pure CO is also available from other processes and can be used with advantage for rinsing. If this is a possibility, the definition of recovery in terms of X and Y parameters changes as follows.
(2) For rinsing with pure CO

$$X = \text{Moles of CO out in DE step} \tag{5}$$

When pressurizing with feed before adsorption:

$$\begin{aligned} Y = {} & \text{Moles of CO used in PF step} \\ & + \text{Moles of CO used in FA step} \\ & + \text{Moles of CO used in RI step} \end{aligned} \tag{6}$$

When pressurizing counter-currently with raffinate fraction before adsorption:

$$\begin{aligned} Y = {} & \text{Moles of CO used in FA step} \\ & + \text{Moles of CO used in RI step} \end{aligned} \tag{7}$$

$$\%\ \text{CO Recovery} = 100\frac{X}{Y} \tag{8}$$

Operating cost in PSA is mainly the power consumption for compressor and vacuum pump. These can be estimated by suitable relations (Perry and Green 1997). To achieve the performance targets as defined above, design can be developed by simulations encompassing a range of values for various parameters listed earlier.

3.2 Preliminary considerations

Majority of the applications of CO require pressures exceeding 10 bara and do not justify operation at temperature far higher than 303.15 K which was the ambient value at site (Wikipedia 2011). Two temperatures 303.15 and 323.15 K are considered in the simulation-based design here.

An adsorbent material like Activated Carbon (AC) on which CO adsorbs weakly as compared to CH_4 has advantages when feed has predominantly CO content because raffinate PSA system can be designed to remove the non-major component CH_4. On such an adsorbent, the adsorption step can be carried out at high pressures to give product CO in raffinate at high pressures. For typical Ammonia plant tail gas, removing all the CH_4 will give CO purity of at best 65 % (with other content predominantly N_2, H_2, Ar and inerts, etc.). The selectivity of CH_4/CO offered by AC is low to give a raffinate having 65 % CO (Lopes et al. 2009). Hence a raffinate PSA system based on AC adsorbent cannot be used for recovering CO from the feed gas composition given in Table 1 (Mhaskar 2012).

The application of Phosgene synthesis requires a CO pressure of around 2 bara. This can be the desorption pressure of an extract PSA if one uses an adsorbent on which the strongest adsorbate is CO and a cycle where product CO will come out as extract stream during regeneration steps such as DE. If vacuum is used for desorption, it could give a better performance. The separation is possible using all the variations such as PSA, PVSA and VSA. Several cycles implementing these were simulated to check their separation performance. With consideration to operating and capital costs, compressor requirement needs to be minimized (Douglas 1988). Four values of feed pressure which is also the pressure used for adsorption, namely, P^{ADS}—1.1, 3.5, 6.5 and 10 bara, have been used. A ratio of adsorption pressure to the desorption pressure ($P^{\text{ADS}} : P^{\text{DES}}$) equal to 10:1 is maintained. This, so called, pressure ratio is known to have strong correlation to separation performance. The extract tank pressure is thus related to feed pressure.

As CO purity of at least 80 % is tolerable in this case, an adsorbent that only adsorbs CO or offers a very high selectivity towards CO by using mechanisms like chemical adsorption, may not be required. A two-stage process in which first stage uses a material to remove CH_4 and the raffinate

Table 2 Bed dimensions, specifications of adsorbent material and other input data used for adsorption breakthrough curve simulation

Viscosity of gas mixture (Pa-s)	0.00001675 @303.15 K, 0.00001759 @323.15 K
Feed gas pressure (bara)	3.5
Adsorbent layer height (m)	1.5
Total bed height (m)	1.5
Inner diameter of the bed (m)	0.15
Adsorbent particle shape	Spherical
Adsorbent particle diameter (m)	0.003
External voidage	0.27
Adsorption pressure (bara)	3.5
Monolayer saturation capacity (moles adsorbed per m^3 of particles)	3756.15 for all components at both temperatures
Adsorption equilibrium constant for CO (m^3/mole)	0.001634 @ 303.15 K; 0.000836 @ 323.15 K
Adsorption equilibrium constant for CH_4 (m^3/mole)	0.000669 @ 303.15 K; 0.000431 @ 323.15 K
Adsorption equilibrium constant for N_2 (m^3/mole)	0.000067@ 303.15 K; 0.000043 @ 323.15 K
Adsorption equilibrium constants for H_2, Ar and other inerts (m^3/mole)	0.0 at both temperatures

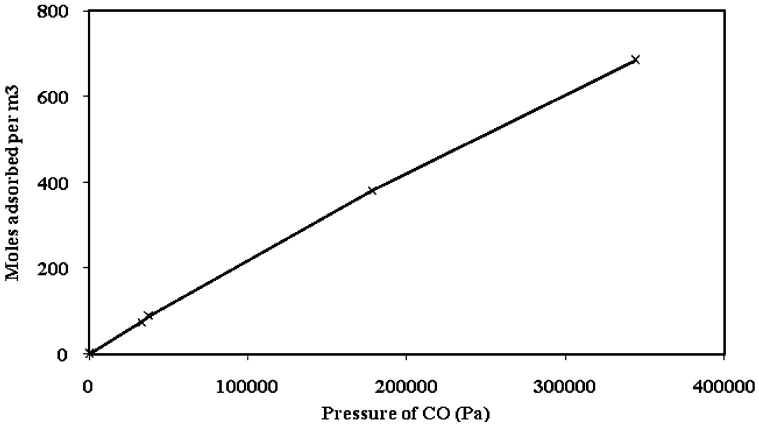


Fig. 1 Extended Langmuir isotherm for CO adsorption at 303.15 K on adsorbent material specified in Table 2

from which is fed to another PSA stage having CO-selective adsorbent is also possible analogous to the old process for recovery of CO from LD converter gas. But this will be costly. So the primary objective of this work was to check if the separation performance targets could be achieved by using a single-stage process and a physically adsorbing material on which CO is the strongest adsorbate. Product CO will be obtained during DE step and will have to be compressed for downstream use.

3.3 Adsorption breakthrough curve and its utility

The selected adsorbent physically adsorbs the components in the following preference order: CO $>$ CH_4 $>$ N_2 $>$ H_2 $>$ Ar $+$ other inerts. Extended Langmuir isotherm was used to describe the multi-component adsorption behavior and its parameters for each component on this adsorbent were estimated from the studies on H_2 purification (Lopes et al. 2009). More details of the model used in all the simulations of this work are given by Mhaskar et al. (2012). The bed dimensions, the specifications of the adsorbent material and other input data used for the simulation is given in Table 2. Simulation of adsorption breakthrough curve and most of the subsequent cycles was done by using these isotherm parameters. From Fig. 1, the isotherm for CO appears to be quite linear at 303.15 K. Mass transfer limitations were neglected and isothermal operation was assumed in the simulation model. Heats of sorption of CO, CH_4 and N_2 are nearly the same on the adsorbent (Lopes et al. 2009). Adsorption selectivity of CO/CH_4 is low. CH_4 and N_2 together account for 32 % of the feed gas. Morever, the columns are not insulated and CO will adsorb by desorbing out CH_4 and N_2. Hence the temperature changes will be less to justify isothermal operation. Simulations carried out with mass transfer controlled adsorption did not improve the match between simulated and predicted breakthrough curves as compared to equilibrium governed adsorption (Lopes et al. 2009). Equilibrium governed adsorption was therefore assumed in calculations.

The bed size used for breakthrough curve simulation is that of a pilot unit. The initial bed conditions for generation of breakthrough curves to be used for initial guess of a PSA

Table 3 Adsorption breakthrough time against feed rate

Q^F (NLPM)	t_b @ 303.15 K CO (s)	t_b @ 303.15 K CH_4 (s)	Q^F (NLPM)	t_b @ 323.15 K CO (s)	t_b @ 323.15 K CH_4 (s)
81	133	90	17	325	242
71	167	106	26	244	178
37	222	154	38	161	116
21	544	379	48	122	87

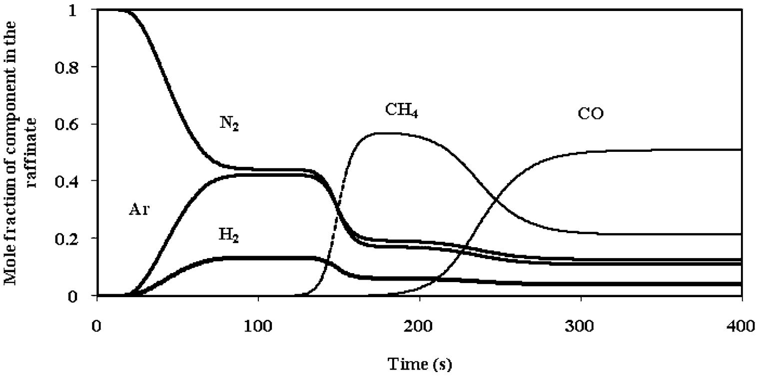


Fig. 2 Model predicted adsorption breakthrough curve at 303.15 K, 81 NLPM feed rate, composition as per Table 1 and other input data as per Table 2

cycle should normally be a pressure same as feed pressure, 3.5 bara in this case and the bed was assumed to contain only N_2 in the adsorbed and bulk phases. Using step-sizes of 0.05 m for spatial discretization and a second for temporal discretization, breakthrough curve simulations were verified to give convergent solutions of model equations. These step sizes were retained for all further simulations including the cycle simulation. Effect of feed rate on adsorption breakthrough times of CO and CH_4 was studied and the results are summarized in Table 3.

The breakthrough time (t_b) of a component reported in the table is the first instance at which a non-zero value of its mole fraction is recorded in the simulated effluent. Thus, at 81 NLPM feed rate, no CO was present in the outgoing fluid for the first 132 seconds but it started coming out from the 133rd second (t_b of CO = 133 seconds) as seen in Fig. 2. CH_4 starts to breakthrough from the 90th second as indicated by its lower equilibrium constant.

As the feed rate increases or the temperature increases, breakthrough starts to occur earlier. At 303.15 K, the feed rate in range of 37–81 NLPM should be tried for cycle simulation as the breakthrough time of CO is such that at least four cycles each of 15 minutes duration can be operated per hour using a two-bed unit. The bed dimensions and flow rates used in these breakthrough curve simulations are typical of pilot-scale units. At 323.15 K, the adsorption capacity drops as indicated by the lower value of equilibrium constants in Table 2. Table 3 shows that the breakthrough occurs earlier at 323.15 K for nearly same feed rate (flow averaged over the feeding time). Thus lower feed rates or lower feeding durations will have to be used in the cycle at 323.15 K. In an actual plant, a certain feed rate has to be obtained so the option left is to change the feeding duration. Breakthrough curve simulation can be carried out using the actual feed rate and industrial dimensions to decide the feeding duration.

In the adsorption breakthrough curve, CO content in the raffinate starts to rise from zero value at the breakthrough time. In an actual PSA cycle, after the cyclic steady state (CSS) has been achieved, CO content in the raffinate during the FA step will start to rise from a non-zero value and that too much earlier than the breakthrough time. This is because, at the end of depressurization step not all the CO and CH_4 are removed from the bed, the bed will not be pressurized with pure N_2 before the start of adsorption step and CO and CH_4 will get adsorbed during the pressurization step. Adsorption of CO during step FA will thus be over and above the residual levels of CO prior to this step. What should be the duration of step FA can be approximately deduced form the breakthrough curve as per the following logic.

Desired extract purity and recovery are stipulated as performance goals. These allow the calculation of maximum CO content that could escape into the raffinate stream by doing simple mole balance. This is done for several values of purity in the range of 80–100 % and recoveries in the range of 70–100 %. Figure 3 shows the plotted results for Ammonia Plant tail gas feed composition. For getting 80 % CO content in extract at 80 % recovery from this feed composition, raffinate can have up to 21 % CO. This is of course a mixed cup composition in a raffinate stream over its entire collection time. This content drops to 17 % if one wants an extract having pure CO at 80 % recovery. The same raffinate

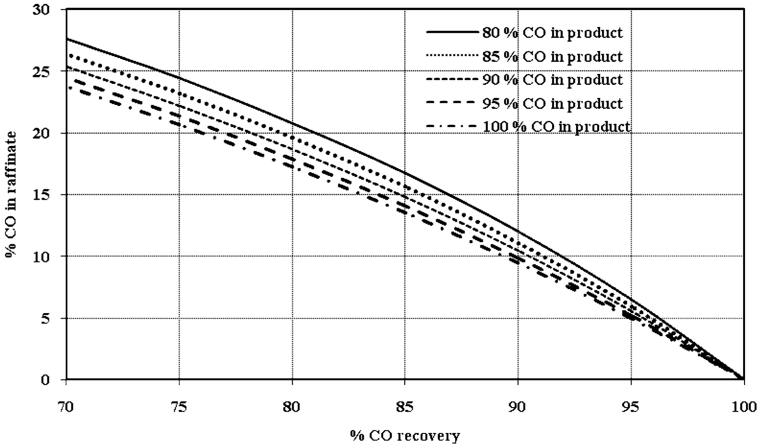


Fig. 3 Maximum permissible mixed-cup CO content in the raffinate for getting a specific recovery-purity combination from PSA based treatment of ammonia plant tail gas feed mixture

quality is permissible if one wants 85 % recovery at 80 % purity. These findings imply that adsorption step time can in reality exceed the breakthrough time of CO if one wants to have product CO purity in the range of 80–100 % and recoveries in the range of 70–99 %. If 100 % CO recovery is desired irrespective of its purity in the extract or if the desired product is a CO-free raffinate, then no CO should be allowed in the raffinate, which means that adsorption step time has to be less than the breakthrough time of CO as defined earlier.

A synthetic multi-component breakthrough generated using feed composition and bed dimensions as actual thus helps to establish an upper limit on adsorption step time or duration over which fresh feed should be drawn by the adsorbent bed to produce raffinate. In reality, the bed regeneration is never complete. The bed returning to production steps such as PF, FA and DR is having some residual concentration of adsorbates. Therefore, if the duration estimated from the breakthrough curves is fully utilized in PSA simulation, raffinate quality will be inferior to what is desired. Therefore, the bed should take in feed for a duration somewhat less than this upper limit indicated by breakthrough curve analysis. For this system, what was found as a good strategy by us was to set the total duration of steps PF, FA and DR to about 80 % of this upper limit in the first simulation. The pressurization step (PF) is generally of a shorter duration and its estimate can be fixed by experience to about 10 seconds or so. Similarly, if step DR is used, it also is a short step of similar duration. The balance is the FA step duration. The above logic allows to guess the production step time duration. If a two-bed system is to be used, then the regeneration steps together must also be of this duration together. If a three bed system is to be considered because desorption is perceived to be very difficult due to non-linearity of isotherm etc., then the regeneration steps together (RI, DE, PU, PR) should be together twice the duration of production steps. Steps RI and PR are of smaller durations compared to DE and PU steps. Accordingly the regeneration part of the cycle can be adjusted. The above logic is explained next with an example.

Multi-component breakthrough curve as given in Fig. 2 was generated using a bed of dimensions given in Table 2 and initially having only N_2 in both the phases. The feed composition, temperature and the adsorption pressure were kept same as the feed specifications for the actual PSA separation. This was used to find the time at a certain average feed rate, which keeps the integrated effluent composition below 21 % of CO. As discussed earlier, this composition is the upper limit on raffinate composition so as to get an extract at 80 % purity and recovery (see Fig. 3). The calculation of this time was as per Eq. (9). By analysis of the breakthrough, the time t^* was found to be 400 seconds as calculated by Eq. (9). This equation considers $z = L$ to be the raffinate end of the bed, and uses the model predicted instantaneous values of the linear superficial velocity of the fluid (u), pressure (P) and mole fraction of CO in the fluid coming out from the raffinate end in the FA step (y_{CO}).

The instantaneous CO percentage in the bed effluent at the end of 400 seconds is actually 50.9 %. However, because of lower concentration of CO before this and almost no CO in bed effluent up to about 140 seconds (see Fig. 2), the average concentration of the stream is still 21 %. Average flow rate of feed during the breakthrough curve generation was 81 NLPM. The proposed cycle had the steps of FA, RI by extract composition, DE and PR. FA step comprised the half cycle during which raffinate is produced and the other three steps comprised the other half of the cycle. Obviously, a 2-bed system is envisaged. The FA step must be 80 % or less than t^* as argued earlier. Duration of 300 seconds was therefore arrived at as the first guess for this step. The other three steps durations were 70, 220 and 10 seconds for RI, DE and PR steps respectively. The rinse pressure was taken as the adsorption pressure of 3.5 bara and desorption pressure was taken as 0.35 bara. A PVSA simulation was done with this initial trial cycle. The feed gas rate during FA step was adjusted to 81 NLPM through the adjustment of raffinate valve coefficient. The rinse-in rate during RI step was adjusted to 17 NLPM through the adjustment of the rinse-out valve coefficient. The PVSA cycle performance at CSS was obtained as 80 % CO in the extract, 20.5 % CO in the raffinate and 81.2 % recovery which matched the expectation. Keeping all the other conditions same, if the duration of FA and DE steps in the simulation are changed to value of 400 seconds and 320 seconds respectively then the predicted mixed-cup CO content in the raffinate rises to 31 %, that in the extract remains 80 % and CO recovery drops to 66 %. This indicates that the first guess of 300 seconds for the FA step duration was a good starting point. A simulated breakthrough curve is thus very useful to arrive at the first trial PSA cycle which guarantees the performance in the expected range.

$$\frac{\int_{t=0}^{t=t^*} (uPy_{\mathrm{CO}})_{z=L}\,dt}{\int_{t=0}^{t=t^*} (uP)_{z=L}\,dt} = 0.21 \qquad (9)$$

The very first trial may not always be successful. Once this initial guess of PSA cycle is made, the simulation to CSS can be carried out. Once a simulation is done, one has enormous data to look into what is actually happening in each step. One can view the spatial-temporal profiles over the cycle steps and visualize if a particular step is over-designed or under-designed. For example, one can reduce the extract tank pressure, or increase the duration of the DE step or adjust the duration of the PU step or purge rate or both etc. At a gross level also, if the raffinate purity is less than desired, one can reduce the duration of FA step or even reduce the coefficient of raffinate/feed valve thereby allowing less feed flow into the bed, etc. The possibilities are many, but after first and subsequent simulations give enormous insight into PSA operation to take an educated decision about the next simulation. Simulated based design thus gets targeted towards achieving the performance goals. This is very important because blindly carried out simulations can be very taxing due to computationally intensive nature of the rigorous simulation. This approach to synthesis and design was followed in the present work. The tabulated results in subsequent sections give only the CSS performance for inputted PSA cycles. However, the thought process behind starting simulations somewhere was as above.

For cases where the desired product is the extract such as CO recovery from various tail gases, RHS term of Eq. (9) depends on the CO content in the feed gas and the required purity and recovery for CO. So for LD converter gas which has 68 % CO on an average, to get 80 % recovery and 80 % pure CO in extract, RHS term of Eq. (9) becomes 43 % or 0.43 instead of 0.21. For cases, where the desired product is the raffinate, RHS term of Eq. (9) is mostly known. In general, Eq. (9) can be applied to any PSA process application. RHS of this equation will be the allowable content of the desired product for getting a recovery-purity combination of the desired product from a feed gas having a certain content of the desired product. y_{CO} in Eq. (9) will be replaced by the fluid phase mole fraction of the desired product.

3.4 Bed dimensions, adsorbent particle shape and dimensions

These were same as used for the studies for generation of adsorption breakthrough curve. Use of smaller bed heights allowed quicker and many simulations as large heights will require more number of divisions for spatial discretization of the adsorbent layer and thus more computational time. After the pressures, temperature, steps of the cycle, sequence of these steps, direction of pressurization, the composition of the stream to be used for pressurization and the composition of the stream to be used for rinsing or purging were finalized from the results of small size, four simulations were done on beds having commercial sizes. These beds also allow larger fluid velocities in the bed. A rough guideline used in the present work was to choose same ratio of bed height to linear velocity in larger beds also as used in pilot scale units. A shortcut procedure based on actual volumetric feed rate, amount of moles to be adsorbed, typical superficial velocity in FA step, space time in FA step and working capacity could be used to get a preliminary estimate of bed volume (Ribeiro et al. 2010, 2012a, 2012b).

3.5 PSA cycle configuration

Since CO is the desired product and the strongest adsorbate, typical steps of an extract PSA cycle are used (Kasuya and Tsuji 1991; Ruthven et al. 1994). Counter-current pressurization with fraction of raffinate (PR) instead of co-current pressurization with feed gas (PF) and varying the composition of stream used for rinsing instead of using an extract of constant composition have given higher recovery values (Miyajima et al. 2005; Zhu et al. 1991). Based on commonly adopted basic steps in any type of cycle, hierarchy of steps starting from only two steps to seven steps has been developed (Zhang and Webley 2008). The same approach will be followed in this work but starting with three steps.

The three steps are (1) PF + FA + DE or (2) PR + FA + DE. If any of these 3-step cycles give the required separation performance in terms of recovery and purity, then there is no need to go for a cycle having more steps (Shin 1995). More steps could often mean more number of valves, pipe-lines and surge tanks. Arriving at a cycle with minimum steps is thus economically a good decision. The results of 3-step cycles are given in Table 4.

Additionally the effect of CO content in the feed gas on the separation performance was also studied. CO content in the Ammonia plant Tail Gas varies in the range of 46–54 %. A simulation was also done with 45 % CO content. Similarly, one may intend to use a different feedstock such as

Table 4 Results of 3-step cycle at 303.15 K and CSS

Q^F NLPM	% CO in feed	P^{ADS} bara	P^{DES} bara	Duration of steps (PF/PR) + FA minutes	Duration of DE step minutes	Cycle time minutes	% CO in extract (Purity)	% CO recovery
84	51	3.5	0.35	5	5	10	78.4	69.3
89	51	3.5	0.35	5.3 (PR + FA)	4.7	10	78.4	75.7
162	51	10	1	4	4	8	76.1	84.2
124	51	6.5	0.65	4	4	8	76.9	80.6
101	51	6.5	0.65	5	5	10	77.1	83.0
115	51	6.5	0.65	5	5	10	77.3	75.5
100	51	6.5	0.65	5	10	15	77.0	82.3
79	51	3.5	0.35	6	6	12	78.4	62
80	68	3.5	0.35	6	6	12	87.1	56.7
71	54	3.5	0.35	6.2 (PR + FA)	5.8	12	80.2	76

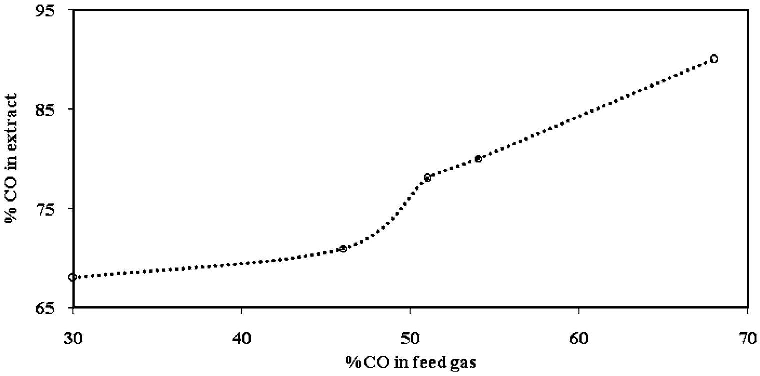


Fig. 4 Predicted purity at CSS vs CO content in feed gas for a single-stage process

LD converter gas which has CO content in the range of 60–70 %. This case was also considered for simulation. Relation of extract purity with CO content in feed as predicted by the model is given in Fig. 4 which shows that higher content gives higher purity for same cycle configuration and bed sizes. This is as expected. The effect of CO content in the feed on product CO purity and recovery can also be concluded from results given in Table 4.

Using a feed gas having 51 % CO on an average basis and CO selective adsorbent but a 3-steps cycle of PF + FA + DE steps gives 78 % purity at 69 % recovery in a single stage. Using a 3 step cycle of PR + FA + DE gives 78 % purity at 75 % recovery. The CO content in raffinate for the first case was 28 % and that for the second case was 25 %. The second case also had a slightly higher feed rate. The cycle with PR step gives higher recovery than the cycle with PF step. 3-step cycle with feed gas having 51 % CO proves to be insufficient for getting 80 % purity. Using a feed gas having 68 % CO gives 87 % purity and that having 54 % CO gives 80 % purity. However the recovery for 68 % CO feed content is only 57 %. This is as expected because in a single-stage PSA, purity comes at the expense of recovery and vice versa. Both can be improved only by use of cascaded PSA and thus at more costs. Similarly the feed gas having 54 % CO proves to be sufficient for getting 80 % purity but insufficient for getting 80 % recovery. Feed gas having 68 % CO is a better choice as the feed gas for getting a high purity CO for the same cycle steps, adsorbent material, step durations, bed sizes and the feed rate. Most of the simulation results discussed hereafter are for the feed gas composition given in Table 1.

Because three steps cycle was observed as inadequate as per simulation studies in achieving the targeted performance, effect of RI step after adsorption as the added fourth step was studied to see whether the required separation performance can be obtained by doing so. RI step will be executed with fraction of extract collected in DE step. In the particular technology task we encountered, pure CO was also available as a process stream. Rinsing with pure CO could also be tried due to this. Cycles having one or more steps of DR (pre-rinse/post-rinse) were also tried. 55 more cycles were simulated using the bed dimensions given in Table 2.

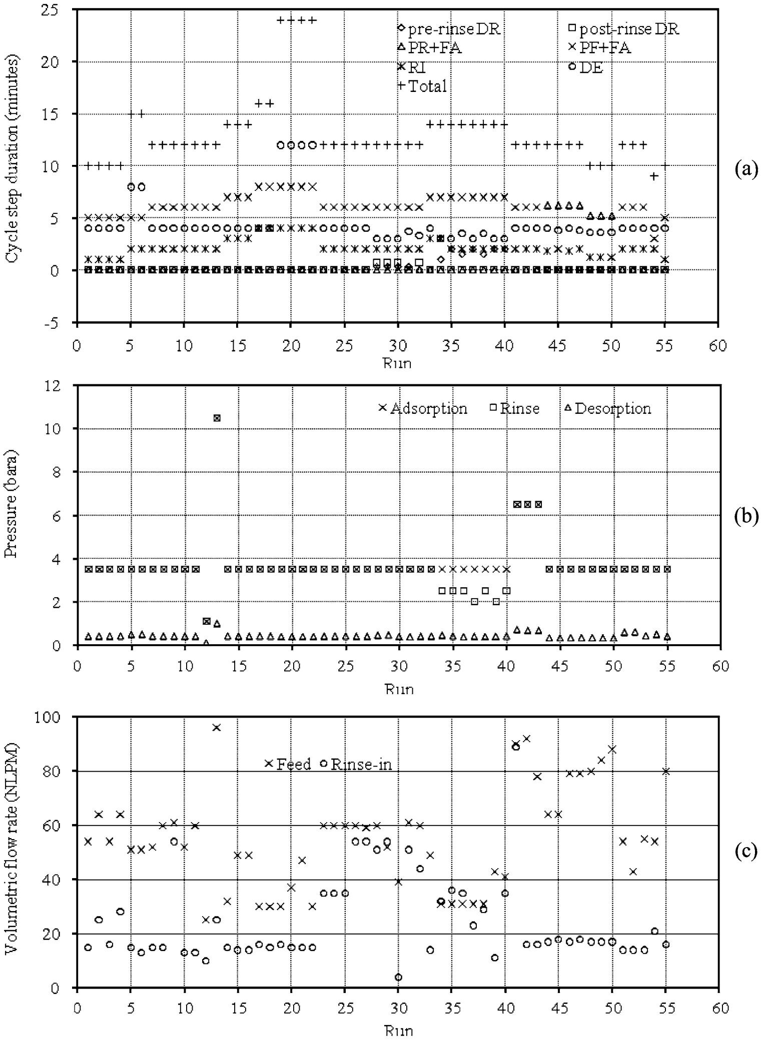


Fig. 5 (**a**) Constituent steps of the cycle run and their durations, (**b**) Adsorption/Rinse/Desorption pressure and (**c**) Volumetric flow rates of the feed gas stream and rinse-in streams for each cycle run

3.6 PSA cycle and number of beds

7 simulations (Runs 5, 6, 19–22 and 54) are done for a 3-bed system while 48 simulations are done for a 2-bed system. Step times are selected so that feed utilization is continuous. For a 3-bed system, the adsorption time is half of the desorption time. The ranges of durations of FA step, RI step and the cycle were 3–8 minutes, 1–4 minutes and 9–24 minutes respectively. Figure 5(a) shows the component step and its duration for each of these runs. The number of beds for each cycle can be found from the total cycle time and the duration of FA/FA + PF steps. For a 4-step cycle, RI step was after the end of FA step and DE step followed the RI step. Two runs used a 5-step cycle wherein DR step was either before or after RI step. A run simulated 6-step cycle that had DR steps before and after RI step.

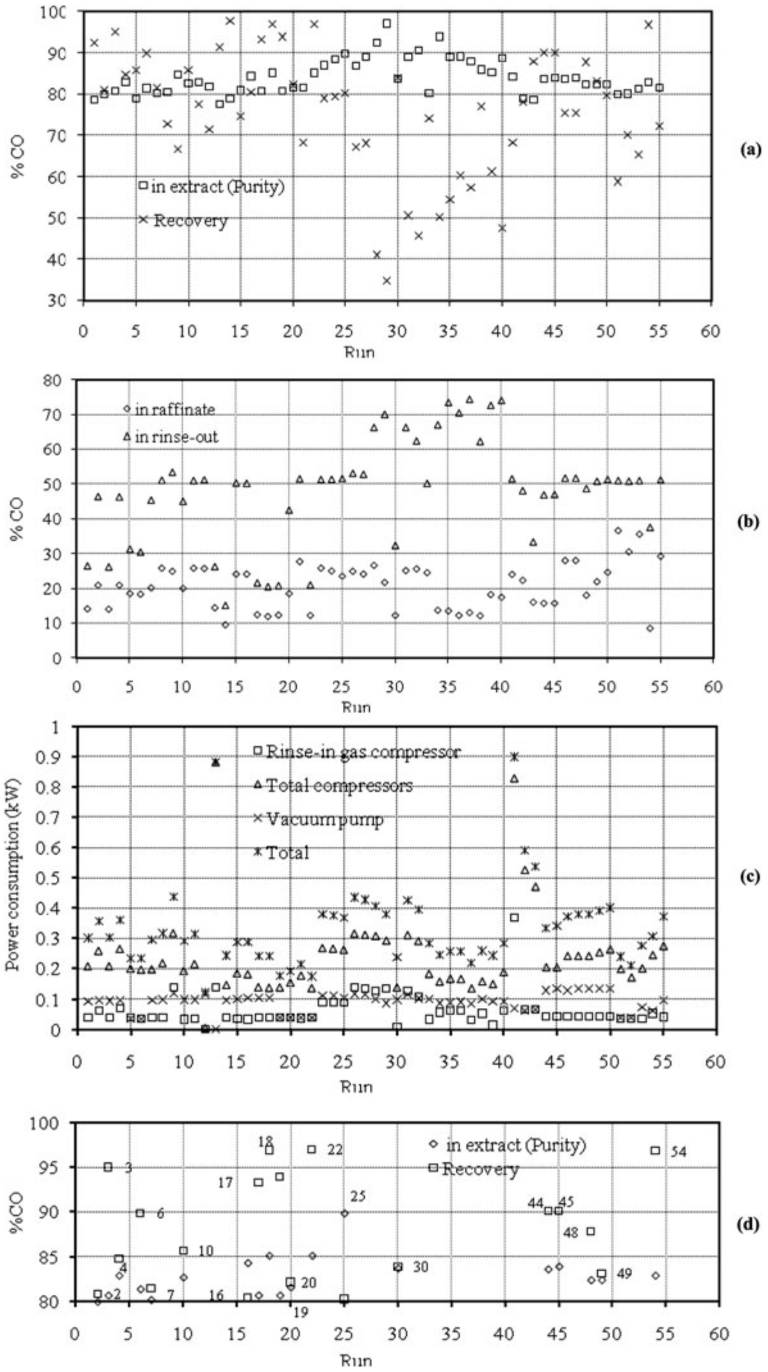
3.7 Rinse pressure

This has to be at least equal to adsorption pressure. If the rinse stream pressure is less than feed pressure, the bed has to be depressurized before rinsing. This will add step DR (pre-rinse DR) to the cycle. Rinse pressure values used in this work are 1.1, 2, 2.5, 3.5, 6.52 and 10.5 bara but most of these are taken equal to the adsorption pressure. It was assumed that pure CO was available in the plant and that too at pressure at least equal to the adsorption pressure. Rinsing with extract or rinsing with low pressure CO will need a compressor.

3.8 Pressurization and rinse steps

Pressurization can be done co-currently with feed gas or counter-currently with fraction of raffinate. Runs 44–50 used counter-current pressurization with raffinate stream. The remaining runs used the feed gas stream for pressurization. Pressurization with raffinate is beneficial as compared to pressurization with feed because raffinate has a lower CO content as compared to feed. Rinsing is done with compressed extract stream or with pure CO. Pure CO as a rinsing stream offers advantages in terms of extract purity without

Fig. 6 (**a**) %CO recovery and %CO purity, (**b**) %CO in raffinate and rinse-out and (**c**) Power consumption, for each run at CSS and (**d**) Runs satisfying 80 % recovery and 80 % purity



detrimentally affecting recovery. Runs 3, 4, 6, 10, 11, 16, 18, 22–25 and 44–55 use pure CO for rinsing. The remaining runs use extract for rinsing.

Figure 5(b) shows the pressures during FA and RI steps and at the end of DE step for each run. This figure helps to classify the cycles as PSA/VSA/PVSA. In the model, a valve is considered at both the ends of the bed. The coefficients of the open valves in a step decide the flow rate in that step. Figure 5(c) shows the predicted normal volumetric flow rates of the feed gas stream (averaged over FA step duration) and of the rinse-in stream (averaged over RI step duration) respectively for each run. Figure 6(a) and Fig. 6(b) show the model predicted separation performance after the achievement of CSS for every run. Figure 6(c) gives the estimated power consumption for each run. For VSA and PVSA cycles, the extract is available at the discharge pressure of vacuum pump (which is 1.013 bara). This becomes the inlet pressure for the power estimation if a rinse-in compressor is needed. For PSA cycle, the inlet pressure of the rinse-in compressor is same as the desorption pressure. Rinse-in

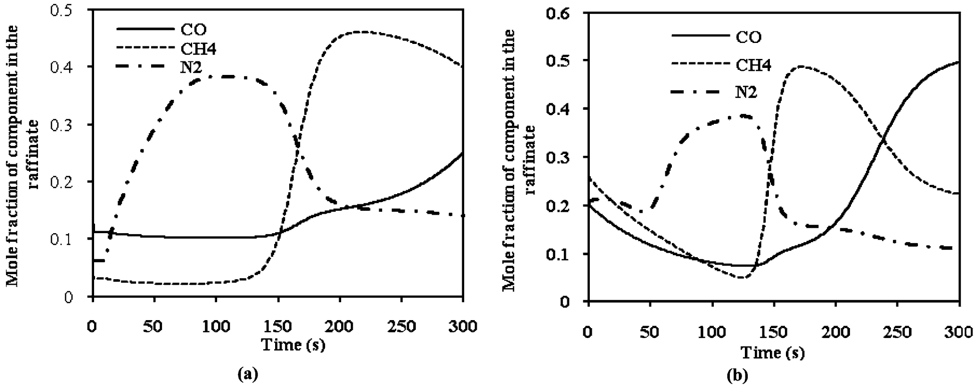


Fig. 7 Raffinate composition profile (**a**) during PF + FA step and FA + RI + DE + PF step sequence and (**b**) during FA step and FA + RI + DE + PR step sequence for 2 bed cycles of 600 seconds duration

compressor power estimation has also been done assuming that pure CO is also available at 1.013 bara. The total power consumed by the compressors is the sum of the powers consumed by the feed gas compressor and the rinse-in stream compressor. The total power consumed is the sum of the powers consumed by the vacuum pump, feed gas compressor and the rinse-in stream compressor. Figure 6(d) gives the runs that satisfy the performance targets given in Table 1. The data points shown in these figures have been tabulated in other work (Mhaskar 2012).

3.9 Runs meeting performance criteria of 80 % recovery and 80 % purity

The simulation results in Fig. 6(d) show that the required separation performance is achievable using a 2-bed cycle. 19 out of the 55 runs met the performance criteria. Stiffer performance specifications of 80 % purity and 85 % recovery leave only 12 runs as relevant. Similarly, only two runs (Run 18 and Run 22) satisfy the more stiffer requirements of 85 % purity and 90 % recovery. These high-end performances come at the price of more adsorbent requirement and/or power consumption. These simulations have helped to get an idea of achievable performance targets and tighter performance targets based on the adsorbent material specified as per Table 2 and use of a single-stage unit.

4 Results and discussions

4.1 Effect of adsorption step duration

Logic to get indicative adsorption duration was discussed earlier. A duration of 300 seconds (5 minutes) was found to be adequate for the expected performance in terms of purity and recovery. Keeping the feed rate and rinse rate unchanged, if the adsorption time for a 2-bed PSA is increased within the range given by Run 1 and Run 15 (5–7 minutes), purity increases further at the cost of recovery (see results of Runs 1, 7 and 15 in Fig. 6(a)). The power consumed by the vacuum pump increases as the amount to be desorbed is more for higher adsorption time (see values for the above indicated runs in Fig. 6(c)). Adsorption step time should be selected based on allowable CO content in raffinate for the required purity and recovery as shown in Fig. 3.

Another advantage of simulation is that one can see the entire time series of raffinate composition. For example, for the above runs, such profiles are shown in Figs. 7(a) and 7(b) for two different PSA cycles. CO profile is monotonically non-decreasing in the case of feed pressurization (Fig. 7(a)), while in the case of raffinate stream being used for pressurization (Fig. 7(b)), the profile goes through a minimum. This is indicative of the possibility that the adsorbed phase concentration profile in the bed at the beginning of adsorption step itself may not be monotonous. As raffinate enters the regenerated bed counter-currently, CO from raffinate will actually get adsorbed. The concentration of CO would thus drop as one goes deeper into the bed from raffinate end. As feed flows into the bed and pushes this bulk phase out of the bed as raffinate, this inverted profile comes out. Although it may not be as simple as that because there is also adsorption/desorption taking place as feed enters, this does indicate a possibility of raffinate concentration of CO going through a minimum with time.

With feed pressurization which has flow direction co-current with that in FA step, this possibility does not exist because what is pushed towards the raffinate end is what was already there at that end of the bed. Watching the effluent concentration time series and also the spatial profiles in the bed at various time, one can actually visualize the interplay of various factors and the impact of co-current and counter-current flows.

Another advantage of observing the raffinate profiles is in taking a decision whether the collection of the raffinate could be in different tanks. For example, during the initial part of the adsorption step, raffinate is much leaner in CO than towards the end of the step and this can be used for pressurization. If one needs a purer CH_4 also as a desirable product, the initial raffinate could be collected into a different tank. Same holds for extract also. Looking at extract

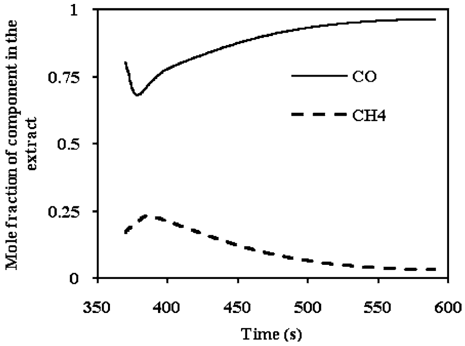


Fig. 8 Extract composition profile during DE step: Cycle time of 600 seconds with FA + RI + DE + PR steps

profile, one may decide to divert extract to different streams to get a high and low purity extract rather than a combined extract of average quality. These finer changes can add value to the product without having to change PSA cycle and are adopted in some value added separations.

4.2 Effect of rinse step time/rinse rate and composition of stream used for rinsing on the separation performance

The step after FA step is rinsing with an appropriate stream composition to displace out and push upwards (towards raffinate end) the CH_4 and N_2 adsorbed up to the FA step. Since CO is the desired product as well as the strongest adsorbate, rinsing must be done with a stream having CO partial pressure greater than the corresponding partial pressure in the feed gas. When such a stream is used, more CO will adsorb by displacing the other components from the bed. Using pure CO instead of extract for RI step gives higher purity as well as higher recovery. Pure CO is the best stream for rinsing (if available) as CO is the desired product. Pure CO was assumed to be available at pressure equal to the adsorption pressure. This also saves the costs related to rinse compressor. If pure CO is not available, then part of the extract has to be used for rinsing as it is the next CO rich stream available for use. Even here, the extract collected during a specific part of extract producing step could be used as it is considerably richer in CO than the entire extract stream. Extract CO concentration profile was indeed observed to go through minimum as shown in Fig. 8. The part after the minima could be used for rinsing.

In this case, later part of extract is richer in CO which could be saved separately and used for rinsing. The advantages can be significant in terms of product purity. The extract fraction has to be compressed before rinsing as it is at the lowest pressure used in any PSA/PVSA cycle.

Duration of step RI and/or flow rate (adjusted through valve coefficient) are also important parameters (Refer to results of Run 8 and 9). As expected, increasing the rinse step time or the rinse rate for the same step time increases purity but recovery drops. Both alternatives also increase the power requirement of the rinse compressor. For example, if Run 1 and Run 3 are compared, then Run 3 gives a higher purity due to rinsing by pure CO but vacuum pump requires more power. This is because by rinsing with pure CO than with an extract having 80 % CO, more CO has to be desorbed out in the depressurization step which is an added burden on the vacuum pump. For PVSA and PSA cycles, rinsing with the fraction of extract increases the costs related to compressors. Hence the use of this step should be minimized by using appropriate co-current depressurization steps before DE step. The effects of using co-current depressurization steps are discussed in Sect. 4.6.

4.3 Effect of using a 3-bed cycle

The results of Run 17 and Run 19 show that the separation performance has remained unchanged and hence going for 3-bed cycle is not worth the capital investment of the third bed and extra adsorbent in the present case. However, as the system offers more time for adsorbent regeneration, there is an operating cost advantage. The 3-bed cycle consumes lesser power for the vacuum pump decreasing the total power consumption. Like purity and recovery, capital cost and operating cost also offer a trade-off in all variations of PSA process.

4.4 Effect of implementing VSA, PSA and PVSA

Refer to the results of Runs 11–13, 41, 42 and 43 in Figs. 6(a) and 6(c). Keeping a pressure ratio of 10 between the adsorption pressure and the desorption pressure but the other variables unchanged, PVSA, PSA and VSA cycles were simulated. For same adsorbent inventory, the feed processing rates were minimum for VSA, intermediate for PVSA and highest for PSA for acceptable CO content in the raffinate. PVSA cycle was tried at adsorption pressures of 6.5 bara and 3.5 bara. The PVSA cycle using an adsorption pressure of 3.5 bara and desorption pressure of 0.35 bara gave the best separation performance. Solid phase concentrations of CO in adsorption step and in rinse step were 4.9 times and 8.7 times higher respectively than that at 0.35 bara. VSA cycle was the lowest consumer of power and required no capital investment on compressors. PSA cycle was highest consumer of power and could also require more investment on beds as the required bed wall thickness may increase. For desorption at vacuum, product CO is discharged at atmospheric pressure. The pressure ratios for the compressors in PVSA cycles were 3.5 and 6.5 as compared to 10 in the PSA cycle. Consequently, the compressor power and costs are highest for the PSA cycle even at the same feed rates. PSA cycle consumed 7 times more power than VSA cycle. PVSA cycle consumed 3 times more power than

VSA. Figure 6(c) shows that the major consumers of power were the compressors particularly the feed gas compressor for this system.

As expected, increasing the adsorption pressure will cause early breakthrough. Lowering the desorption pressure will improve the extract purity. VSA cycle gives a purity above 80 % but recovery is low at a feed rate as low as 25 NLPM. This low recovery is due to low adsorption capacity for CO at 1 bara pressure. As a result the raffinate has 26 % CO. This of course could have been improved using lesser adsorption step time. However, it will come at further reduced recovery. Using an adsorption pressure of 10 bara allows feed rates as high as 96 NLPM. However the extract purity is low. This is due to the fact that the bulk phase in the bed has more gas moles which end up in extract during depressurization. The recovery is high due to the higher adsorption capacity at 10 bara and less CO escapes into raffinate as indicated by low CO concentration in raffinate (14 %). PSA and VSA cycles did not give the required separation performances.

4.5 Effect of CO/CH_4 and CO/N_2 selectivity

The effect of using an adsorbent more selective for CO on the separation performance was also studied using the ratio of adsorption equilibrium constants of CO to CH_4 (b_{CO}/b_{CH_4}) values of 2.44, 2.87 and 3.48 respectively but keeping the value of b_{CO}/b_{N_2} constant to 24.4. The higher selectivity values were indicated by some adsorbent samples which could not be reproduced. The results of Run 23 to Run 25 cover this aspect. The value of 2.44 is the actual value as estimated from the equilibrium constants in Table 2 (Run 23). Purity at a ratio of 3.48 (Run 25) was higher by about 2.8 percentage points than the purity at the actual selectivity value of 2.44 while the recovery at the ratio of 3.48 was higher by 1.3 percentage points than the recovery at the value of 2.44. The power consumption is also the lowest among the three runs for Run 25. It is trivially apparent that an adsorbent more selective for CO will be preferred. Simulation studies could help quantify the advantage and judge whether further efforts on adsorbent development are worth or not. These runs were carried out to provide such a feedback to the adsorbent developers.

N_2 is not an inert in this separation. One has to consider another selectivity value due to the adsorbing N_2. Compare the results of Run 15 and Run 33. The value of b_{CO}/b_{N_2} was reduced from the actual value of 24.4 to 12.9 but keeping the value of b_{CO}/b_{CH_4} constant to 2.44. This reduction increased the content of N_2 in the extract from 1.3 % to 2.0 % while that of CH_4 decreased by equal units. There was no significant effect on recovery, purity and power consumption.

4.6 Effect of co-current depressurization and rinse pressure

Steps of DR were added in order to (i) reduce the rinse pressure and thus the compression requirements, (ii) check if the purity improves as the other components get pushed out and (iii) check its impact on recovery. Cycles were tried with the additional steps of co-current depressurization pre-rinse (Runs 31 and 36–42) or post-rinse (Run 32) or before and after rinse (Runs 28–30). The range of duration of pre-rinse DR step was 0.3–2 minutes. The duration of post-rinse DR step was 0.7 minutes. Run 30 gave the best results. Purities exceeding 90 % were also obtained using DR step but the corresponding recoveries were unacceptable. For the maximum obtained purity value of 97 %, the recovery value was only 35 % (Run 29). Run 30 used DR step before and after rinse, a rinse rate approximately one tenth of the feed rate and fraction of extract for rinsing. In Run 36 to Run 40, DR step is implemented before RI step and rinsing is done at low pressure. This allowed rinsing to be done with extract fraction compressed up to 2.5 and 2 bara respectively (see Fig. 5(b)).

4.7 Comparison of counter-current raffinate pressurization and co-current feed pressurization

The results of Run 44 to Run 50 are relevant here. The step of co-current pressurization with feed was replaced by the step of counter-current pressurization of the bed by fraction of raffinate. Raffinate is not the desired product here and proves to be more than sufficient to pressurize the bed. This allowed use of higher feed rates for same performance in terms of purity and recovery or better purity/recovery for same feed rates. For Run 45, purity was 84 % and recovery was 90 % at the feed rate of 65 NLPM. For Run 10, which used the same cycle time but used PF step instead of PR step gave lower purity and recovery. Results reported in Table 4 also indicate a similar behavior. The raffinate is leaner in CO as compared to the feed (see Fig. 6(b)). CO adsorbs in PR step but less than what will be adsorbed by using PF step before FA step. Also in case of cycle with PR step, the portion towards feed end has less CO as CO is adsorbed mostly towards the raffinate end. So in FA step that follows the PR step, more CO can be adsorbed than that adsorbed when FA step follows the PF step. This effect was seen earlier from the profile of CO fluid phase mole fractions in Figs. 7(a) and 7(b). Profile in Fig. 7(a) is flatter compared to that in Fig. 7(b). Figure 9 shows the solid phase concentration profiles for CO and CH_4. The PF step is carved out of the first half of the cycle. The PR step is carved out of the second half of the cycle in this work. Thus, the duration of FA step is 290 seconds for the cycle having PF step but 300 seconds for the cycle having PR step. Adsorbed phase concentration profile for CO and CH_4 along the bed length

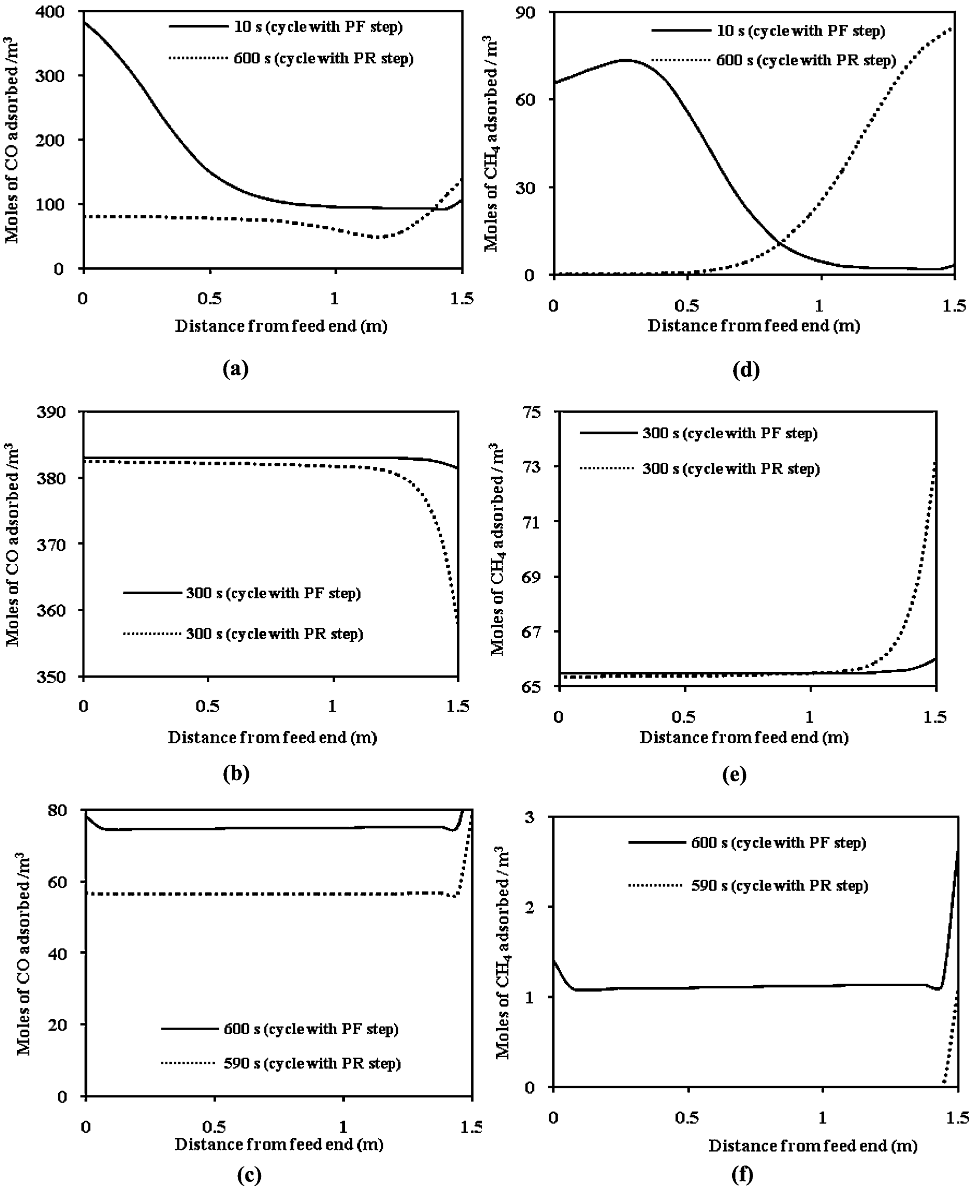


Fig. 9 Axial solid phase concentration of CO and CH_4 at the end of pressurization (**a**, **d**), adsorption (**b**, **e**) and depressurization (**c**, **f**)

at the end of PF/PR, FA and DE steps show the comparison between the two cycle configurations. The effect on separation performance that results by replacing PF step with PR step agrees with the findings reported in earlier works (Zhu et al. 1991).

Alternative stream for pressurization can be the rinse-out stream. The composition of stream flowing out from the bed in rinse step is nearly same as that of the feed stream composition and the moles going out are lesser than that required to pressurize the bed. CO content in rinse-out stream is also higher than that in the raffinate. So recycling the rinse out stream will not be sufficient for pressurization and will not prove beneficial for getting high extract purity. However the rinse out stream can be compressed, recycled and mixed with fresh feed gas during FA step. This will improve the CO recovery. Rinsing the bed with any stream that is richer in CO than the feed and pressurizing the bed with any stream that is leaner in CO than the feed will benefit. Mixing the rinse-out stream with the raffinate stream will give a stream having higher CO content than in the raffinate stream. Using an inert for pressurization will have the drawback that CO in raffinate is still lost instead of getting recycled back to the bed. So raffinate stream is the preferred stream for pressurization in the present separation task.

For this system, raffinate is not the desired product yet has CO in it. Recycling back some fraction of this raffinate for pressurizing the bed improves the CO recovery by eliminating the need for fresh feed gas during pressurization and by reducing the amount of CO permanently lost as part of the raffinate.

4.8 Effect of temperature

Though the adsorption capacity decreases, high temperature operation increases the linearity of the isotherm, makes desorption favorable and reduces mass transfer resistances. The selectivity may increase or decrease or remain unchanged. Run 51 to Run 54 use a higher temperature of 323.15 K. At 323.15 K, if we use the adsorption time and feed rate used in the run at 303.15 K, CO content in the raffinate will increase and its recovery will drop. This is because at the higher temperature, the equilibrium constants have decreased. CO starts to breakthrough earlier. So a 9-minutes cycle employing three beds was also considered at 323.15 K and this gave the desired performance (Run 54). Majority of the applications of CO require a temperature of at least 323.15 K. The feed gas considered here comes at slightly lower than ambient temperature value from the liquid N_2 washing section and does not have any condensable components. Nor does it require recycle of a product stream from the PSA unit back to the upstream unit. Hence operation at ambient temperature of 303.15 K seems to be okay.

4.9 Effect of increasing bed volumes and velocities simultaneously

The bed dimensions and flow velocities used in the 55 simulations were typical of what are used in PSA studies in bench-scale and pilot-scale units. The difference between these units and large-scale units is generally that the flow velocities can be of an order of magnitude higher. Large-sized units are governed by capacity requirement. However, in PSA, there is a practical limit on bed diameter and height of the beds that can be used. The limit on diameter is generally due to the distribution considerations. PSA units rarely use a bed diameter of more than 1.5 m because of the concurrent difficulties in effective distribution of inlet/outlet streams to/from the bed. If distribution is not adequate, adsorbent is not utilized properly. Similarly, the limit on height is mainly due to the crush strength of the adsorbent particles (Geankoplis 1997). Normally, heights of beds are not more than 10 m. Taller beds also require more elaborate mechanical design due to wind load, seismic load etc. in addition to pressure load and call for wall thickness higher than what is required from pressure design point of view (Megyesy 1995). As mentioned earlier, flow rates could be such that the ratio of adsorbent layer height to flow velocity is similar to what is used in pilot plant units. This simple hydrodynamic scale-up criteria is often effective.

The simulations for small-scale offered one advantage in that the number of divisions along the bed for simulation were less and hence the simulation times were reasonable. Large-scale units differ considerably in flow velocities. Of course, the bed sizes are much larger. Simulation studies were also carried out for large-scale flow rates and bed sizes for the same adsorbent-adsorbate system. These studies were time consuming. Nevertheless, they offered a useful insight into a large-scale PSA system design and also allowed development/verification of some design heuristics. Some salient results are summarized here.

The results of small-scale simulations are used to decide the operating pressures, temperature, cycle steps, the step sequence, the number of beds, the stream composition for rinsing if this step is required, the stream composition for purging if this is step is required, the stream composition for pressurization and the flow direction in pressurization that should be used for the simulation of larger bed volumes and flow rates. These results also justified the use of single-stage process based on a single material that physically adsorbs the components and offers a CO/CH_4 selectivity of 2.44 only. For the operating temperature of 303.15 K, the lowest cycle time considered for simulation on this small-size and small-velocity units was 10 minutes. The large-scale simulations were done at temperature of 303.15 K. Since the large-scale volumes and velocities are higher, we started with a cycle time lower than 10 minutes. The total cycle duration of 6 minutes was comprised of component step durations: PR (10 seconds) + FA (180 seconds) + RI (30 seconds) + DE (140 seconds). Two bed units were considered as these were found adequate earlier.

With the above cycle, bed height was adjusted to get the desired performance. Rinsing was done by extract or by pure CO assumed to be available at feed gas pressure of 3.5 bara. The extract tank pressure was 0.35 bara and that of raffinate and rinse-out tanks was 3.4 bara. The start-up conditions were same as those used for adsorption breakthrough curve and PSA cycle simulations done for small-scale units. Large columns have linear superficial velocities in the range of 0.1–0.5 m/s during the FA step (Geankoplis 1997). The valve coefficients were adjusted to get a velocity in this range. The inner diameter of the column was taken as 1 metre. The adsorbent layer height was varied in the range of 4–6 m so that bed volume lies in the range of 3.1–4.7 m^3. Convergent temporal step size was found to be a second for the steps of FA and RI and 0.5 seconds for the steps of PR and DE. Convergent spatial step size was found to be 0.08 m for all the layer heights. The simulation results are shown in Table 5. Important concentration profiles are shown in Fig. 10 for the case offering the desired performance.

Cases which differed in bed heights and flow rates from this case are also reported to indicate that the design was indeed optimal. Case 1 uses the lowest height and also has highest feed rate. Smaller height and high feed rate have given a higher purity but CO content in raffinate is high enough to reduce the recovery to 51 %. Cases 2 to 4 use same feed rates and rinse rates. Increasing the height has decreased the purity and correspondingly increased the recov-

Table 5 Results of simulation at larger bed volume and larger velocities

Case	Bed volume (m^3)	Q^F (NCMPH)	Rinse stream composition, Q^{RI} rate (NCMPH)	% CO in extract (Purity), % CO recovery, % CO in raffinate	Feed compressor, Rinse compressor, vacuum power (kW)
1	3.1	1671	Pure CO, 846	85.9, 51, 40.4	70, 0 , 25
2	3.9	1248	Pure CO, 743	84.3, 78.9, 25.1	52, 0, 29
3	4.7	1210	Pure CO, 750	83.3, 92.6, 12.1	51, 0, 34
4	4.7	1210	Extract, 703	80.2, 89.6, 12.1	51, 29, 33

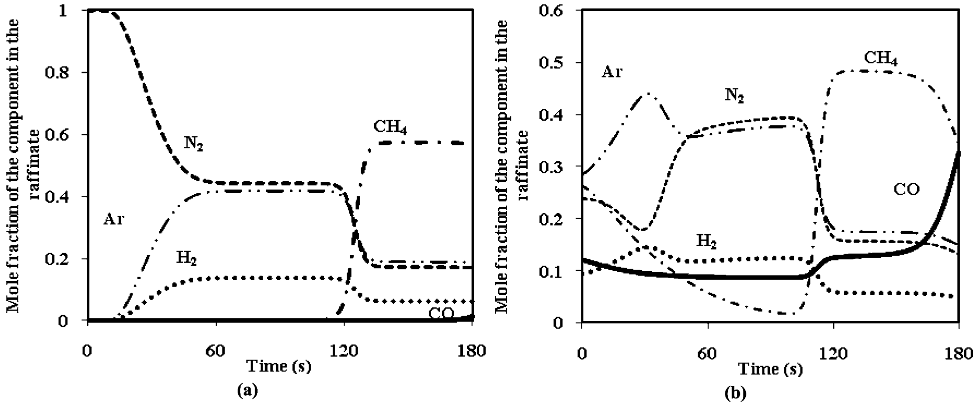


Fig. 10 Raffinate concentration profile in FA step (**a**) of first cycle and (**b**) at CSS for Case 3

ery. Case 3 and Case 4 give the desired separation performance. Pure CO (Case 3) gives higher purity and recovery than that given by using extract (Case 4) for rinsing. Extract rinsing also requires additional compressor power of 29 kW. Using more rinse rate will further improve the purity at the expense of recovery and more compressor power requirement.

Refer to Fig. 10, which is obtained from the simulation results of Case 3. This happens to be the best case. Looking at the adsorption breakthrough behavior in cycle 1 (Fig. 10(a)), CO starts to come out of the bed from 133 seconds after FA step has started. At 180 seconds, CO content in the outgoing fluid is only 1.27 %. However, after CSS is achieved (Fig. 10(b)), it is seen that CO content in the bed outlet stream starts to increase after 91 seconds of FA step have elapsed. This is due to incomplete regeneration of bed at the end of depressurization step and due to adsorption occurring in the step of pressurization. The value of t^* for the feed rate and bed dimensions used in Case 3 and Case 4 was found using Eq. (9) to be 293 seconds. Selected duration of FA step was around 60 % of this value and proved to be a good selection. Table 6 gives the comparison between the small scale (Run 48) and large-scale (Case 3) simulations with respect to crucial points. The small-scale unit differs with respect to bed volume, velocity, step duration and the step size used for spatial and temporal discretization. Component steps of the PSA cycle were the same in both the cases. As mentioned earlier, the larger PSA unit uses lower cycle times than those used in small scale units earlier. Residence times (ratio of bed height to superficial feed velocity in step FA) in larger units were approximately 60 % of the corresponding value used in small scale unit simulation. The cycle duration was correspondingly reduced also to 60 % of corresponding values for small bed PSA. The small-scale unit required 30 times less CPU time for a cycle simulation on a 2 GHz processor with 3.3 GB memory and 32-bit operating system. Case 4 gives 80 % pure CO at 90 % recovery. This is the next best case and uses extract for rinsing.

4.10 Strategy for handling feed gas having lower CO content

It was also tried out whether by changing bed dimensions and/or PSA cycle configuration, a tail gas feed leaner in CO could be processed to get same product purity and recovery. The average composition of this leaner feed gas was 30 % CO, 20 % CH_4, 19 % N_2, 5 % H_2 and rest as Ar and other inerts.

Purity was targeted first. It was possible to get at the most 68 % pure CO in a 2-bed PVSA cycle at a recovery of 70 %. This is so because of lower content of CO in the feed and competitive CO-CH_4 adsorption due to selectivity ratio as low as 2.44 (Peter et al. 2010). The PSA cycle for achieving this performance comprised of the four steps in sequence as FA + RI with compressed fraction of extract + DE + PR of durations 300, 70, 220 and 10 seconds respectively. The feed rate was 87 NLPM and the rinse rate was 43 NLPM. There seemed to be no other alternative but to use cascaded

Table 6 Comparison between small-scale and large-scale simulations

Scale	Large (Case 3)	Small (Run 48)	Ratio
Adsorbent layer height (m)	6	1.5	4
Bed inner diameter (m)	1	0.15	6.6
Bed volume (m^3)	4.7	0.027	178
Range of superficial linear velocity in FA step at the feed end of the bed (m/s)	0.1–0.4	0.016–0.044	6–9
Q^{F} (NCMPH)	1210	4.8	257
Time at which CO content in raffinate starts to rise during FA step at CSS (s)	92	136	0.68
Feed end residence time range (s)	15–60	34–93	0.4–0.6
CPU time (s) per cycle	6328–7902	220–236	27–33

PSA to achieve the minimum purity target of 80 % (Peter et al. 2010). This was achieved as follows.

The earlier PSA process where 80 % purity and 81 % recovery were achieved was seen as the secondary stage of the cascaded PSA. It would therefore need a feed with 50 % CO. The primary unit of the cascaded PSA should therefore process the tail gas containing 30 % CO to get an extract stream of 50 % CO. To retain the overall recovery of the cascaded PSA to 80 %, it is also imperative to operate the primary PSA unit at almost 100 % CO recovery. This means that the raffinate in the primary stage should be almost CO-free. Such a system was designed using the simulation model. A PVSA cycle comprising the step sequence of FA + DE + PU by fraction of raffinate + PR with durations 240, 170, 60 and 10 seconds respectively offered extract purity of 52.5 %. The feed rate was 81 NLPM, the purge-in rate was 37 NLPM and the CO recovery was 99.7 %. This extract after compression will serve as feed stream to the secondary PSA. The extract was produced from this stage at the rate of 48 NLPM. The cycle discussed in previous paragraph and the primary stage discussed in this paragraph used the pressure range of 0.35–3.5 bara and temperature of 303.15 K. Bed and adsorbent dimensions were as given in Table 2 for all these simulations.

To integrate the two stages of the cascaded PVSA, it is important to have extract flow rate of the first stage to match with the input stream requirement of the second stage. The primary stage should thus be scaled up to produce 64 NLPM extract (Feed rate in Run 2 of Fig. 5(c)). The bed and the feed rate in the primary stage should thus be enlarged by a ratio of 64/48 or 1.33 times. This can be achieved easily by increasing the bed volume in the first stage to 1.33 times as compared to the secondary stage value and by increasing the feed rate to the first stage to 108 NLPM from the earlier value of 81 NLPM. This simple hydrodynamic scale-up with primary stage using 33 % more adsorbent than the secondary stage would help produce 80 % pure CO at 80 % recovery starting with a leaner tail gas with only 30 % CO. There was no use of a recycle of a stream from the second stage to the first stage.

The design of cascaded PVSA system may still not be optimal. For example, it may be possible in this case to enrich CO to an intermediate purity level different than 50 % and still achieve the overall goals of purity and recovery. It could also be possible to keep the bed sizes same in all stages and play with PVSA cycle configuration to achieve the overall goal. Ultimate design will also have to take into account the process economics. This exercise was not carried out in the present work.

5 Heuristics for simulation-based synthesis and design

These extensive simulation studies aimed at optimal design offered deeper insight into the functioning of various PSA cycle steps and their roles in deciding overall performance. Some heuristic rules for design were arrived at. Even a single PSA simulation is quite computationally intensive. This is so because of the simultaneous solution of mass and momentum transfer equations and the necessarily iterative approach to CSS performance. Many such simulations would be called for if one were to arrive at an optimal combination of design and operating parameter values that give the desired performance for a given separation task. This design exercise would be helped a great deal if initial guess for a candidate design is itself made based on minimal information about the characteristic parameters of the adsorbent/adsorbate system. Some useful rules that could be extracted out of these extensive simulation studies are as follows.

1. A breakthrough curve is a very powerful and information-rich data on any adsorbent-adsorbate system. Design is greatly helped if a breakthrough curve is generated using appropriate velocity range for flow of adsorbate through the adsorbent bed. The initial bed condition before the feed is passed through the bed could be

a fully regenerated bed. This could mean a bed saturated with pure N_2 if one is designing a system for recovery of CO_2 from flue gases. In the case of the PSA considered in this section, the bed was initially assumed to be initially saturated with N_2 only because it was a least preferred adsorbate among the major feed components. Breakthrough curve is a packed bed's response to adsorption/desorption and comes closer to what happens during adsorption step of any PSA process.

2. The bed dimensions for generation of such breakthrough curves could be those of a pilot plant set-up or a proposed industrial unit depending on whether one is carrying out pilot plant verification of separation strategy or designing a commercial scale unit. For pilot plant scale, the bed dimensions could be actual dimensions. For commercial unit design, the bed diameter could be decided through consideration of distribution and bed height could be decided using adsorbent crush strength and mechanical design implication of tall columns.
3. The adsorbent-adsorbate system characteristic parameters such as equilibrium and kinetic parameters could be extracted from analysis of experimental breakthrough curve generated in a lab-scale unit. Parameter values that strike a least squares fit between experimental and simulated breakthrough curves can be accepted as more representative of the system as compared to their estimates from simpler particle level studies such as gravimetric studies (Mhaskar 2012). This is so because bed hydrodynamics is brought into picture while analyzing breakthrough data.
4. The desired purity and recovery for a given feed composition gives the maximum content of desired component that can be allowed to escape in the raffinate stream for an extract PSA or in an extract stream for a raffinate PSA. For extract PSA, the time on the breakthrough curve up to which the mixed-cup composition of the effluent stream (raffinate) is within this limit serves as the maximum possible adsorption step time. For raffinate PSA, the breakthrough curves can be used to similarly decide the time beyond which the undesired component will start affecting the raffinate quality. Actual duration of the adsorption step would have to be actually less than this as the adsorbent bed would never return for adsorption in fully regenerated condition. 80 % of the estimated time turned out to be a good starting guess for the duration of the feed adsorption step in this case. Non-isothermal effects could mean that practical duration of adsorption steps in PSA will have to be shorter than the one arrived at using isothermality assumption. In cases where significant temperature effects in the bed can be legitimately neglected, the suggested procedure to get a first guess of adsorption step time could be very useful. In the present case, the heats of adsorption of the competing adsorbates (CO and CH_4) were nearly same and so were there adsorption capacities. The separation was mostly by displacement of one component by the other and the thermal effects of adsorption/desorption would be moderate. With the PSA beds generally non-insulated, the isothermality assumption was reasonable.
5. PF and DR steps could be carved out of this adsorption step time estimate as small duration steps. About 10 seconds are normally considered sufficient for these steps but may need more duration. PF step along with the FA step constitutes the feeding part of a raffinate PSA cycle. Valve dynamics and velocity constraints play an important role in practical implementations. Large sized valves also take finite time to open and close, and could necessitate suitable gaps between the end of one step and the beginning of the next step. In another related PSA system design of surge-less PSA systems, the authors used on-off valves and flow control valves in series and could achieve shorter duration steps effectively by implementing control valve closure as per pre-designed time series (Mhaskar 2012).
6. The other major PSA cycle steps are the regeneration steps. These should be chosen such that all regeneration steps (DE, PU, RI, PR, DR, PE) together are of same duration as the sum of all feeding steps (FA and PF) for a minimal PSA system, i.e. a 2-bed system. For adsorbent-adsorbate systems which offer difficult desorption and call for more time for desorption, the next possible number of beds is 3. Here, the regeneration steps should together be of twice the duration of the production steps etc. How difficult the desorption is, can be decided by either generating a desorption breakthrough curve or even from the non-linearity of adsorption isotherm. Or else, it could be quantified by trying first with a 2-bed system and then opting for 3-bed or 4-bed system if required. The input stream compositions are important for steps of pressurization, rinsing and purge. Flow direction is important in the step of pressurization. These depend on which stream is the desired product. In extract PSA, using the feed for pressurization or extract for rinsing will reduce the recovery of the desired product. Instead, pressurizing with raffinate improves recovery as well as purity and also saves energy. Rinsing the bed with extract is an energy intensive step and should be used carefully in extract PVSA and PSA cycles. Using co-current depressurization steps before counter-current depressurization or rinse steps will help to improve the purity and reduce the compression costs in the rinse step.
7. Simple PSA cycles with major steps of adsorption and depressurization can be tried first. Other supportive steps such as feed or raffinate pressurization and rinsing/purging are generally of small duration and enhance

product purity. These can be added in the cycles after the number of beds are arrived at through simulations. While these steps are added, the ratio of durations of regeneration and production steps must be kept constant.

8. Temperature of adsorption is important. Higher temperature will generally reduce adsorption capacity and call for more adsorbent inventory for same throughput. At the same time, desorption isotherms could be more favorable for the desired separation at higher temperature because of improvement in selectivity and/or decrease in non-linearity. Reduction in adsorption capacities and whether selectivity improves or not are solely decided by the heats of adsorption of competing components. Mass transfer coefficients will increase with increasing temperature. Higher or lower operating temperature than the ambient value would increase capital/operational costs and this would generally negate any advantage offered by PSA operation at temperatures different from the ambient value except in cases where the upstream unit is itself at a much higher or lower temperature (than the ambient value) and requires recycle of an outlet stream from the adsorber back to the upstream unit or deals with condensable components like water, ethanol, n-pentane, etc.
9. The feed pressure and the depressurization pressure selection is a major task. For a given feed composition, adsorption capacities would be higher for higher feed pressure and regeneration would be more complete for lower pressures. Pressure ratios of 8 or above are recommended if possible. However, most appropriate pressure levels for PSA can be arrived at through simulations. Ideally, one should keep an eye on the effect of this decision on the process economics also. The pressures of the upstream and downstream units may help in selecting the pressure levels. VSA is a first choice to be evaluated for a single stage unit and for every additional stage of a cascaded unit.
10. Depending upon the selectivity of adsorbent towards the component expected to be concentrated, a raffinate or extract PSA could be chosen. For example, if adsorbent is less selective towards the desired product, a variation of PSA termed as raffinate PSA in this work, would be designed. Extract PSA would be the choice otherwise. Raffinate PSA is a better option as desired product (raffinate) is at higher pressure close to feed pressure and compressor associated costs are less. The performance obtained by using a single adsorbent material that adsorbs physically in a single-stage should be assessed first. Tighter separation targets may need the use of layered bed or cascaded unit or highly selective materials such as those based on chemical adsorption. Situations involving low adsorption selectivity or low content of the desired product in the feed gas may require the use of cascaded unit.

Some of these rules helped in minimizing the simulation effort for designing a system for a targeted performance. However, the rules themselves had to be arrived at through extensive simulations in the beginning.

The generic simulation model was also used to study several other challenging separation tasks belonging to raffinate and extract PSA categories, systems with low selectivity values, systems with several adsorbable components, etc. (Mhaskar 2012; Mhaskar and Moharir 2011; Peter et al. 2010). These studies led to additional heuristics regarding lumping strategies for PSA systems for multicomponent separation, cascaded PSA for systems with low selectivity, pressure and flow surge minimization through model based control and a possible import of SMB concept to PSA systems.

6 Conclusions

A case study involving enrichment of CO from a tail gas containing CH_4 and N_2 as competitive adsorbates was studied extensively using simulations. The case study posed a challenging separation performance achievable only through judicious choice of a PSA cycle. A way to carry out simulation based synthesis and design has been proposed such that the simulation effort is targeted towards fast convergence to the final acceptable design of a suitable PSA cycle. Several important heuristic rules for synthesis and design of a PSA system have been derived and presented in this paper.

The paper also studied the importance of minor steps such as rinsing, purging, pressurization, etc. from their impact on performance parameters such as purity and recovery and on operating costs. The insight should be useful for most PSA systems.

The work here shows the complexity involved in design of PSA processes and also shows how a PSA process model can be effectively utilized for the design.

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