Operation of irreversible series reactions in pressure swing reactors

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Chapter 3

Selectivity Effects on Series Reactions by Reactant Storage and PSA Operation

This work evaluates adsorptive reactors used to improve the operation of a sequential reaction scheme, \( A \xrightarrow{D} B \xrightarrow{D} C \), for the total removal of A from a stream with an excess of B. In the adsorptive-reactor concept, the reactor is filled with a physical mixture of catalyst and an adsorbent, the latter being thermodynamically selective toward primary reactant A. In this case, the sorbent is periodically regenerated using the principles of pressure swing adsorption and purged with secondary reactant D. This concept is restricted to low temperatures to have sufficient adsorption capacity. Improved reaction selectivity arises from the accumulation of A in the unit. The reaction of A maximizes the driving force for regeneration and thus accelerates the regeneration half-cycle. The adsorptive reactor is compared to a conventional plug-flow reactor (PFR) and to a PSA & PFR unit in series. Reaction selectivity improved and recovery of pure B over these alternative reactors under realistic conditions are demonstrated. The volume-based productivity is lower than that of a PFR but higher than that of a PSA. The purge gas flow rate can be manipulated to balance the sorption flux and reaction rate, thereby maximizing the conversion of A. The influence of differences in sorption kinetics is discussed and the required sorbent characteristics are identified.

3.1 Introduction

Pressure-swing adsorption (PSA) is an established separation technology based on selective, reversible adsorption of one or more components in a gas mixture onto an adsorbent (Ruthven, 1984; Ruthven et al., 1994; Yang, 1987). Selective adsorption may either be based on differences in sorption equilibria or on different sorption kinetics. PSA operation consists of alternating adsorption and regeneration steps, and the unit is run in a cyclic invariant state. The design of PSA units is not straightforward due to the large number of operating parameters and its intrinsic dynamic character. Although a few rules of thumb are known, detailed simulation is essential for design (LaCava et al., 1998).

Vaporciyan and Kadlec (1987) were the first to extend PSA to chemical reactors, thereby employing in-situ separation of products/reactants during chemical conversion. They proposed to use a mixture of a catalyst and a sorbent in the reactor vessel and operate it under a pressure-swing cycle. Such a reactor is now known as the pressure-swing reactor (PSR), pressure-swing adsorber reactor (PSAR), sorption-enhanced reaction process (SERP), or adsorptive reactor. The in-situ separation can be used to improve the performance of a chemical reactor. Several operating principles can be utilized.

Equilibrium-limited reactions can be driven to completion by separation of the reaction products. In contrast to equilibrium-limited reversible reactions, irreversible reactions have received little attention in PSR research and the focus has been on rate improvement. Alpay studied the reaction \( A \rightarrow B \) in a rapid PSR, where the adsorption affinity of \( A \) dictates the residence time in the vessel and thus conversion (Alpay, 1992). Vaporciyan and Kadlec (1989) showed that the rate of CO oxidation can be increased by adsorbing \( 0 \), since the reaction rate is inversely proportional to the CO partial pressure.

In the present work we focus on sequential irreversible reactions, where selectivity toward reaction intermediates is the crucial parameter. An example is the selective hydrogenation of ethynes (Derrien, 1986). In chapter 2 we have shown that by selectively adsorbing the reaction intermediate \( B \) in a sequential reaction scheme: \( A \rightarrow B \rightarrow C \), selectivities beyond those obtained in a steady-state operated plug-flow reactor can be obtained under pressure-swing operation.

In the sequential irreversible reaction scheme: \( A \xrightarrow{+D} B \xrightarrow{+D} C \), where selectivity toward \( B \) is the crucial parameter, separation of \( B \) and \( D \) by selective adsorption of \( B \) can also increase the selectivity toward this product. The soundness of this principle was illustrated for batch operation in a chromatographic reactor (Liden and Wamling, 1989).

In case of a feed mixture with both \( A \) and \( B \) present, application of the preceding
Principle II: Accumulation of the desired reactant (isothermal)

principle has some pitfalls. Component B from the feed can saturate the sorbent and minimize the operating capacity of the sorbent.

For such systems we propose to enhance the selectivity toward B by reactant storage. When feeding a mixture of A and B, A will accumulate in the reactor vessel by adsorption onto the sorbent, and is thus not available for reaction; A will be absent before the adsorption front. These conditions are unfavorable for operation as the availability of the desired reactant A is reduced. We therefore propose to start the reaction as the adsorption front of A reaches the product end and reactant D is introduced as purge gas in the regeneration step. At this moment the ratio of A over B present in the vessel is much more favorable than the feed composition, resulting in improved reaction selectivities over an ordinary PFR. Secondly, the conversion of A by reaction will further lower its gas-phase concentration, and thus maximize the driving force for regeneration and improve the productivity of the unit. With the proposed operation, separation and reaction are integrated in space, but separated in time.

In this work we investigate whether this operating principle can be put to work in a PSR unit and employed to yield improved performance over traditional reactor configurations.

3.2 Reactor models

Three reactor configurations are compared in this work: (1) A PSR reactor where equal volumes of catalyst and adsorbent are perfectly mixed, (2) a PFR with an identical amount of catalyst as in (1), (3) a PSA with the sorbent followed by a PFR with the catalyst. The stream enriched in A from the PSA is fed to the PFR.

A reactor model was derived using the following assumptions: (1) Isothermal operation; (2) Ideal gas law is obeyed; (3) Axially dispersed plug flow in the bed; (4) Negligible pressure drop over the bed; (5) Adsorbent and catalyst of constant voidage, bulk density and particle size; (6) No radial concentration gradients; (7) Perfect mixing of the catalyst and adsorbent particles; (8) Adsorption isotherm of the Langmuir type; (9) Mass-transfer resistance is described by the linear driving-force model; (10) Reactions are first order in reactant partial pressures; (11) The specific time constant for catalytic reactions is negligible to that of other processes in the reactor. Isothermicity clearly is the most stringent assumption and will be relaxed in chapter 4.

In parametric studies, it is convenient to write the governing equations in their corresponding dimensionless form. The adsorption step \( P_{\text{high}}, v(\text{prod}) \) and PSR reactor length \( L \) are used as a reference state. The resulting variables and parameters are given in the
notation section.

The single-species mass balance reads:

$$\frac{\partial}{\partial \tau} (y_i P) = -P \frac{\partial}{\partial x} (V y_i) + \frac{P}{Pe} \frac{\partial^2}{\partial x^2} (y_i) - \chi_i \frac{\partial}{\partial \tau} (\theta_i) + v_{i,1} R_1 + v_{i,2} R_2 \quad i = 1 \ldots N \quad (3.1)$$

The overall mass balance reads:

$$\frac{\partial}{\partial \tau} (P) = -P \frac{\partial}{\partial x} (V) - \Sigma_i \chi_i \frac{\partial}{\partial \tau} (\theta_i) + \Sigma_i v_{i,1} R_1 + \Sigma_i v_{i,2} R_2 \quad (3.2)$$

Sorption kinetics using the linear driving force model:

$$\frac{\partial}{\partial \tau} (\theta_i) = \Phi_i (\theta^*_i - \theta_i) \quad i = 1 \ldots N \quad (3.3)$$

The sorption equilibrium using the Langmuir isotherm:

$$\theta^*_i = \frac{\kappa_i y_i P}{1 + \kappa_j y_j P} \quad i = 1 \ldots N \quad (3.4)$$

The reaction rates:

$$R_1 = K_1 y_A y_D P^2 \quad (3.5)$$
$$R_2 = K_2 y_B y_D P^2 \quad (3.6)$$

The pressure ramp is imposed:

$$\frac{\partial P}{\partial \tau} = \zeta_{\text{press}} \quad \text{pressurization}$$
$$P = 1 \quad \text{adsorption}$$
$$\frac{\partial P}{\partial \tau} = \zeta_{\text{depress}} \quad \text{depressurization}$$
$$P = \Omega \quad \text{purge} \quad (3.7)$$

The boundary conditions are given in Table 3.1. The PFR model is the steady state equivalent of the PSR model with the boundary conditions for the adsorption stage. The PSA model is identical to the PSR model without reaction terms.

The PSA and PSR units in this study are operated in the single-bed version of the four step Skarstrom cycle (Skarstrom, 1960)(Figure 3.1). For the PSA, part of the product gas is temporarily stored in a well-mixed tank. During pressurization/depressurization a
Principle II: Accumulation of the desired reactant (isothermal)

<table>
<thead>
<tr>
<th>press.</th>
<th>ads</th>
<th>depress.</th>
<th>purge</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0</td>
<td>x = 1</td>
<td>x = 0</td>
<td>x = 1</td>
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<tr>
<td>y</td>
<td>eqn. 3.2</td>
<td>V = 0</td>
<td>eqn. 3.2</td>
</tr>
<tr>
<td>x = 0</td>
<td>eqn. 3.2</td>
<td>V = 0</td>
<td>eqn. 3.2</td>
</tr>
</tbody>
</table>

(a) \( \frac{\partial}{\partial t} (y_i) = Pe \left( y_i - y_i(\text{feed}) \right) \)
(b) \( \frac{\partial}{\partial t} (y_i) = 0 \)
(c) \( \frac{\partial}{\partial t} (y_i) = Pe \left( y_i - y_i(\text{purge}) \right) \)

Table 3.1: Boundary conditions for the vessel model

The performance indicators used for all units are the conversion of A \( (X_A) \), the reaction selectivity \( (R_1/R_2) \), and the productivity \( (Pr) \). Productivity is based on the amount of feed gas processed per time and multiplied by the reference state \( \left( \frac{\text{mol feed}}{\text{s} \ \text{kg ads}^{-1}} \right) \) for the PSA and PSR and \( \left( \frac{\text{mol feed}}{\text{s} \ \text{kg cat}^{-1}} \right) \) for the PFR unit. Further performance indicators are the product stream purity of A over A, B & C \( (P_{UA}) \), the recovery of B \( (R_{VB}) \). The definitions of these are given below.

The cumulative flux of a component in a stream is defined as an auxiliary variable:

\[
J_i(\text{stream}) = \int_{\tau_{\text{cycle}}} \pm y_i \left. V \right|_{x=0 \wedge x=1} \text{P} d\tau
\]

Figure 3.1: The Skarstrom cycle for pressure swing operation. For the PSA S represents a ideally mixed storage tank where part of its contents is used as purge gas at low pressure. For the PSR component D is introduced via the purge feed at low pressure.
where the cycle time is given by \( \tau_{\text{cycle}} = \tau_{\text{pres}} + \tau_{\text{ads}} + \tau_{\text{depres}} + \tau_{\text{purge}} \). The net consumption of a component over one cycle is given by

\[
\Delta J_i = J_i(\text{feed}) - J_i(\text{prod.}) + J_i(\text{purge}) - J_i(\text{exh.}) \tag{3.9}
\]

The performance indicators defined in terms of \( J \) and \( \Delta J \) are:

\[
X_A = \frac{\Delta J_A}{J_A(\text{feed})} \tag{3.10}
\]

\[
R_1/R_2 = \frac{\Delta J_A}{\Delta J_C} = \frac{\int_{\tau_{\text{cycle}}}^{1} K_{1} y_A y_D P \, dx \, d\tau}{\int_{\tau_{\text{cycle}}}^{1} K_{2} y_B y_D P \, dx \, d\tau} \tag{3.11}
\]

\[
Pr(PSA) = \frac{\sum_{i=A,B} J_i(\text{feed})}{\tau_{\text{cycle}}} \tag{3.12}
\]

\[
Pr(PFR) = \sum_{i=A,B} V_{x=0} y_i(\text{feed}) P \tag{3.13}
\]

\[
Pu_A(\text{prod.}) = \frac{J_A(\text{prod.})}{\sum_{i=A,B,C} J_i(\text{prod.})} \tag{3.14}
\]

\[
Rv_B(\text{prod.}) = \frac{J_B(\text{prod.})}{J_B(\text{feed})} \tag{3.15}
\]

\[
Pu_A(\text{exh.}) = \frac{J_A(\text{exh.})}{\sum_{i=A,B,C} J_i(\text{exh.})} \tag{3.16}
\]

\[
Rv_B(\text{exh.}) = \frac{J_B(\text{exh.})}{J_B(\text{feed})} \tag{3.17}
\]

The inventory of species \( i \) in the vessel is given by:

\[
A_i = \int_{0}^{1} (\chi_i \theta_i + y_i P) \, dx \tag{3.18}
\]

The initial state is a vessel completely filled with reactant D. The relaxation to cyclic steady state is calculated by successive integration. Convergence to the cyclic steady state is assumed on the basis of the following balances:

\[
\Delta J_A + \Delta J_B + \Delta J_C = 0
\]

\[
\Delta J_A + \Delta J_C - \Delta J_D = 0
\]

The first expression represents a check on the conservation of the main reactant/product and the second is a check on the consumption of auxiliary reactant D. Convergence was assumed when the residues equaled \( 10^{-7} \) (ten times the integration accuracy).
3.3 Numerical solution of the model

The model was implemented in gPROMS Version 1.6 (Process Systems Enterprise Ltd, London, U.K.). The built-in schemes for discretization for problems with flow reversal (central finite differencing or orthogonal collocation) proved unsuitable. In contrast to the cases in Chapter 2 steep concentrations gradients are encountered in the cases described in this chapter and application of the built-in scheme’s resulted in significant numerical oscillations in the composition profiles. Therefore a second-order upwind scheme (see Gaskell and Lau, 1988, Table 1) was manually implemented in the gPROMS environment. The discretization scheme was formulated on a staggered grid (Analogous to the treatment in Patankar (1985, page 80ff)). On a staggered grid the axis is divided into small volumes. Component fluxes are defined at the border of two adjacent volumes whereas pressure temperature and composition are defined at the centre of the volume. A staggered grid is preferred since the boundary conditions of the balances are expressed in terms of fluxes. The axial reactor axis was discretized using 200 equal volumes. An IBM RS6000 43P workstation, SP2 platform and a Pentium III PC were used in the simulations.

3.4 Model parameters

The objective of the unit is to remove all A from the feed stream which consists of 10% A in B, and obtain high recovery of B. To enable a proper comparison the allowed impurity level of A in the product stream is fixed at 5 ppm for each case. The adsorption step is terminated when the preset purity of the product stream is reached. Likewise, the regeneration time is coupled to the extent of regeneration (PSR) or to the amount of product stream gas (PSA).

The parameters are given in Table 3.2 and discussed below. The Peclet number in industrial adsorbers is usually high. Reaction occurs in a PSR when A or B and D are both present in the gas phase. During pressurization and adsorption this situation only occurs at the unretended front, and thus the extent of reaction depends strongly on the Peclet number. In reality the reaction zone may be broader due to the finite residence time of the species on the catalytic surface. Therefore a relatively small Peclet number of 200 was chosen for the PSR system. This Peclet number still gives rise to mass transfer predominantly by convection, and requires a reasonable number of grid points using non-dedicated algorithms.

Prior to presenting the results on the bench marking of the reactor configurations discussed here, we need to address the matter of the comparison basis for these reactors. For
Table 3.2: Parameters in the simulations.

<table>
<thead>
<tr>
<th>symbol</th>
<th>PSR cases I</th>
<th>PSR cases II</th>
<th>PSR cases III</th>
<th>PSA cases IV</th>
<th>PSA cases V</th>
<th>PFR cases VI</th>
<th>PFR cases VII</th>
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<th>$\zeta_{\text{depres}}$</th>
<th>$\tau_{\text{ads}}$</th>
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<td>0.0</td>
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<td>$\frac{1}{6}$</td>
<td>(a)</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

a: The step is terminated when the following criterion is met: $P_{\text{prod}} > 5 \times 10^{-6}$
b: The step is terminated when the following criterion is met: $A_A < 10^{-3}$
c: The step is terminated when the following criterion is met:
   $\Sigma J(\text{purge})/\Sigma J(\text{prod.}) = 0.7$
d: Values used: 0.5, 1, 2, 5, 10, 20, 50, 100
e: Values used: 1, 2, 5, 10, 20, 50, 100, 200, 500, 1000
f: Optimal value see Figure 3.2.
the PSR, we have consistently assumed a total volume $V_R$, with the volume fraction taken up by the catalyst and the sorbent each being 0.5. For the PSA & PFR and the single PFR two options exist:

a. The PSA (filled with adsorbent) and PFR (filled with catalyst) each take up a volume equal to $1/2V_R$ and the single PFR takes up a volume equal to $1/2V_R$. In this case the volumes of catalyst and/or sorbent are equal for all reactor configurations.

b. The PSA (filled with adsorbent) and PFR (filled with catalyst) and the single PFR each take up a volume equal to $V_R$. In this option the residence time at reference conditions is equal for all vessels.

For the single PFR the performance hardly depends on the choice of reference state since the flow and corresponding actual Peclet numbers are high.

In the one-dimensional model at hand, reactor volume is linked to reactor length. In option a), the reference flow rate is divided by two to maintain an equal residence time. Since the axial dispersion coefficient is assumed constant, the Peclet numbers are altered. For the isothermal PSA, option b proved to be only slightly superior. Therefore, the PSR was compared to the PSA (in the PSA & PFR in series) on the basis of equal amount of sorbents (option a). The parameter values used for the PFR and PSA are also listed in Table 3.2.

In Table 3.3 the sorbent properties selected for the present case are compared to values used in experimentally verified simulations of equilibrium-based PSA systems. The values for saturation capacity ($\chi^s$) and adsorption kinetics ($\Phi_t$) used in the base case are within the range of experimental values reported in the literature. The most important comparison is the retention factor $\left(\frac{y_A \theta_A^s \left(\frac{f(\text{feed})}{P_{\text{high}}}ight)}{y_A \text{ (feed)}}\right)$ which is influenced by both adsorption and process parameters. The resulting retention factor is comparatively high, but much higher values (nC6 on zeolite 5A) have been reported. The resulting sorption selectivity chosen in the base case is very modest compared to the PSA systems.

The reaction selectivity ratio ($k_1/k_2$) of the catalyst was fixed at 10. Since the molar ratio of A to B in the feed is set at 9, a net conversion of B already becomes apparent at low conversion levels.

In the PSA and PFR in series case, the purpose of the PSA unit is to purify the feed stream and optimize the A to B ratio in the exhaust stream. The purge gas velocity was chosen at its optimal value ($\psi = 2$), as both the recovery of B in the product stream
Table 3.3: Comparison of key adsorption parameters with selected PSA systems.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PSA in this work</th>
<th>(Farooq et al., 1989) [exp. no. 8]</th>
<th>(Yang et al., 1997) [run C']</th>
<th>(Yang et al., 1997) [run C]</th>
<th>(Silva and Rodrigues, 1998) [PSA case]</th>
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<tr>
<td>A</td>
<td>O₂</td>
<td>CH₄</td>
<td>CO</td>
<td>nC5/nC6</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>N₂</td>
<td>H₂</td>
<td>H₂</td>
<td>iC₅</td>
<td></td>
</tr>
<tr>
<td>sorbent</td>
<td>zeolite 5A</td>
<td>zeolite 5A</td>
<td>zeolite 5A</td>
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<td>( y_A (\text{feed}) )</td>
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<td>0.21</td>
<td>0.3</td>
<td>0.3</td>
<td>0.139 / 0.046</td>
</tr>
<tr>
<td>( y_B (\text{feed}) )</td>
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<td>0.7</td>
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<td>0.815</td>
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<tr>
<td>( \chi_B^a )</td>
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<tr>
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<td>0.17</td>
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</tr>
<tr>
<td>( \Phi_B )</td>
<td>0.5</td>
<td>9.1</td>
<td>2.10</td>
<td>2.11</td>
<td>(a)</td>
</tr>
<tr>
<td>( \chi_A \theta_A(y_{A(\text{feed})}, p_{\text{high}}) )</td>
<td>200</td>
<td>5.74</td>
<td>18.11</td>
<td>25.61</td>
<td>73 / 800</td>
</tr>
<tr>
<td>( \chi_B \theta_B(y_{B(\text{feed})}, p_{\text{high}}) )</td>
<td>28.58</td>
<td>18.1</td>
<td>0.59</td>
<td>0.44</td>
<td>0</td>
</tr>
<tr>
<td>( \Omega )</td>
<td>0.333</td>
<td>0.230</td>
<td>0.091</td>
<td>0.091</td>
<td>0.133</td>
</tr>
</tbody>
</table>

a: variable.
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Figure 3.2: The influence of purge gas flow rate ($\psi$) on PSA performance. Legend: $+$: $t_{\text{ads}},$ $O$: $t_{\text{ purge}},$ $\Delta$: $Pr,$ $\triangledown$: $Rv_{B}(\text{prod.}),$ $\lozenge$: $Pu_{A}(\text{exh.}).$ Parameters: PSA case IV in Table 3.2

($Rv_{B}(\text{prod.})$) and the enrichment of A in the exhaust stream ($Pu_{A}(\text{exh.})$) reside at their local maxima (Figure 3.2).

To keep realistic gas-flow velocities in the pessurization step, the pressurization rate ($\zeta_{\text{press}}$) is set to a low value. The depressurization rate ($\zeta_{\text{depres.}}$) is fast to minimize initial slip of A.

3.5 Results

3.5.1 Reactor performance: recovery, selectivity and productivity

The overall performance of the PSR is compared to the PSA and PFR in series and the PFR in Figures 3.3, 3.4, and 3.5 which show the recovery of B, reaction selectivity and productivity respectively. In Figure 3.3 the three configurations are compared as separators by plotting purity versus recovery. For the PSR, A is removed by adsorption and over 80% of B is recovered at high purity in the high pressure half-cycle. This combination of recovery and purity cannot be obtained in a PFR. The recovery of B in the product stream of the PSA unit is much lower, as part of this gas is used as purge gas. Due to the selective adsorption, A is accumulating in the PSR, and the ratio of A over B present in the vessel ($A_{A}/A_{B},$ see eqn.3.18) rises from 0.111 to 0.57 during the adsorption step.

Figure 3.4 compares the three configurations as reactors by comparing conversion with
reaction selectivity. In the PSR the reaction takes place almost exclusively in the regeneration step. At the onset of pressurization, the vessel contains predominantly D. The feed velocity during pressurization is dominated by the net consumption of moles during reaction at the concentration front of B until all D is converted. Since A is retarded, it is hardly converted at this stage. The regeneration behavior can be manipulated both by the catalyst activity and the residence time of the reactants. The residence time of the reactants is directly related to the purge-gas velocity. High conversions can only be obtained when both parameters are large compared to the desorption rate of A and B (see Figure 3.4). For high purge-gas flow rates the PSR demonstrates an overall selectivity to B far in excess of that observed for both the PFR and the PSA and PFR in series.

A second advantage of the PSR is that it leads to acceleration of the regeneration by conversion of the desorbed gas. The resulting shorter purge times and more thorough regeneration enhances the productivity of the unit. Figure 3.5 shows that this is indeed the
Principle II: Accumulation of the desired reactant (isothermal)

Figure 3.5: Productivity versus conversion of A for different reactor configurations. Legend: dotted line: PFR case VI, \(\Delta\): PSR case I \(\bigcirc\), PSR case II, continuous line PSA case IV. Parameters see Table 3.2. For PFR case VII the productivity is ten times the value for PFR case VI shown here.

Figure 3.6: Outgoing flow of A during regeneration in a PSR. Legend: i:\(\psi=10\), ii:\(\psi=50\), iii:\(\psi=1000\) Parameters: PSR case II (Table 3.2). The letters refer to the cases shown in Figure 3.7.

case. The PSR has much higher productivity compared to the PSA. The required purge time hardly depends on purge-gas velocity \((\tau_{\text{purge}} \approx 19.5)\) and is close to the theoretical minimum \((\tau_{\text{purge}} = \frac{1}{\phi_A} e^{\log \left(\frac{A_{A,\text{end}}}{A_{A,\text{start}}}\right)} \approx 18)\). The productivity of the PSA unit is limiting in the PSA & PFR in series. Therefore its productivity is independent of conversion. The PFR has the highest productivity. In the PFR the molar fraction of A in the gas phase is in the order of a few percent, whereas it is usually below 0.1% during regeneration in the PSR. Compared to the PSA & PFR case, which is the traditional choice for maximizing selectivity, the PSR offers a productivity improvement by a factor of three.

3.5.2 Optimal operation: balancing the sorption flux and reaction rate

A distinct optimum exists in conversion with respect to purge-gas velocity (Figure 3.4). This can be understood by the dynamics of the regeneration. Figure 3.6 shows qualitative differences in regeneration behavior for the three cases. In case i a significant initial outflow of unconverted A is observed until two-thirds of A is removed, followed by a period of regeneration without outflow of A. In the optimal case slip only occurs in the depres-
Figure 3.7: Profiles in the reactor during regeneration. Legend: △: y_D, ○: desorption flux of A (S_A), ▽: flow of A (F_A). Parameters: PSR case II, A,B:ψ=10, C:ψ=50, D:ψ=1000. For each case the extent of regeneration is illustrated in Figure 3.6.

Surization step. In the case of higher purge flows, the out-going flux of unreacted A is constant in time. These three cases are illustrated in Figure 3.7.

In the case where purge gas velocity is too low, it takes a significant time for D to penetrate through the reactor. During this time, desorption of A is balanced by the reaction after this front only (Figure 3.7A). The slip of A drops once D reaches the end of the vessel (Figure 3.7B).
The maximum conversion of A is reached when sorption and reaction are balanced throughout the regeneration. This case is shown in Figure 3.7C.

Upon a further increase in the purge-gas flow, the reaction rate can no longer balance the desorption flux. This results in significant outflow of A throughout the regeneration step (Figure 3.7D). Thus, optimum conversion can be reached by balancing the adsorption kinetics and the catalyst activity. The conversion of A is constrained by the amount of A released during depressurization and the molar fraction present in the gas phase at the end of the adsorption step.

3.5.3 Combined thermodynamic and kinetic sorption selectivity

Since the sorption rate is a key parameter in PSR operation, kinetic selectivity can be exploited. Swift removal of adsorbed B may result in additional enhancement of the reaction selectivity. This was evaluated by a series of simulations where the sorption rates of B and C were ten times that of A resulting in a system that is thermodynamically selective toward A and kinetically selective toward B (PSR case III in Table 3.2).

Figure 3.8 shows that the selectivity improvement is comparable to the non-kinetic case (PSR case I). A slight improvement is found over the non-kinetic case at low purge velocities, but the conversion of A is lower. Compared to the base case the ability of the sorbent to separate A and B is reduced, and hence the accumulation of A in the vessel by adsorption drops from $A_A=8$ to around 6. This reduces the potential for selectivity enhancement. The underlying phenomena are discussed shortly. Upon depressurization
the initial rise of $y_A$ observed in the base case is absent, due to the fast desorption of B (not shown). As a result the extent of reaction 1 ($A + D \rightarrow B$) during the initial stage of the purge step is reduced. Later on B is nearly fully removed and the selectivity rises to end at slightly higher values. The latter two phenomena are illustrated in Figure 3.9, which shows that the initial drop in selectivity is reversed in course of the regeneration.

Hence, the increased reaction selectivity during the major part of the regeneration cycle is largely counteracted by a reduced accumulation of A during the adsorption cycle and the unfavorable onset of the regeneration half-cycle.

As mentioned before, the inclusion of kinetic selectivity toward B reduces the ability of the sorbent to separate A and B. On a tenfold increase in catalyst activity compared to the kinetically selective case discussed above (PSR case III, △ in Figure 3.8), the required purity of the product stream cannot be met. This is illustrated in Figure 3.10, which shows the resulting concentration profiles of component A ($y_A$) during pressurization in the cyclic

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**Figure 3.9:** The development of the reaction selectivity during the regeneration for kinetically and non-kinetically selective cases. The incremental reaction selectivity is given by the slope of the lines. Legend: The numbers are also shown in Figure 3.8. continuous lines & a: PSR case I (Figure 3.8: △), dotted lines & b: PSR case III (Figure 3.8: ▲), i: $\psi=5$, ii: $\psi=100$.

**Figure 3.10:** Profiles of the molar gas fraction of A ($y_A$) over the reactor during the pressurization step in case of combined kinetic and thermodynamic sorption selectivities. A to J: The lines are plotted starting at $\tau=0.195$ with increments of 0.1 until $\tau=1.095$, Parameters: PSR case III modified with $K_1=K_1*10$, $K_2=K_2*10$, $\psi=2$. K: PSR case III, $\psi=2$ after an identical total amount of feed gas was fed ($\tau=3.5$).
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The in-going flow rate is comparatively high due to the high net consumption of moles. Due to differences in sorption kinetics, retention of B is now dominant and A accumulates at the interface with D. This results in molar gas fractions of A above the feed-gas composition. The high conversion rate of A ($R_1$) results in the swift penetration of A through the reactor while it simultaneously reacts. In the course of pressurization, the superficial gas velocity drops and now thermodynamics determine the relative retention of A over B. This results in a broad concentration front of A.

At the reactor end, the concentration of A reaches a maximum of 300 ppm early in the pressurization process. Subsequently it drops to about 10 ppm at the start of the adsorption step, and then rises again. As a result, the purity limit of 5 ppm can never be met and the adsorption step is terminated right after its minimum step time ($\tau_{ads} = 1$).

3.5.4 Performance criteria for the sorbent

For the performance of the PSR, the ability of the sorbent to selectively retain A in the unit is of paramount importance. In this section, the minimum requirements for sorbents are addressed. Sorbent capacity and selectivity were systematically investigated by varying $\chi_A^a$ and $\kappa_B$ respectively. An increase in the sorbent capacity leads to higher reaction selectivities, but it lowers the maximum attainable conversion (Figure 3.11). The retention ratio of A to B ($\frac{A_A}{A_B}$ at $\tau = \tau_{ads}$) increases with increasing adsorbent capacity, which leads to higher reaction selectivities. The flux of desorbing species ($S_A$) is proportional to the saturation capacity ($\chi_A^a$) and will also increase. As shown in Section 3.5.1 a high con-

![Figure 3.11: Influence of sorbent capacity on the performance of the PSR. Legend: dotted line: PFR case VI, continuous line: PSA & PFR case IV, PSR case I modified with: □: $\chi_A^a\cdots D = 10$; △: $\chi_A^a\cdots D = 20$; ◊: $\chi_A^a\cdots D = 40$, +: $\chi_A^a\cdots D = 100$; (cases shown here: $\psi=5,-\rightarrow 10,20,50,100$).](image-url)
version can only be obtained when both the purge flow velocity and catalyst activity are large compared to the desorption rate. This situation is no longer encountered for when the sorbent capacity increases and the sharp maximum in the conversion of A versus the purge gas flow velocity disappears.

When the adsorption affinity of B becomes less, the reaction selectivity and the maximum attainable conversion of A in the PSR increase (Figure 3.12). The former is directly related to the decreased accumulation of B in the unit in the adsorption step. The latter results from the decreased amount of D consumed in the conversion of B during the regeneration, which results in swifter penetration of D into the reactor.

There is no single generic criterion to determine which one of the investigated reactor configurations is optimal. The parameters of PSR case I represent the case where the reaction selectivity at the maximum conversion is just higher than the alternative reactor configurations (PSR case I, $\psi = 50$ in Figure 3.4). A sorbent with lower capacity or selectivity should be operated at a much higher purge velocity to obtain reaction selectivities beyond the alternative reactor configurations, and the resulting conversion drops sharply. The base case presented in this study reflects the case where the sorbent properties are only just appropriate to justify PSR operation.

In this work, we assume the PSR contains equal volumes of catalyst and sorbent. For higher catalyst activities than assumed in this base case, the balancing reaction rate and sorption flux can be achieved by using less catalyst; thus the dilution of sorbent by catalyst particles decreases and the criterion on the sorbent with respect to its capacity ($\chi^d_i$) can be relaxed to minimally approach half the value given here.

![Figure 3.12: Influence of sorbent selectivity on the performance of the PSR. Legend: dotted line PFR case VI, continuous line PSA & PFR case IV; PSR case I modified with: +: $\kappa_B = 5$; $\circ$: $\kappa_B = 2$, $\triangle$: $\kappa_B = 1$, $\square$: $\kappa_B = 0$; (cases shown here: $\psi=5,\rightarrow 10,20,50,100)$.](image-url)
In the case of lower sorbent capacities ($\chi_{A,D}^a = 10$) the required purity of the product stream could not be met in PSA and therefore the PSR data should be compared to the PFR only. In the PSR the purity of the product stream is reached as a result of reaction, which induces a more thorough regeneration in the PSR concept.

### 3.6 Discussion

In the PSR a moderate pressure ratio in the pressure swing cycle is generally sufficient, as sorbent operation is largely driven by partial pressure reduction. This adds to the viability of the concept. A similar observation was made by Yongsunthon and Alpay (1998b) in a study on temperature swing adsorptive reactors. They found that optimal operation required a regeneration temperature below the adsorption temperature, as the desorption was largely driven by concentration swing.

The PSR concept is restricted to low temperatures and easy separation of D from A, B, and C. The former is necessary to meet the sorbent capacity requirement, and the latter to remove D from the exhaust stream.

We have shown that the purge-gas flow rate can be used to balance the reaction rate and desorption kinetics. The sorbent-to-catalyst mixing ratio and temperature level can also be used to achieve this balance.

The Skarstrom-cycle is usually applied in pressure swing adsorption to obtain a pure product stream only. In this study a large recycle ratio was needed in order to meet the required purity. Also the resulting enrichment of A in the exhaust stream was limited to approximately 35% ($y_A^{exhaust} \approx 0.135$). There is a great deal of room for improvement in both the PSA and PSR in this study: a co-current depressurization step may be included to increase the fraction of A in the exhaust stream (Cen and Yang, 1986). This will improve the purity of the low pressure product stream which contains the adsorbed component. A co-current depressurization step in the PFR & PSA in series configuration seems very beneficial. However, co-current depressurization, will have a negative effect on the sharpness of the concentration front, and the purity of the high pressure product stream will be compromised. In the PSR studied, the desired reactant A is accumulated in the reactor. A co-current depressurization step will be effective in a further removal of B in the reactor. A larger part of the desired reactant is, however, accumulated in the gas phase instead of in the adsorbed state and will be swept out by the purge gas rather than converted. For the PSR, variation of purge-gas flow velocity within the purge step can be used to tune the corresponding residence time of the reactants during the regeneration.
However, the use of more sophisticated pressure swing cycles is beyond the scope of this work.

The PSR concept can also be used to improve an existing PSA separation application. The inclusion of a catalyst will lead to a more thorough regeneration in a shorter regeneration time. Furthermore, systematic variation of the adsorption capacity has shown that due to a more thorough regeneration, the requirements on sorbent capacity for the required separation can be relaxed. Finally, a reactive purge gas will increase the recovery of the components in the product stream.

3.7 Conclusions

In this work we have addressed the use of a packed bed filled with a mixture of a sorbent and a catalyst, and operated in a pressure-swing mode. The PSR concept is compared to both a plug-flow reactor (PFR), a pressure-swing separation, and a plug-flow reactor in series (PFR & PSA). In the case presented here, the unit is used to carry out the reaction scheme $A \xrightarrow{+D} B \xrightarrow{+D} C$. The feed stream is a mixture of $A$ and $B$, and the objective is to remove $A$ from the feed by selective adsorption, and then to introduce reactant $D$ to selectively react $A$ and $D$ in the $B$-depleted reactor.

As a reactor, we have shown that the superior selectivity performance of the PSR concept was seen for realistic sorbent properties, and hence the PSR concept is viable in a practical sense for low temperature reactions in particular.

As a separator, the inclusion of a catalyst will allow sorbent regeneration to be carried out in a time close to the theoretical minimum, which leads to a factor $\approx 3$ improvement in the productivity compared to the PSA. The productivity is, however, lower than that of the single PFR unit.

A maximum conversion level in the PSR is obtained when the sorption kinetics and the reaction kinetics are balanced.

For the realistic parameters (PSR case 1) in this study, the selectivity at maximum achievable conversion in the PSR is just higher than the PFR or PFR & PSA. These parameters limit the region where optimal conversion and a small selectivity improvement are combined. In the case of larger sorbent selectivities and higher sorbent capacities, the selectivity enhancement of the PSR at optimal conversion increases.
Acknowledgment
Academic Computing Services Amsterdam (SARA) is gratefully acknowledged for making available CPU time on their SP2 platform.

Notation
All symbols used are grouped in this section. In the third column the unit is given for symbols containing dimensions. For dimensionless symbols the definition is given.

Roman
$A_i$ amount of component $i$ inside the reactor eqn. 3.18
$\frac{\mathrm{mol}}{\mathrm{kg}}$ $\frac{\mathrm{s}^{-1}}{\mathrm{Pa}^{-1}}$

$b$ adsorption affinity

$D_{ax}$ axial dispersion coefficient

$F_A$ axial flux of component A

$J_i(s)$ cumulative flux of component $i$ in stream $s$

$k$ reaction rate constant

$K_j$ amount catalyst & catalyst activity

$K_{LDF}$ adsorption rate constant

$L$ reactor length

$P$ pressure

$P$ dimensionless pressure

$P_e$ axial dispersion coefficient

$\Pr$ productivity

$Pu_i(s)$ purity of stream $s$ with respect to component $i$

$q$ solid phase concentration

$R$ gas constant

$Rv_i(s)$ recovery of component $i$ in stream $s$

$R_{1}/R_{2}$ reaction selectivity

$S_A$ desorption flux of component A

$t$ time

$T$ absolute temperature

$v$ superficial gas velocity

$\chi_A$ $\frac{\partial \theta_A}{\partial \tau}$ s

$\varepsilon$ $\frac{\varepsilon^c \rho_c k_j P_{high}^2 LRT}{\varepsilon^g P_{high} v(\text{prod})}$ s$^{-1}$

$\varepsilon^c$ $\varepsilon^g$ $\varepsilon^g$
\( \mathbf{V} \) interstitial velocity

\( x \) length

\( X_A \) conversion of A

\( y \) molar gas fraction

\( z \) axial distance from reactor feed

**Greek**

\( \varepsilon^i \) volume fraction of phase \( j \)

\( \theta_i \) amount adsorbed

\( \kappa_i \) adsorption equilibrium

\( v_{i,j} \) stoichiometric coefficient of component \( i \)

in reaction \( j \)

\( \rho \) mass density

\( \tau \) time

\( \zeta_{\text{depress}} \) depressurization rate

\( \zeta_{\text{pres}} \) pressurization rate

\( \Phi_i \) adsorption rate

\( \chi_i^3 \) amount adsorbent & capacity

\( \psi \) purge flow

\( \Omega \) pressure ratio

**Superscripts**

* equilibrium value

\( a \) adsorbent

\( c \) catalyst

\( g \) gas phase

\( \text{sat} \) saturation

**Subscripts**

\( i \) component (A,B,C,D)

\( j \) reaction (1,2)

\( \text{ads.} \) adsorption step
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depres. depressurization step
high upper pressure
low lower pressure
pres. pressurization step
purge purge inlet stream step

Arguments
exh. exhaust stream at $P_{\text{low}}$
prod. product stream at $P_{\text{high}}$
feed feed stream
purge purge inlet stream
PSR pressure swing reactor
PFR plug flow reactor
PSA pressure swing adsorber