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Modelling, Design and Optimisation of a Hybrid PSA-Membrane Gas Separation Process

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Abstract

Pressure swing adsorption (PSA) and membrane-based gas separation processes are two different alternatives for effective, continuous bulk gas separation at the industrial scale. Both these processes possess characteristics that render them advantageous over conventional cryogenic processes, and they can be combined into a Hybrid Separation System (HSS). Dynamic simulation and optimisation of a HSS must rely on all mathematical equations describing the dynamic behaviour of PSA and membrane permeation modules in a single flowsheet. The mathematical model is a set of Partial Differential and Algebraic Equations (PDAE) and has been used to investigate two HSS classes, considering the case of air separation. The paper considers two HSS concepts (for same and opposite separation selectivity), and presents dynamic simulation and optimisation results, focusing on the performance of the HSS flowsheet and demonstrating significant improvements over the standalone PSA and membrane processes.

Keywords: PSA, membrane, gas separation, modelling, design, optimisation.

1. Introduction and Motivation

Advances in non-cryogenic gas separation process applications over the past 20 years have been driven by the need to improve efficiency and reduce cost, via

alternatives to several traditional, energy-intensive gas separation processes (distillation, chemical absorption). High-purity hydrogen, which is foreseen as the fuel for the future, is commercially produced by pressure swing adsorption (PSA), a typically low product recovery process. Previous studies (Sircar et al., 1999; Sircar & Golden, 2000) identified that integrating a membrane module into PSA can improve the overall recovery of the separation process. Membrane gas separation processes are also shown to be cost-effective in separating greenhouse gases from gaseous mixtures at high purity (CO_2 capture and sequestration). Numerous studies (Bhide et al., 1998; Naheiri et al., 1997, Zolandz & Fleming, 1992) show that combinations of a membrane module and another separation process offer lower cost and better separation performance than an all-membrane separation system. The first combination of a membrane and an adsorption separation process is attributed to Mercea and Hwang (1994); a PSA unit was used to improve the O_2 enrichment performance of a Continuous Membrane Column (CMC), and the combination featured superior economics and separation performance over both PSA and CMC processes. Feng et al. (1998) proposed an integrated process in which gas permeation is included in the sequential steps of PSA, hence considering permeation occuring in a cyclic fashion. Hydrogen purification from a gaseous mixture has also been studied: results show that a hybrid PSA-membrane achieves higher purity compared with a standalone PSA process. Other PSA-membrane combinations are shown to improve the performance of either of the two units (Sircar et al., 1999; Esteves & Mota, 2002), yet none presents a detailed mathematical model and numerical solution procedure for simulation and optimisation. The main goal of this paper is thus to study the potential of a PSA-membrane HSS by developing a rigorous mathematical model for its dynamic simulation and optimisation, and by using it to obtain relevant results and design conclusions. Air separation is the exemplary case study for the hybrid gas separation process.

2. Process Description: Hybrid Separation Systems (HSS)

All hybrid PSA-membrane processes are classified into two categories in the literature: (a) ***Membrane followed by PSA (Class I)***, (b) ***PSA followed by membrane (Class II)***. Rigorous mathematical models combine all equations describing the dynamic behaviour of the membrane separation module into the cyclic operating steps of the PSA process; such models are sets of Integral Partial Differential and Algebraic equations (IPDAEs) and their implementation for dynamic simulation and optimization is often challenging and cumbersome.

HSS I: In a Class-I HSS flowsheet, the membrane comes before the PSA (Figure 1a). The first processing step is feeding fresh compressed gas into a hollow fibre module: the permeate is obtained at the shell side (atmospheric pressure), while the residue stream (assumed to be at feed pressure) is obtained at the tube side of the fibre module. Depending on PSA selectivity, the

membrane residue *or* permeate is used as PSA feed: in N_2 production (HSS with same selectivity) the N_2-rich (residue) stream is fed to PSA; in O_2 production (HSS with opposite selectivity) the O_2-rich (permeate) stream is used. Either the residue or the recompressed permeate is fed in the first step (pressurisation), yet the high-pressure residue stream is the only fed in the second step (adsorption).

HSS II: In a Class-II HSS flowsheet, the membrane comes after the PSA (Figure 1b); Sircar et al. (1999) considered such a HSS to improve the recovery of a H_2 PSA process. The cyclic steps of this HSS start with fresh feed introduction into the PSA unit; then, the purge gas from each PSA bed passes through the membrane to increase recovery. The membrane residue stream obtained can be recycled as fresh feed to the PSA bed or (in the case of multiple beds), the permeate stream can be used for purging other beds. Generally, feed conditions for the PSA unit depend on the membrane module (HSS I); feed conditions for the membrane unit depend on the PSA beds effluent (HSS II).

The present study is based on separation selectivity towards the target species. A binary gas mixture Hybrid Separation System (HSS) in which the gas more adsorbed in the PSA is more permeable through the membrane is a ***HSS with same selectivity***; when the same gas is the least permeable, then we have a ***HSS with opposite selectivity***. Polymeric membranes are usually only selective to O_2 (O_2 being obtained as permeate), but for PSA, either O_2 or N_2 can be more adsorbed (depending on the adsorbent used). The combined HSS mathematical model of this paper thus considers (Akinlabi, 2006): (a) A dual-bed PSA unit (producing N_2 on carbon molecular sieve and O_2 on zeolite 5A), and (b) A steady-state, isothermal, cross-flow permeation hollow fibre membrane module.
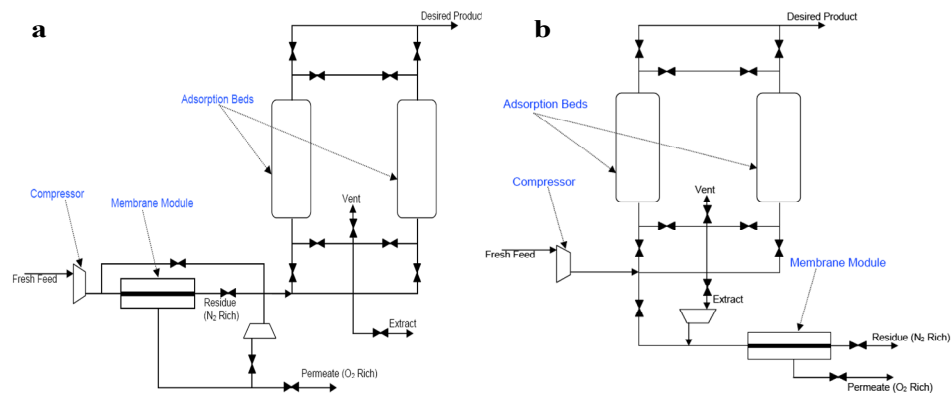

Figure 1**:** The two Hybrid Separation System (HSS) flowsheets considered: (a) HSS I, (b) HSS II.

3. Mathematical Model Formulation and Dynamic Simulation

The dynamic behaviour of standalone PSA beds and membrane modules is studied for various operating conditions, to obtain a base case for comparison. An experimentally used polysulphone membrane (Ettouney & Majeed, 1997) is

considered, to analyse the cross-flow isothermal membrane model dynamics. For PSA, feed pressure and product flow rate are varied, and a standard model is used (Nilchan, 1997; Sircar et al., 1999; Sircar & Golden, 2000). Both PSA and membrane units are studied at low pressure ratios (feed to permeate/purge pressure ratio), assuming isothermal conditions without any pressure losses. Models and simulation conditions for both modules are presented in Table 1.

Table 1: Mathematical models for membrane separation and Pressure Swing Adsorption (PSA).

Membrane unit mathematical model		*Pressure Swing Adsorption (PSA) mathematical model*	
Air separation via PERMEA membrane		*Nitrogen/N$_2$ Production on Carbon Molecular Sieve*	
$-d(Qx_i) = J_i dA$	(1)	$\dfrac{\partial C_i}{\partial t} - D_L \dfrac{\partial^2 C_i}{\partial z^2} + \dfrac{\partial(\upsilon C_i)}{\partial z} + \dfrac{1-\varepsilon_{BED}}{\varepsilon_{BED}} \dfrac{\partial q_i}{\partial t} = 0$	(13)
$J_i = \dfrac{P_i}{\delta}\left(P^H x_i - P^L y_i\right)$	(2)	$-\dfrac{\partial P}{\partial t} = \dfrac{180\mu(1-\varepsilon_{BED})^2 \upsilon}{\varepsilon_{BED}{}^3 D_{PARTICLE}{}^2} = 0$	(14)
$y_i \dfrac{dQ}{dA} = \dfrac{d(Qx_i)}{dA}$	(3)	$\dfrac{P}{RT} = \displaystyle\sum_{i=1}^{c} C_i$	(15)
$\displaystyle\sum_{i=1}^{c} \dfrac{dx_i}{dA} = 0$	(4)	$\dfrac{\partial q_i}{\partial t} = \dfrac{\Omega_i D_{i0}}{r_c{}^2}\left(q_i^* - q_i\right)$	(16)
$x_i(0) = y_{feed,i}$	(5)	$q_i^* = \dfrac{b_i q_{iS}}{1 + \displaystyle\sum_{i=1}^{c} b_i C_i}$	(17)
$Q(0) = Q_f$	(6)	*Oxygen/O$_2$ Production on Zeolite 5A*	
$Q(0) = Q_f$	(7)	$\varepsilon_t \dfrac{\partial C_i}{\partial t} - D_L \dfrac{\partial^2 C_i}{\partial z^2} + \dfrac{\partial(\upsilon C_i)}{\partial z} + \rho_b \dfrac{\partial q_i}{\partial t} = 0$	(18)
$\alpha_i = \dfrac{Q_r x_i}{Q_f y_{feed,i}}$	(8)	$\varepsilon_t = \varepsilon_b + \varepsilon_p\left(1 - \varepsilon_b\right)$	(19)
$dA = \pi D_0 N dL$	(9)	$D_{i0} = \dfrac{\varepsilon_p}{\tau_p} \dfrac{D_k D_m}{D_k + D_m}$	(20)
$Purity_i = \dfrac{Q_{product,i}}{\displaystyle\sum_{i=1}^{c} Q_{product,i}}$	(10)	$D_k = 48.5 d_{PORE}\sqrt{\dfrac{T}{MW_i}}$	(21)
$Recovery_i = \dfrac{Q_{product,i}}{Q_{feed,i}}$	(11)	$q_i^* = m_i C_i RT$	(22)

4. Dynamic Simulation Results and Optimal Base-Case Design

Membrane Simulation: A membrane unit is studied for various module areas (Figure 2). The following straightforward conclusions emerge from inspection:

(a) N_2 enrichment increases with membrane area but decreases with feed gas flow rate, (b) O_2 enrichment decreases with membrane area but increases with feed gas flow rate, (c) The membrane area required for separation increases with increasing stage cut, (d) The membrane area required for separation decreases with increasing pressure ratio, (e) Permeate (O_2) quality increases and residue (N_2) quality decreases at low stage cut. Thus, we conclude that this is a design suitable for limiting feed gas loss, hence reducing the area requirements.
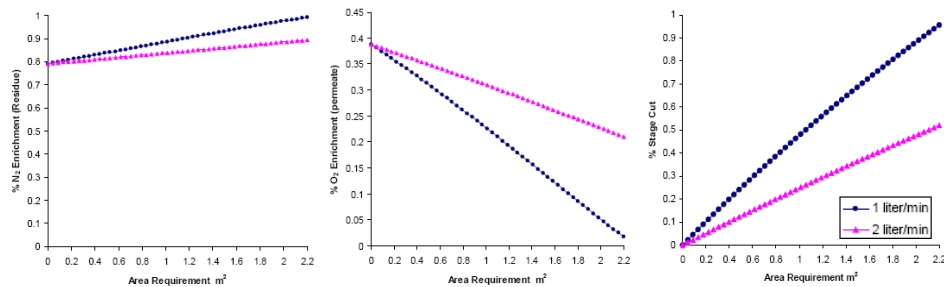
Figure 2: Dynamic simulation for design of a standalone membrane separation unit ($P^H/P^L = 3$).

PSA Simulation: A PSA unit is studied for various adsorption bed heights (Figure 3), considering the same pressure ratios and variable product flow rate, subject to balances. The following straightforward conclusions are now derived: (a) The product purity increases with pressure ratio (at the expense of product recovery), (b) Higher product recovery is attainable by increasing the volumetric product flow rate, (c) Power requirement increases with pressure, bed size (height) and product flow rate, (d) The N_2 and O_2 production units reach CSS at 40 cycles and 60 cycles, respectively, (e) Pressure and PSA bed mole fraction trends conform to Skarstrom cycle standards (Sircar et al., 1999).
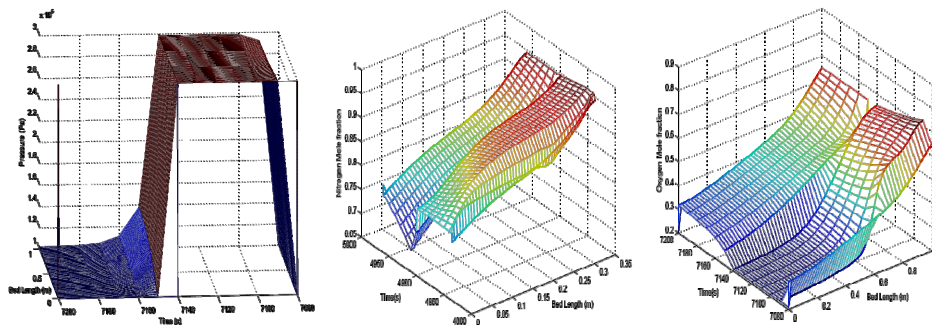
Figure 3: Dynamic simulation for design of a standalone PSA separation unit at CSS conditions.

Optimal base-case design: The base-case design for the membrane hollow-fibre module and the PSA bed focuses on minimising the combined operational and investment costs, achieving the desired target gas purity at minimum unit size and energy consumption. The N_2-enriched air for commercial applications must

be of high purity (95-99% N_2); O_2-enriched air must also be of >35% purity. The base case is the *maximisation of O_2 enrichment (membrane) and of N_2 purity (PSA)*, assuming there are minimum power requirements: (a) ***Membrane:*** Q=1.667·10⁻⁵ m³/s, N_2:O_2=79.1:20.9, A=0.22 m², P^H:P^L =(3:1)·10⁵ bar, (b) ***PSA:*** Q^{prod}=1.0·10⁻⁵ m³/s, Q^{purge}=0.5·10⁻⁵m³/s, N_2:O_2=79.1:20.9, P^H:P^L =(3:1)·10⁵ bar.

Table 2: Performance of standalone PSA units vs. volumetric feed flow rates and pressure ratios.

Nitrogen/N_2 production (standalone PSA unit)				*Oxygen/O_2 production (standalone PSA unit)*			
Q=1·10⁻⁵ m³.s⁻¹	*P^H/P^L = 3*	*P^H/P^L = 4*	*P^H/P^L = 5*	*Q=1·10⁻⁵ m³.s⁻¹*	*P^H/P^L = 3*	*P^H/P^L = 4*	*P^H/P^L = 5*
N_2 purity (P)	95.30 %	95.88 %	95.88 %	O_2 purity (P)	68.15 %	70.51 %	71.32 %
N_2 recovery (P)	29.02 %	22.32 %	18.38 %	O_2 recovery (P)	14.10 %	9.87 %	7.55 %
O_2 purity (E)	27.30 %	22.60 %	22.25 %	N_2 purity (E)	71.50 %	79.31 %	79.22 %
Avg. power/W	1.04 W	1.79 W	2.60 W	Avg. power/W	4.35 W	8.47 W	13.46 W
Q=1.5·10⁻⁵ m³.s⁻¹	*P^H/P^L = 3*	*P^H/P^L = 4*	*P^H/P^L = 5*	*Q=1.5·10⁻⁵ m³.s⁻¹*	*P^H/P^L = 3*	*P^H/P^L = 4*	*P^H/P^L = 5*
N_2 purity (P)	93.06 %	94.31 %	94.65 %	O_2 purity (P)	63.63 %	67.68 %	69.37 %
N_2 recovery (P)	37.63 %	29.92 %	25.12 %	O_2 recovery (P)	19.26 %	13.96 %	10.86 %
O_2 purity (E)	24.78 %	23.98 %	23.42 %	N_2 purity (E)	80.30 %	79.94 %	79.72 %
Avg. power/W	1.17 W	1.97 W	2.82 W	Avg. power/W	4.46 W	8.63 W	13.65 W
Q=2·10⁻⁵ m³.s⁻¹	*P^H/P^L = 3*	*P^H/P^L = 4*	*P^H/P^L = 5*	*Q=2·10⁻⁵ m³.s⁻¹*	*P^H/P^L = 3*	*P^H/P^L = 4*	*P^H/P^L = 5*
N_2 purity (P)	91.42 %	93.15 %	93.75 %	O_2 purity (P)	59.56 %	65.00 %	67.47 %
N_2 recovery (P)	44.29 %	36.13 %	30.81 %	O_2 recovery (P)	23.48 %	17.57 %	13.89 %
O_2 purity (E)	25.99 %	25.14 %	24.44 %	N_2 purity (E)	80.96 %	80.49 %	80.19 %
Avg. power/W	1.30 W	2.14 W	3.04 W	Avg. power/W	4.56 W	8.77 W	13.84 W

5. Dynamic Optimisation Results

Dynamic optimisation focuses on maximising HSS recovery at the maximum purity; we seek optimal hybrid gas separation process conditions that minimise operational costs, because operational costs vary inversely with product recovery (as in most separations). Operational costs of PSA processes are due to maintenance, energy and raw materials; investment costs are due to columns, adsorbent, compressor and valves (Cruz, 2005). Dynamic optimisation via successive substitution is very expensive (Jiang et al., 2004); thus, simultaneous spatial and temporal discretisation (Nilchan, 1997) has been used to accelerate convergence to CSS (all beginning and end bed conditions have to be identical). A literature heuristic cycle time constraint prescribes that adsorption and desorption times must be equal, to allow that both beds attain equal performance (Jain et al., 2003). The optimisation decision variables are selected to be the PSA ***bed height***, ***cycle time*** and ***membrane area***, and they have been determined at specified volumetric flow rates and at desired pressure ratios.
Dynamic optimisation is performed on the gOPT®/gPROMS® platform, via 2ⁿᵈ-order 6-point orthogonal finite element collocation (OCFEM) for the spatial

domain and 1st-order, 40-point backward finite differencing (BFDM) for the temporal domain, yielding improved result accuracy. Dynamic optimisation results for the HSS vs. standalone units are presented in Table 3, and the resulting optimal design measures (HSS re-simulation) are presented in Table 4. HSS product purity and recovery (for same selectivity) are sharply increased, at reduced PSA power consumption (since recovery is inversely proportional to the power required). The improvement comes at the cost of increased membrane area, a fact implying lower recovery in the module and a larger number of fibre capillaries required for enrichment, increasing the fixed investment requirement.

Table 3**:** Performance comparison of HSS vs. standalone units for same and opposite selectivity.

Nitrogen/N_2 production			*Same Selectivity*		*Oxygen/O_2 production*			*Opposite Selectivity*	
	PSA (standalone)		*HSS I*	*HSS II*		*PSA (standalone)*		*HSS I*	*HSS II*
N_2 purity	P	95.30 %	95.79 %	–	O_2 purity	P	68.15 %	83.27 %	–
N_2 recovery	P	29.02 %	28.89 %	–	O_2 recovery	P	14.10 %	11.44 %	–
O_2 purity	E	27.30 %	20.95 %	–	N_2 purity	E	71.50 %	68.02 %	–
	Membrane (standalone)		*HSS I*	*HSS II*		*Membrane (standalone)*		*HSS I*	*HSS II*
N_2 enrichment	81.15 %		–	78.34 %	O_2 enrichment	35.47 %		–	65.81 %
O_2 enrichment	35.47 %		–	22.40 %	N_2 enrichment	81.15 %		–	68.52 %
N_2 recovery	91.11 %		–	90.70 %	O_2 recovery	80.11 %		–	88.62 %

Table 4: Dynamic optimisation results and performance of the Hybrid Separation System (HSS I)

HSS Decision Variables		**HSS: PSA Performance**		**HSS: Membrane Performance**	
τ pressurization	1.1374 s	Product purity/N_2	98.42 %	Residue enrichment/N_2	95.08 %
τ adsorption	55.4138 s	Product recovery/N_2	49.63 %	Residue recovery/N_2	27.16 %
τ blowdown	1.0000 s	Extract purity/O_2	6.05 %	Stage cut	77.41 %
τ purge	55.5413 s	Average Power/Watts	0.52 W	Number of fibers	6077
τ cycle	113.0925 s	L (PSA bed height)	0.1348 m	A (membrane area)	1.7183 m^2

6. Conclusions

A dynamic simulation and optimisation strategy has been developed and used for a hybrid (pressure swing adsorption combined with membrane) gas separation process. The HSS combines the two processes in a single flowsheet and considers the dynamics of each process unit, to achieve design for optimal bulk gas separation performance. Dynamic simulation of Class-I and Class-II HSS (with same or opposite selectivity) covers previous integrated PSA-membrane flowsheets published in journal and patent literature. The IPDAE model requires a robust numerical algorithm (DASOLV, gPROMS$^{®}$), as the discretisation method greatly affects accuracy (due to boundary discontinuities). This implementation improves the accuracy of results and ensures robustness. Dynamic simulation results obtained reproduce the HSS behaviour and known

tradeoffs between product recovery and purity in both PSA and membrane separation processes, and allow the use of the model for optimisation studies.

Advantages of the two processes combined in the integrated HSS plant are complementary: this is illustrated by comparing the HSS to both standalone PSA and membrane units (feed and product flow rates of compared systems are equal, to establish a fair basis). The HSS gas separation process has definite benefits over both standalone unit types: (a) HSS with opposite selectivity are preferable when high product purity and recovery are required; this in turn implies slightly higher energy costs for effective performance. (b) HSS with same selectivity have inferior separation performance, but appear less energy intensive and more economical, due to elimination of permeate recompression. Adsorption mass transfer and equilibrium isotherm assumptions affect model accuracy; research is ongoing towards ensuring robust dynamic optimisation and quantitative validation. Experimental validation of the HSS and the model results with the use of a pilot plant is the current goal that will be vital in order to use present optimisation results for the design of a viable industrial process.

Acknowledgement

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