Optimization of a Pulsed Operation of Gas Separation by Membrane

Jean-Pierre Corriou, Christian Fonteix, and Eric Favre
LSGC-CNRS-ENSIC, 1 rue Grandville, BP 20451 54001 Nancy Cedex, France

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A pulsed cyclic membrane process, originally proposed by Paul for gas separations, has been investigated through a simulation and optimization study. For carbon dioxide hydrogen separation, it is shown that cyclic operation, based on an already reported material, could potentially compete with the most selective, still virtual, polymers, both in terms of selectivity and productivity. The use of asynchronous cycling operation, unexplored up to now, has been more specifically investigated. This mode of operation offers an extended range of performances from the point of view of the selectivity-productivity trade-off. A dedicated optimization study based on either nonlinear or genetic algorithm approach shows that, for this system, synchronous operation offers the best performances. These results have been confirmed by multiobjective optimization by means of the genetic algorithm. © 2008 American Institute of Chemical Engineers *AIChE J,* 54: 1224–1234, 2008

Keywords: separation, membrane, gas, unsteady, optimization, genetic algorithm, multiobjective

Introduction

Membrane processes are nowadays one of the key technologies for gas separations in industry (Baker, 2004). The fact that a binary mixture can be, in some cases, treated in a one stage membrane unit working under steady state conditions is often presented as a decisive advantage compared to technologies which require transient operation and multiple units, such as adsorption processes. As a consequence, the separation of gaseous mixtures has been almost exclusively investigated for stationary conditions as soon as industrial applications are considered. Transient regimes remained limited for a long time to investigation purposes, especially when a detailed transport analysis is aimed. To that respect, the well known time lag technique is a classical example (Vieth, 1991).

Looking at transient operation for industrial membrane gas separations may thus appear, at first glance, as a deadlock. To our knowledge, the first theoretical study dedicated to a membrane separation process working under cyclic transient operation was performed by (Paul, 1971). Based on a series of simplifying assumptions, the author could obtain an analytical solution to the separation performances of a novel cyclic process working under pulsed feed conditions. For the practical case of helium recovery from natural gas, Paul showed that a considerable increase in selectivity could be obtained compared to the steady state performances, at the expense, however, of a loss in productivity. Transient membrane permeation under pulsed feed conditions was also studied later by Higuchi and Nakagawa (1989) for air separation (O_2 N_2 mixture) through a thick silicone rubber membrane. Similar conclusions to those proposed by Paul were obtained.

Alternative strategies for improved membrane gas separation performances under transient operation have been also reported. Ueda et al. (1990) proposed a cyclic process for air separation based on a repetition of pressurization of the feed and evacuation of the permeate. The key idea is to take advantage of a higher pressure difference under transient operation, compared to the steady state situation. Moreover, pressurization and feed evacuation can be carried out by

Correspondence concerning this article should be addressed to E. Favre at Eric.Favre@ensic.inpl-nancy.fr.

Table 1. Conditions of Simulation: Membrane Performances are Reported in Bandrup and Immergut (1988)

Number of membranes		1	
Thickness of the membrane (m)		10^{-5}	
Diffusion coefficients (I.S.)		Component H_2	Component CO_2
	Membrane	$0.247\ 10^{-9}$	$0.00031\ 10^{-9}$
Sorption coefficients (I.S.)			
	Membrane	$0.277\ 10^{-6}$	$10.6\ 10^{-6}$
Volume fraction of upstream components		0.5; 0.5	
High upstream pressure (Pa)		$1.01315\ 10^5$	
Initial downstream pressure (Pa)		0	
Temperature (K)		293.15	
Surface area of the membrane (m^2)		10^{-4}	
Downward left and right volumes (m^3)		10^{-3}	
Number of discretization points in the membrane		51	

using the same pump. Another unsteady state process has been described by LaPack and Dupuis (1994). In that case, dynamic operation is used in order to induce the preferential accumulation of the fast compound in the membrane, before the slow diffusing component reaches steady state. Alternatively, the difference in desorption rates, also due to differences in diffusivities, is utilized for the permeate recovery step. More recently, a novel and promising process, so called pressure swing permeation, was disclosed by (Feng et al., 2000). With two or more membrane modules operated in a cyclic fashion, the low-permeate pressure can be elevated by pressurization with high pressure feed gas. An economy on compression costs, is, thus, obtained. Feng applied the concept to H_2/N_2 separation to demonstrate the possibility to recover the permeate product at a pressure as high as the feed, without using a compressor. Moreover, this study pointed out a potential limitation of cyclic membrane operation, which occurs when fast diffusing compounds (typically showing a diffusion coefficient D above 10^{-12} $m^2 \cdot s^{-1}$) permeate through a very thin membrane (below 0.1 μm).

Surprisingly, a systematic investigation of the potentialities of the pulsed feed approach proposed by Paul has remained unexplored. It is the intention of this work to extend the analysis developed by Paul beyond the set of working hypotheses, which are needed for an analytical solution to be obtained. To that respect, a rigorous numerical study, based on finite volume computing, which allows a broad range of physical situations to be covered, has been undertaken. The process time constant (i.e., time needed to reach steady cyclic operation), which has remained unexplored up to now, can, thus, be estimated through simulation. Furthermore, the incidence of compound back diffusion, which can potentially affect the separation performances, has been also rigorously implemented in the simulation framework. Numerical simulation enables to investigate a broad range of operating conditions, including asynchronous modes, which cannot be assessed through analytical approaches. Finally, a series of optimization methods have been developed in order to systematically explore a broad range of operating conditions when a target objective is defined. The association of numerical resolution to novel optimization methods enables operating conditions for a given objective criteria to be quickly identified. This methodology will be illustrated with respect to two different objectives: finding operating conditions which generate maximal selectivity or productivity, and finding a compromise between selectivity and productivity (a multivariable optimization problem, which is typical of separation processes on a broad sense).

Similarly to the previous simulation studies performed in pulsed membrane separation processes, a choice has to be done for a given problem to be explored. An illustrative case study, namely the CO_2/H_2 separation through a polyisoprene-co-acrylonitrile membrane, has been selected for that purpose. A rigorous analysis of the pros and cons of unsteady vs. steady operation, in terms of selectivity (i.e., hydrogen purification) and productivity will be detailed for that case.

Framework and objectives of the study

The selective permeation of gases through polymeric membranes is classically interpreted by means of the so-called solution diffusion model (Freeman, 1999). According to this approach, the steady-state separation factor for two species is the product of the ratios of diffusion coefficients and solubility coefficients. Nevertheless, in numerous cases, these two ratios have opposite behaviors, which result in a decreased overall steady state selectivity. For instance, rare gases pairs can show a very high-diffusion selectivity which is almost completely annihilated by an inverse sorption selectivity. In that case, only transient operation can enable to make use of this potentiality. Given the number of mixtures and variables which play a role, an exhaustive analysis of the performances and limitations of cyclic vs permanent membrane separation cannot be achieved.

In this study, the CO_2/H_2 gas pair separation through an elastomeric polyisoprene-co-acrylonitrile membrane has been selected, for illustrative purposes, as a target problem. The key parameters of the separation problem are summarized in Table 1. The CO_2/H_2 mixture shows in fact several advantages:

- it corresponds to the key problem of hydrogen production from natural gas steam reforming, which is currently considered as one of the major challenge for separations (Noble and Agrawal, 2002). The difficulties associated to the identification of efficient hydrogen selective materials are often mentioned (Adhikari and Fernando, 2006). A novel and promising approach, based on reverse selective materials ((i.e., showing a selectivity towards carbon dioxide), has been recently reported in order to circumvent this problem (Lin et al., 2006). This study will, however, be deliberately restricted to hydrogen selective materials, based on realistic performances.

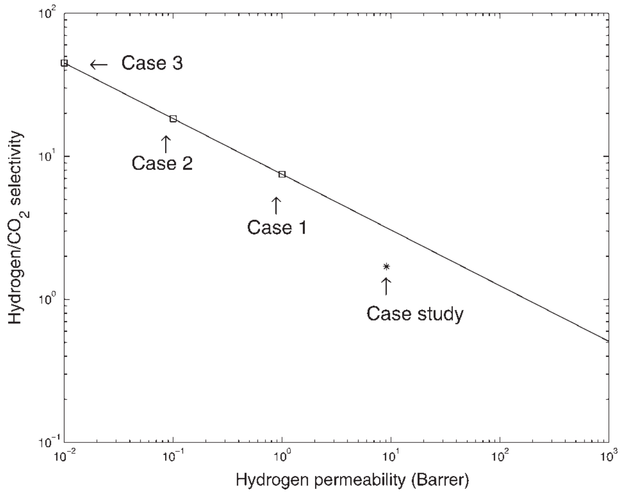

Figure 1. Theoretical CO_2–H_2 curve at 293.15K computed from a classical predictive approach.

- depending on the process constraints, either hydrogen alone or hydrogen and carbon dioxide have to be recovered under a given purity. The former case corresponds to a classical hydrogen production framework. The latter one corresponds to the clean power plant problem, for which carbon dioxide should be enriched in order to achieve carbon capture and sequestration.
- polymeric membranes show a low selectivity toward this mixture, due to the antagonistic contributions of solubility (which favors carbon dioxide) and diffusivity (which favors hydrogen). The so-called trade-off curve for CO_2/H_2, computed from a classical predictive approach (Freeman, 1999), is shown on Figure 1. It can be seen that highly permeable membrane materials are more likely to be selective towards CO_2, while low permeable ones show a preferential permeation toward hydrogen. The conditions used for the present case study, which correspond to a compromise (and, as a consequence, a poor selectivity) are shown on Figure 1. They correspond to a steady permeation selectivity close to 2 (1.7), which is considered as representative for polymeric membranes and remains too low for industrial application (Adhikari and Fernando, 2006). Points 1, 2 and 3 of Figure 1 correspond to virtual membrane materials, not yet available, but which would present improved performances in terms of hydrogen purification.
- for elastomeric membrane materials, such as the one selected in this study, the constant permeability behavior, one of the working hypotheses of the simulation, can be considered as correct (Baker, 2004). Polyisoprene-copolyacrylonitrile (74/26) shows indeed a glass transition temperature of -10°C (van Amerongen, 1950). Furthermore, low pressure conditions have been deliberately selected in order to prevent the occurence of a variable permeability, especially for carbon dioxide. This type of deviation has been alreay reported in glassy and rubbery polymers (Yampolskii et al., 2006). Nevertheless, plasticization by carbon dioxide is known to occur especially in glassy polymers and for partial pressures of several bar (Ghosal and Freeman, 1994).
- flux coupling may be significant in any multicomponent mass-transfer situation. Nevertheless, the absence of flux coupling is expected to hold in the present case, as it is classically postulated for membrane gas separations (Pan, 1986). This effect does not significantly affect indeed separation performances for the CO_2/H_2 pair in elastomers up to partial pressures of 15 Bar (Lin et al., 2006). Again, the low-partial pressure used in our simulations corresponds to a low carbon dioxide volume fraction in the membrane. This criterion is often proposed to be the key factor which will affect deviations from the pure gas behaviour. Additionnally, we notice that mixed gas permeability values for the frequently studied gases (H_2 and CO_2) have been reported to be very similar to pure gas permeabilities over a large range of operating conditions, both in rubbery and glassy polymers (Merkel et al., 2001).

We expect that the two aforementioned simplifying assumptions (negligible plasticization and no flux coupling) remain acceptable in order to achieve realistic flux computations. To that respect, it should be noted that a similar computation framework enabled a very good prediction of the experimental fluxes obtained with a polyimide (i.e., glassy) membrane hollow fiber module with hydrogen and carbon dioxide under high pressure conditions (Kaldis et al., 2000).

More generally, the objectives of the study are the following:

- evaluate, through a rigorous numerical study, the performances, the limitations and the potentialities of a cyclic membrane process working with a realistic material.
- explore considerations which could not be addressed by an analytical solution, such as the time needed in order to reach cyclic operation, the incidence of back-diffusion effects or the performances of asynchronous operation.
- tentatively identify, through optimization methods, optimal operating strategies, with particular concern to the productivity/selectivity trade-off.

Even though the results which will be developed, hereafter, remain limited to a simulation study at this stage, it is expected that a realistic evaluation of the potentialities of a cyclic operation can be provided.

Description of the Process

Paul's process

Paul (1971) describes a process represented in Figure 2 where two tanks are disposed upstreams and two tanks backwards. Paul studies the possibility of separation when the

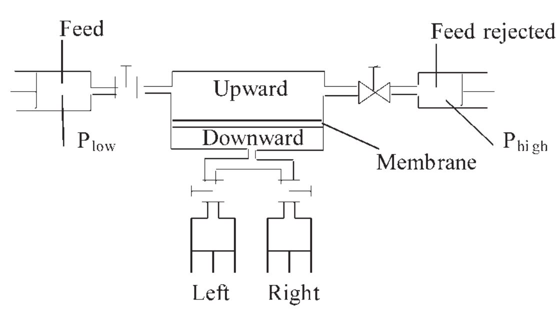

Figure 2. Process of pulsed separation according to Paul (1971).

valves are operated in a cyclic manner consisting of steps of the upstream pressure alternatively high and low. In this article, Paul considers that the valves are synchronous and that the duration of the steps is the same for high- and low-pressure. Another aspect of Paul study is that it remains mainly qualitative and describes more a principle than the actual conditions of operation. However, Paul underlines the fact that a cyclic operation can enhance the selectivity.

Model of the process

The following hypotheses are considered for the membrane

1. The resistance to mass transfer is only located in the membrane,
2. The process is strictly diffusional in the membrane,
3. Interfacial equilibrium is instantaneous upstream,
4. Conditions are isothermal.

In these conditions, it results that the behavior of the membrane can be modeled by Fick law for each compound

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial z}\mathcal{D}(c)\,\frac{\partial C}{\partial z} \tag{1}$$

where $\mathcal{D}$ is the diffusion coefficient which eventually can depend on concentration $C(z,t)$. In the simple case of a single membrane of thickness L submitted to an upstream pressure P_0, when vacuum is initially done in the upstream and downstream tanks, the initial and boundary conditions are

$$\begin{aligned} &C(z,0) = 0 \qquad \forall 0 \le z \le L \\ &C(0,t) = C_0 = SP_0 \qquad \forall t \\ &C(L,t) = C_1 = SP_1 \qquad \forall t \end{aligned} \tag{2}$$

where S is the sorption coefficient, P_0 the upstream pressure, P_1 the downstream pressure.

Furthermore, for the downstream tank, the mass balance results in the following equation

$$\frac{dP_1}{dt} = \frac{dn_{in}}{dt}\,\frac{RT}{V_{\text{downstream}}} \tag{3}$$

with the molar flux entering into the downstream tank

$$\frac{dn_{in}}{dt} = -\mathcal{D}(C_1)\frac{\partial C}{\partial x}\bigg|_L A \tag{4}$$

where A is the surface area of the membrane offered to transfer.

In this study, two downstream tanks are present which are alternatively open and closed for receiving the diffused gases. A brutal change of boundary condition occurs when the downstream left valve closes and the downstream right valve opens and vice-versa. Just before the instant of closure of the left valve, the partial pressure of component k in the downstream left tank and the concentration of the same component at the membrane-gas interface noted $z = L$ are related by the condition

$$C_k(z = L) = sorpt_k\, P_{k,\text{downstream,left}} \tag{5}$$

When the commutation of the valves occurs, the downstream right tank is put in communication with the membrane, and a new boundary condition is imposed for the interface concentration

$$C_k(z = L) = sorpt_k\, P_{k,\text{downstream,right}} \tag{6}$$

It has been assumed that in certain conditions where a concentration gradient is favorable, the gas can diffuse backwards from the downstream tank toward the upstream tank. This physical consideration is very important when step responses are to be obtained. It can occur, for example, when the upstream pressure becomes low after having imposed a high-pressure to the membrane.

These equations together with the initial and boundary conditions are solved by the finite volume method (Patankar, 1980, Patankar et al., 1998). The numerical procedure has been first validated in a simple case where an analytical solution is available.

The integration time step is chosen as 0.1s and 51 points are chosen for spatial discretization in the membrane. It is important to stress at this stage that care has been taken to select realistic operating conditions. This applies particularly for the minimal opening or closing time of the valves, which will remain systematically larger than one second (Feng et al., 2000). Consequently, a rather large membrane thickness (10 μm) has been deliberately chosen, in order to be compatible with the characteristic diffusion time in the membrane. Composite membranes used for gas separations in industry obviously are typically hundred times thinner. This peculiarity, which could be seen as a decisive penalty for the cyclic operation, will be discussed after.

Definition of selectivity and productivity

The selectivity can be defined in different manners. Here, it is defined as

$$\text{selectivity} = \frac{y_{d,l,1}}{1 - y_{d,l,1}}\,\frac{1 - y_{u,1}}{y_{u,1}} \tag{7}$$

where $y_{d,l,1}$ is the mole fraction of component 1 is the downstream left tank and $y_{u,1}$ is the upstream mole fraction of component 1.

Given the principle of the process, the selectivity toward the other compound, which preferentially accumulates in the right tank, could also have been considered. Nevertheless, this possibility has not been taken into account for sake of simplicity. The problem of hydrogen purification will, thus, be the only target of the simulation and optimization study.

The productivity is simply defined as the number of moles of component 1 that are obtained in the downstream left tank divided by the total time of operation.

Operating conditions

Exposure of the Problem. Let us note x_1, x_2, x_3, x_4, respectively, the opening times of the upstream left, upstream right, downstream left and downstream right of the valves of the process. It is assumed that each valve is constrained in the domain [1,100]s, these bounds being denoted as t_{min} and t_{max}. t_{max} has been chosen arbitrarily and could be varied. t_{min} is obviously strictly positive. A constant delay could exist between the cycle of the upstream valves and the cycle

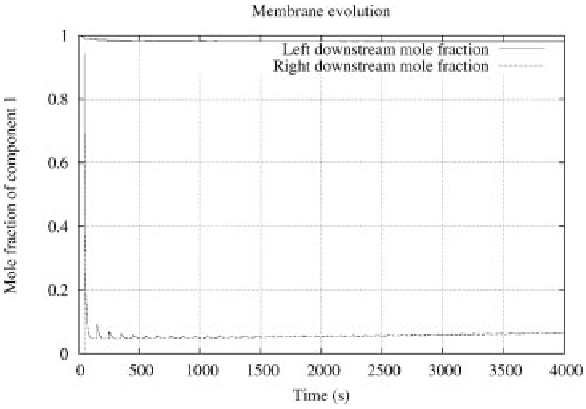

Figure 3. Evolution of mole fractions with respect to time in a standard synchronous operation.

of the downstream valves. In this study, this delay has not been considered. Furthermore, to ensure a cycle for the opening times, x_4 is related to the other opening times by the relation

$$x_1 + x_2 = x_3 + x_4 \Rightarrow x_4 = x_1 + x_2 - x_3 \tag{8}$$

so that there remain only three independent variables x_1, x_2, x_3 which will be considered in the following optimization problem. The optimization variables are constrained by their existence domain and the following constraints

$$\begin{aligned} x_1 + x_2 &\leq t_{max} \\ t_{min} &\leq x_1 + x_2 - x_3 \end{aligned} \tag{9}$$

The different types of operation are defined as follows

$$\begin{array}{rlll} \text{Synchronous if} & x_1 = x_2 & \text{and} & x_3 = x_4 \\ \text{Symmetric if} & x_1 = x_3 & \text{and} & x_2 = x_4 \\ \text{Asynchronous if} & x_1 \neq x_2 & \text{and} & x_1 \neq x_3 \end{array} \tag{10}$$

For a given set of opening times, for example $x_i = 50\text{s}\ \forall i$, the mole fractions of component 1 in the left and right downstream tanks have been studied with respect to time. Figure 3 shows that after about 500s, a quasi steady state resulting from the cyclic operation occurs. Consequently, for the rest of the study, it was decided to consider the values of selectivity and productivity at a final time equal to $t_f = 1{,}000\text{s}$, representative of a quasi-steady operation.

Conditions of Simulation. An equimolar binary mixture H_2, CO_2 has been considered for separation and the objective is to obtain H_2 with a good selectivity and productivity by means of cyclic steps performed for the upstream pressure. The conditions of simulation are resumed in Table 1.

First Preliminary Study of Selectivity and Productivity. A first and naive approach for the pulsed operation of the process would be to operate at equal opening and closing times for all upstream and downstream valves, in a synchronous manner, so that x_i does not depend on valve i. This corresponds to the case described by (Paul, 1971). Even, in this simple case, the duration of each positive or negative step simply denoted as x is an operating parameter for the process. The influence of this parameter is given in Table 2.

Table 2. Influence of Step Length on Selectivity and Productivity for a Synchronous Operation

Step length x (s)	Selectivity	Productivity (mol · s^{-1})
10	41.6	1.66 10^{-10}
20	44.7	1.69 10^{-10}
30	51.4	1.71 10^{-10}
40	54.8	1.71 10^{-10}
45	56.3	1.72 10^{-10}
50	55.6	1.75 10^{-10}
55	54.3	1.72 10^{-10}
60	52.2	1.75 10^{-10}
75	47.3	1.72 10^{-10}
100	40.2	1.72 10^{-10}
200	28.3	1.73 10^{-10}
500	23.3	1.73 10^{-10}

Note that the final time to calculate the selectivity and productivity has been increased, when the step length is increased to be certain to reach a quasi-steady state. It has been chosen at least as long as twenty times the step length, and equal to an even number of times the step length in order to finish at the end of a low-upstream pressure step.

Clearly, the productivity depends very little on the duration of the step length, whereas the selectivity is much more sensitive and even presents a maximum around 50s (Figure 4). Small fluctuations in productivity in Table 2 must be attributed to numerical inaccuracy.

Second Preliminary Study of Selectivity. In the following study, it is assumed that the upstream valves have the same opening and closing duration equal to 50s, so that the length of a single cycle is 100s. The duration of opening and closing of the downstream valves is varied between 5 and 95s, the sum of the opening and closing of the left valve (similarly for the right valve) being equal to the length of the cycle 100s. The selectivity is calculated after 1,000s, and is represented on Figure 5.

Comparison of Steady-State and Cyclic Operations. In a first step, a direct comparison of steady vs. unsteady operation has been carried out, and is shown on Figure 6. Steady operation corresponds to a classical single module operation,

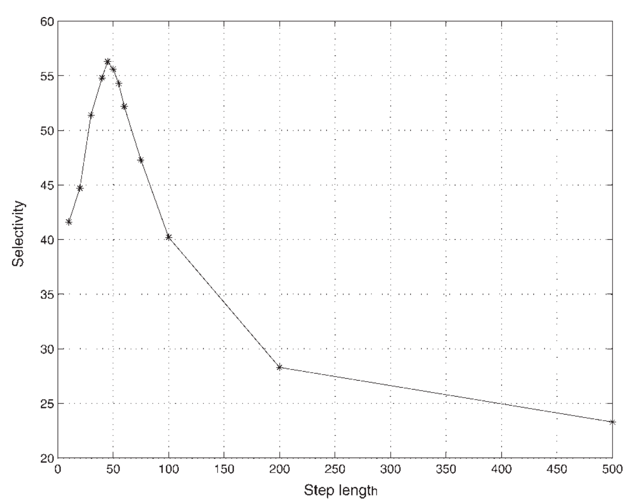

Figure 4. Influence of step length on selectivity for a standard synchronous operation.

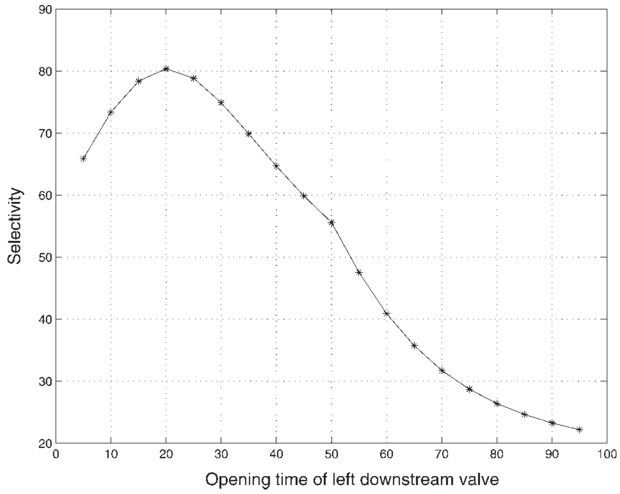

Figure 5. Influence of downstream step length on selectivity in the case of equal upstream step lengths.

with stationary upstream conditions and a constant pressure ratio (Pan, 1986). The unsteady (or cyclic) operation was previously described in the Exposure of the Problem section.

The open steady diamonds have been obtained for different thicknesses of membranes (namely 10 and 0.1 μm) for same material characteristics as used previously for cyclic operations. A much higher productivity results, at the expense, however, of a too low selectivity. The thickness of 0.1 μm has been chosen as representative of thin composite membrane conditions, such as those used in steady operation for industrial application.

Similarly, open circles indicate the performances of more selective virtual membrane materials operated under steady-state conditions, and referenced by numbers 1, 2, and 3 (those already used in Figure 1) on Figure 6. Since steady state conditions only are used for these three membrane materials, the overall permeability only plays a role in the simulations, and each case gives unique performances (in other words, separate contributions of S and D have not to be considered).

Unsteady operation, shown by stars, clearly offers a broad range of performances in terms of productivity and selectivity, depending on the set of operating conditions. For much longer upstream opening times than those explored in this study, it can be logically expected that the unsteady performances would become similar to the steady state ones (Paul, 1971). Given the crucial need to develop a high-selectivity toward hydrogen, simulation conditions which favor this criterion have been chosen. It is important to notice that the performances of unsteady operation can offer improved selectivity with a similar productivity compared to the most efficient materials (upper bound of the trade-off curve, noted case 1 and case 2) operated under steady conditions with a much thinner membrane. Even though such a comparison is not straightforward, it shows that the argument of too low-productivity which has been classically reported up to now for the other case studies (He/CH_4 and O_2/N_2) could possibly be reconsidered for the CO_2/H_2 mixture. In that case, unsteady operation can offer the opportunity to reach, with existing materials, similar performances to those with improved virtual membranes. It has to be stressed, however, that, for a given membrane material, the gain in selectivity offered by the cyclic operation can only be obtained at the expense of a loss of productivity. This key feature of Paul process cannot be circumvented.

Apart from the steady vs. unsteady comparison, an examination of the characteristic performances which can be obtained by each type of unsteady operation (namely symmetrical, synchronous and asynchronous) is also interesting. This is summarized on Figure 7. It can be seen that symmetrical operation covers a tiny area, while synchronous conditions systematically correspond to the upper threshold, and asynchronous conditions cover the broadest part of the domain. This observation calls for a systematic analysis of the operating conditions which would maximize a given

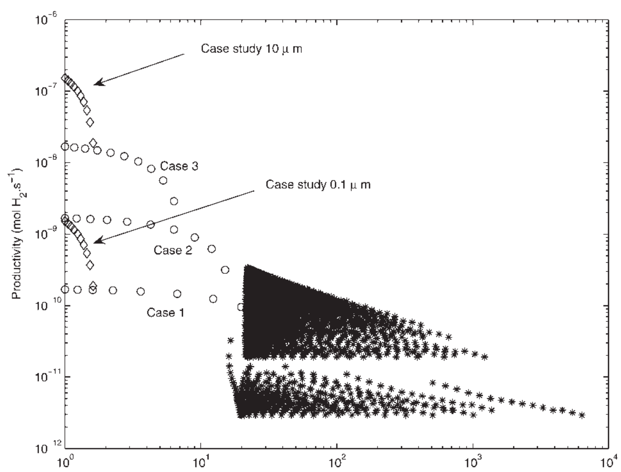

Figure 6. Comparison of separation performances for steady (○ and □), and unsteady (*) operations.

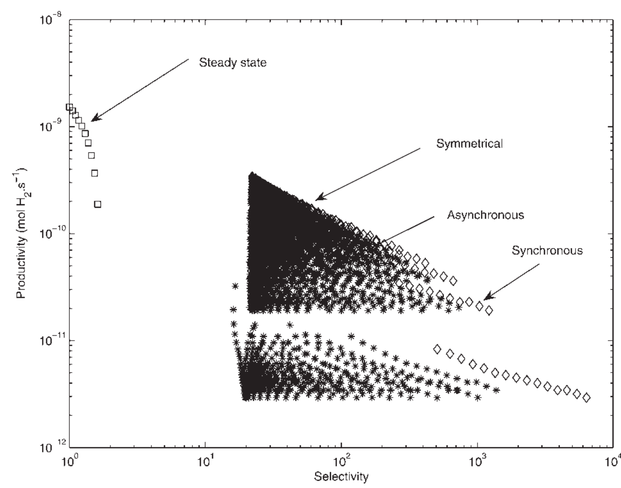

Figure 7. Separation of unsteady performances between symmetrical, synchronous and asynchronous operations and comparison with steady performances.

objective. A dedicated optimization study has been carried out in order to explore this issue.

Optimization

In practice, it is not sufficient to consider synchronous or symmetric operations so that all types of operation including asynchronous ones will be considered in the optimization study.

Optimization problem

The optimization problem with respect to selectivity is set as follows

$$\begin{aligned} &\max_{x_1,x_2,x_3} \text{ selectivity}(t_f) \\ &\text{submitted to:} \\ &t_{min} \le x_i \le t_{max} \\ &x_1 + x_2 \le t_{max} \\ &t_{min} \le x_1 + x_2 - x_3 \end{aligned} \tag{11}$$

The problem of productivity is exactly similar to the problem of selectivity.

Due to the way of calculating the selectivity or productivity by a sequence of finite volume iterations until $t = t_f$, this optimization problem is nonlinear. Furthermore, it is constrained. Two methods are chosen to solve the optimization problem. A genetic algorithm able to take into account the constraints has been designed and used. It possesses the properties of a nearly global optimization (Gen and Cheng, 1997), i.e., due to its random generation of individuals, it sweeps over the domain of variables in a way such that it is likely that local extrema will be found. Another method of completely different character has been used. Developed by Schittkowski, 1985, NLPQL is a nonlinear programming Fortran code based on sequential quadratic programming (SQP), which is efficient for solving nonlinear optimization problems. However, it is local, and, thus, might fail in finding local extrema. A combination of the two methods can be thought of, with first the genetic algorithm to span the domain of variables and then the SQP method to locally refine the result. This optimization strategy has also been used in the present problem.

Optimization by genetic algorithm

The genetic algorithm which has been designed and used is based on real numbers, not chromosomes. It first generates an initial population of a given size of individuals (variables x_1, x_2, x_3) calculated at random, but belonging to the domain $[t_{min}, t_{max}]$. For each of these individuals, the criterion to be optimized can be calculated, as well as the constraints which are not necessarily automatically satisfied. Then, a sequence of mutation and birth of individuals forces the population to evolve in an elitist manner towards a better extremum while respecting the constraints. The parameters of the genetic algorithm code written in Fortran are mainly the size of population, the number of generations, some thresholds for mutation and birth.

The performance of the genetic algorithm is illustrated in Figure 8, where the selectivity is plotted with respect to the number of the individual. Twenty generations of 200 individuals, each were generated. At first, the points are scattered, and then evolve towards an extremum of selectivity equal to 1,640 for individual 1,801 for the triplet $x_1 = 4.97$, $x_2 = 94.8$, $x_3 = 5.15$. In each generation of 200 individuals, only the points belonging to the existence domain are represented and in each generation, the points are classified from the best one to the worst one, which gives that specific allure to the graph. After the 18th generation, the evolution of the selectivity becomes lower.

The productivity is optimized by the genetic algorithm in a similar manner to the selectivity, with the same number of 200 individuals and 10 generations. It converges towards $0.339\ 10^{-9}$ (Figure 9) for the triplet $x_1 = 64.7$, $x_2 = 1.47$, $x_3 = 65.0$. The optimum triplet for productivity is far from the optimum triplet for selectivity, so that a classical optimization conflict appears for the best operation choice.

Optimization by nonlinear programming

In a first stage, the nonlinear programming under the form of sequential quadratic programming performed by NLPQL code (Schittkowski, 1985) has been applied to the selectivity without any *a priori* knowledge about the triplet x_1, x_2, x_3 which is simply taken as (50,50,50), i.e., right in the center of the domain, corresponding to an initial selectivity equal to 55.6, and an initial productivity equal to $1.75\ 10^{-10}$. After many iterations, the algorithm converges toward a selectivity equal to 3,702 for $x_1 = 1.93$, $x_2 = 96.08$, $x_3 = 1.08$, thus, far better than the result of the genetic algorithm. However, the tendency for the location of the extremum is very close, with low and nearly equal values of x_1 and x_3, and a high-value of x_2. In this optimum case of selectivity, the productivity is equal to $0.36\ 10^{-11}$, which is very low.

Study of surface responses

The difficulty of optimization is that there always exists possibilities of multiple extrema for a complex function. Consequently, it was decided to systematically calculate the

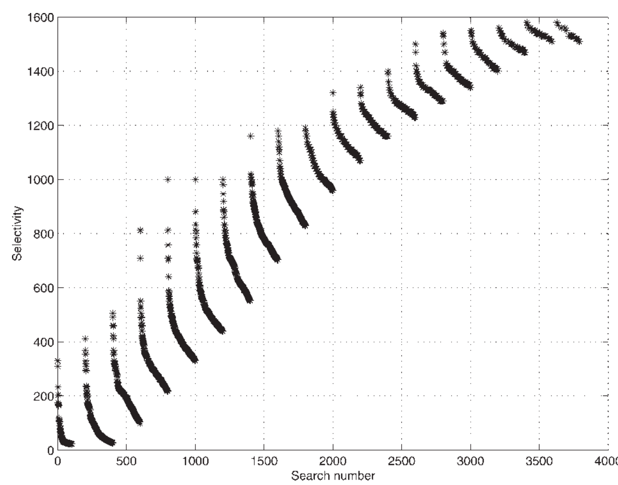

Figure 8. Evolution of selectivity of individuals along the generation procedure of the genetic algorithm.

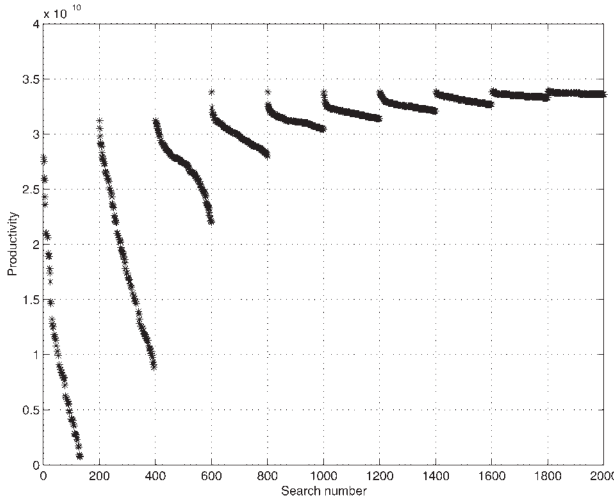

Figure 9. Evolution of productivity of individuals along the generation procedure of the genetic algorithm.

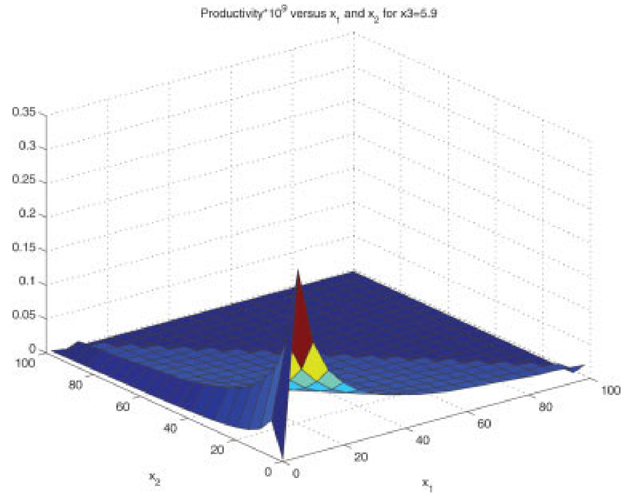

Figure 11. Surface response of productivity (× 10^9) with respect to variables x_1 and x_2 for x_3 = 5.9 s.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

selectivity and the productivity of the membrane operation process by scanning the three variables x_1, x_2, x_3. Nevertheless, constraints on these variables must be respected as stated in Eq. 11. As a representation can be made only for two variables, the third variable is fixed and its chosen value is given in the caption of the Figure. The surfaces responses of Figures 10 and 11 were, thus, obtained. For the values of the triplet x_1, x_2, x_3 not allowed because of constraints, zero values of selectivity or productivity have been assigned. The value of this third variable was chosen so that the swept domain would be sufficiently large. If this value is varied, the tendencies remain the same. The surfaces do not show several extrema but regular variations even if these latter are large. In this manner, the largest value of selectivity is reached when x_1 is taken at its lowest value, and x_2 at its largest value for a fixed x_3. The selectivity varies considerably from around 16 to 6300, thus, is increased by a factor larger than 100. The largest value of selectivity 6,371 is obtained for (x_1, x_2, x_3) = (1,99,1) corresponding to a productivity equal to 0.2934 10^{-11}.

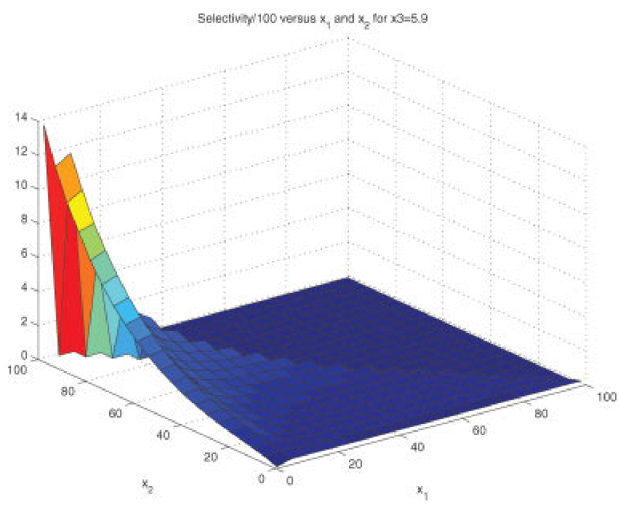

Figure 10. Surface response of selectivity (divided by 100) with respect to variables x_1 and x_2 for x_3 = 5.9 s.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The productivity responds in an opposite manner with regard to the selectivity with its maximum reached when x_1 and x_2 is taken at its lowest value for a fixed x_3. The productivity varies from 2.9 10^{-12} to 3.4 10^{-10}, and is increased by a factor 100. The maximum of productivity equal to 3.4 10^{-10} is obtained for (x_1, x_2, x_3) = (99,1,99) and correspond to a selectivity equal to 22.13.

It is interesting to compare the figures of selectivity (Figure 10), and productivity (Figure 11) for a given couple of varying variables. The remark concerning their opposite tendencies of variations can be easily noticed.

The values of maxima of selectivity and productivity obtained by this systematic approach are close to the values obtained by nonlinear programming, and the optimization by genetic algorithm could not give closer results by far.

In experimental design (Box et al., 1978, Davies, 1979), it is customary to represent a surface response by a linear model without any physical meaning, but which can be exploited statistically. The systematic study which was performed does not follow the usual rules of experimental design as the number of experiments is not minimized. The availability of a comprehensive model was used, but this model needs computing time and a surface response model would be beneficial. Following that point of view, several models have been tried such as

$$y = a_0 + a_1 x_1 + a_2 x_2 + a_3 x_3 + a_4 x_1 x_2 + a_5 x_1 x_3 + a_6 x_2 x_3 + a_7 x_1^2 + a_8 x_2^2 + a_9 x_3^2 \qquad (12)$$

where y is either the selectivity or the productivity. In fact, due to the large and steep variation of the selectivity or productivity, these models gave bad predictions and failed in predicting the steep variations. A much better model for selectivity was obtained as

Table 3. Coefficients of the Statistical Selectivity Model (13)

Coefficient with confidence interval $a_{i,min} \leq a_i \leq a_{i,max}$	Significance
$1.4654 \leq 1.4958 \leq 1.5262$	Yes
$0.0021 \leq 0.0025 \leq 0.0029$	Yes
$0.0074 \leq 0.0078 \leq 0.0082$	Yes
$-0.0073 \leq -0.0070 \leq -0.0067$	Yes
$0.2134 \leq 0.2821 \leq 0.3508$	Yes
$-0.2441 \leq -0.1754 \leq -0.1067$	Yes
$-0.0591 \leq 0.0095 \leq 0.0780$	No
$-0.0017 \leq -0.0006 \leq 0.0005$	No
$-0.0103 \leq -0.0092 \leq -0.0081$	Yes
$0.0054 \leq 0.0065 \leq 0.0076$	Yes
$0.0027 \leq 0.0038 \leq 0.0048$	Yes
$-0.0164 \leq -0.0154 \leq -0.0143$	Yes
$0.0044 \leq 0.0055 \leq 0.0065$	Yes

$$\log(y) = a_0 + a_1 x_1 + a_2 x_2 + a_3 x_3 + a_4 \frac{1}{x_1} + a_5 \frac{1}{x_2} + a_6 \frac{1}{x_3} + a_7 \frac{x_1}{x_2} + a_8 \frac{x_1}{x_3} + a_9 \frac{x_2}{x_3} + a_{10} \frac{x_2}{x_1} + a_{11} \frac{x_3}{x_1} + a_{12} \frac{x_3}{x_2} \quad (13)$$

where the logarithm was used to attenuate the steep variations of selectivity, and the fractional functions were chosen to take into account the shape of the surface responses. With a signification level equal to 5%, the coefficients a_0, a_4 and a_5, were found to be the most statistically significant which confirms the hyperbola shape of Figure 10. The values are gathered in Table 3.

Multicriteria optimization

A multicriteria genetic algorithm has been developed to emphasize about the conflict between optimization of selectivity and productivity. The single criterion genetic algorithm is modified to take into account several criteria as

$$\min \boldsymbol{f}(\boldsymbol{x}) = \begin{bmatrix} f_1(\boldsymbol{x}) \\ \vdots \\ f_p(\boldsymbol{x}) \end{bmatrix} \quad (14)$$

submitted to inequality constraints

$$g_i(\boldsymbol{x}) \leq 0 \qquad i = 1, \ldots, m \quad (15)$$

To create the domination function, each individual of the ranked population is compared to the other individuals of the same population. The domination number is calculated as the number of times a function linked to an individual is larger than the same functions linked to the other individuals. Then the individuals are classified with respect to their domination number. The domination function is used to discriminate the set of nondominated individuals which are retained to form Pareto's zone.

First, the algorithm has been validated by two examples given in Massebeuf et al., 1999. One example is the minimization of the two following functions

$$\begin{aligned} f_1(x, y) &= 200\,(1 + 3x - 2y)^2 + 4\,(1 + 4x - 4y)^2 \\ &\quad \text{Optimum}(-0.5, 0.25) \\ f_2(x, y) &= 200\,(1 - 2x)^2 + 7\,(1 + 4y)^2 \\ &\quad \text{Optimum}(0.5, 0.25) \end{aligned} \quad (16)$$

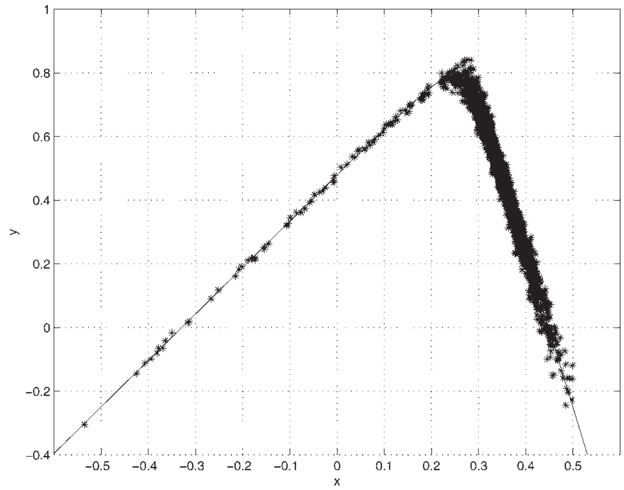

Figure 12. Pareto's zone for the validation example.

The crosses are the points generated by the genetic algorithm. The continuous line corresponds to Eq. 17.

which yields the theoretical Pareto domain

$$y = (5925 - 7538x - (14485361 - 105968388x + 196619844x^2)^{0.5})/4424 \quad (17)$$

On Figure 12, the Pareto's zone obtained by the multicriteria genetic algorithm is compared to the theoretical Pareto domain given by Eq. 17 and the zone obtained from the multicriteria genetic algorithm represents very well the behavior of the theoretical zone, which validates our algorithm.

The same multicriteria genetic algorithm has been used for selectivity and productivity, which constitute the two functions of the three variables which are the time durations x_1, x_2, x_3. Ten generations have been performed with 1,000 individuals each. Due to the mutation, death and birth mechanisms involved in the genetic algorithm, more than 48,000

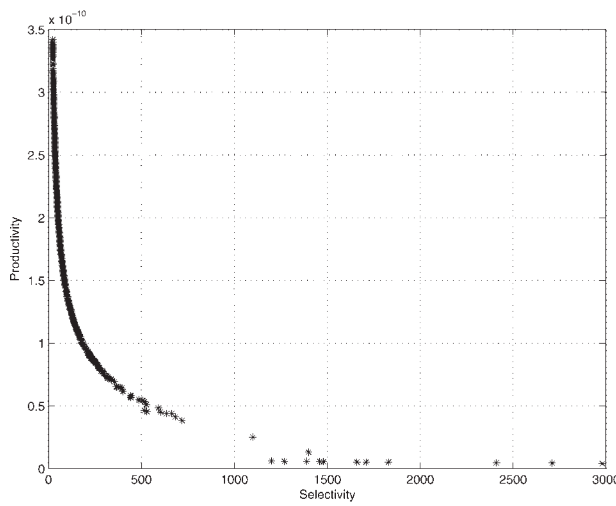

Figure 13. Pareto's zone for the multicriteria genetic optimization with respect to selectivity and productivity.

individuals were tested to finally retain only the ten generations of one thousand individuals each, with only the results of the final generation represented here.

Figure 13 has been obtained as the last of ten generations of 1,000 individuals each. It clearly shows that the Pareto's zone has the shape of an hyperbola. More points are gathered at low selectivities and high-productivities.

Figure 14 shows the Pareto's zone in terms of opening times of the left and right upstream valves. Most points are close to the constraint $x_1 + x_2 \leq 100$, and correspond to medium selectivity and productivity. The scarce points for low values of x_1 correspond to high-selectivities, low-productivity and the reverse for those for low values of x_2.

Figure 15 is remarkable in the sense that all points are gathered along the bisecting line corresponding to equality of opening times for the left upstream and left downstream valves. This confirms the results of monocriterion optimization where these times were very close.

Conclusion

Membrane processes have found many applications during the last decades for the separation of hydrogen, carbon monoxide, nitrogen, ammonia, and the sweetening of natural gas. They attracted a great deal of research interest, particularly for the development of improved membrane materials. The development of better membranes with both high-permeability and selectivity can advance the performances. Nevertheless, most new highly selective membranes possess a very low permeability.

Apart from membrane material development, the exploration of new permeator configurations or operation can open new fields of application. The tentative advantages of a rather unexplored approach, namely the cyclic operation of a single membrane module, has been investigated in this study. One of the most challenging gas pair for membrane separations, hydrogen/carbon dioxide, has been selected as a case study.

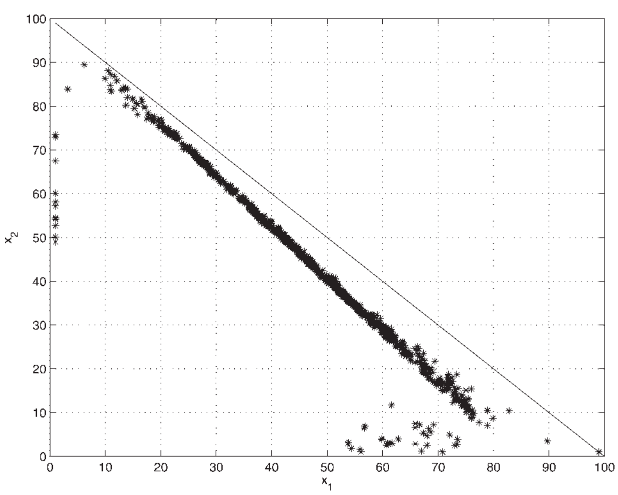

Figure 14. Pareto's zone for the multicriteria genetic optimization with respect to the opening times of upstream valves.

The continuous line corresponds to the constraint on $x_1 + x_2$.

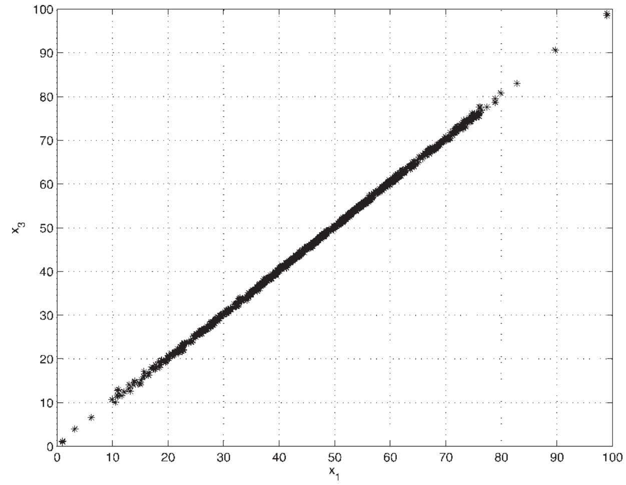

Figure 15. Pareto's zone for the multicriteria genetic optimization with respect to the opening times of left upstream and downstream valves.

It has been shown, through a rigorous numerical approach, that cycling operation offers the opportunity to largely expand the productivity/selectivity domain, compared to steady operation. The gain in selectivity offered by the cyclic operation can, however, only be obtained at the expense of a loss of productivity. We could not circumvent this matter of fact, which is intrinsically associated to the cyclic process proposed by Paul. A much larger domain of selectivity/productivity trade-off might be an interesting opportunity in some cases, but it may also be of no use if the productivity decrease is too strong. There is no systematic answer to this question. For CO_2/H_2, unsteady operation performed with a reported membrane material can potentially compete with the best, still virtual, materials operated under steady state, both in terms of permeability and selectivity. This conclusion differs largely from the previous studies, performed on two other gas pairs (H2/CH_4 and O_2/N_2), for which a too high loss in productivity was obtained in the case of cyclic operation.

More importantly, a novel and dedicated optimization approach has been developed for cyclic membrane operation, in order to quickly and efficiently identify the best set of operating parameters for a given target performance. For the case study (CO_2/H_2), synchronous operation should be chosen in order to achieve maximal productivity and selectivity. It is obvious that the previous conclusion (cyclic competing with steady state and synchronous operation offering the best performances) cannot be extended to any situation. Given the complexity of the process and the number of variables which play a role, other mixtures, membrane materials or operating conditions should be explored in order to identify possible windows of interest of unsteady operation.

Our study offers several perspectives. First, the study of the incidence of more complex permeation conditions, such as variable permeability or flux coupling would be also of interest. It is important to note at this stage that, since a detailed solution-diffusion mechanism is incorporated in the modelling approach, variable permeability conditions could be rigorously taken into account (Mauviel et al., 2005).

Another key issue of cyclic gas permeation processes is the identification of the most appropriate membrane thickness, which can be seen as a dilemma in terms of productivity/selectivity trade-off. Basically, we selected in our study a fixed membrane thickness according to two criteria: a realistic process control strategy and a realistic membrane production facility. For the first criterion, the time lag for the fast permeating compound (i.e., hydrogen) has to be much larger than the shortest acceptable valve operation frequency (fixed at 1 s). For the second one, a thickness of a few micrometers seem to be reasonable for a rubbery active layer. Nevertheless, the identification of the most appropriate membrane thickness would call for a dedicated optimization strategy, as soon as a precise separation process with defined objectives is selected. This target can be achieved thanks to the modeling and optimization approach that we have described.

Thus, the generic and rigorous simulation and optimization tool which has been reported in this study offers a series of promising perspectives.

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