OPTIMIZATION OF A SETUP OF MEMBRANES IN SERIES FOR CO_2 SEPARATION FROM A FLUE GAS STREAM USING GENETIC ALGORITHM – AN ECONOMIC POINT OF VIEW

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***Abstract**. This work presents an optimization case of setup of membranes in series for gas separation. The feed stream of gas is a binary mixture of CO_2 and N_2, coming from the burning process of a generic hydrocarbon. The objective of the optimization is to find the best combination for arrangements of six membrane surfaces. A computational code written in FORTRAN ©, describing the species conservation equations for each membrane is used to obtain the concentrations and the permeated and retained stream molar flow rate. An optimization code using Genetic Algorithms is adapted and coupled to the membrane code. The objective function to be optimized is the profit, given by the difference between the income from the commercialization of the CO_2 permeate and the costs of compression of the permeate flow and of the membrane array. The feed stream condition is known, given for the chemical reaction between the generic hydrocarbon and air, resulting in 15.038% of CO_2 and 84.962% of N_2, at a molar flow rate of 5000 mol/s. Eight types of membrane materials where applied, the permeability and permselectivity of each one relative to CO_2/N_2 are known from the literature, the cost of each material was estimated in inverse proportion to its permeability. The code searches the combination of membrane surfaces materials allowing the variation of the surface area values from 0 to 9000 m^2 (step of 1000 m^2) and calculates the objective function which takes into account not only the volume but also the cost of compression of the CO_2 and N_2, penalizing the concentration of N_2 in the permeate stream. As a result is obtained an optimal combination of the six membranes in series which gives a molar flow rate of 161.1mol/s of CO_2 permeate at 79.32% and a net income of 24,405.30 €/year.*

***Keywords**: Membranes, Genetic Algorithms, Gas Separation, Carbon Sieve Membranes.*

1. INTRODUCTION

All burning processes release greenhouse effect gases into the atmosphere. Today, the political interest in the environmental issues turned the CO_2 a valuable commodity in the market. One way of reducing the release of CO_2 to the environment is by its retention in the site where it is generated. This retention may be done using carbon sieve membranes as gas separator, but it is necessary to optimize the process in order to turn it economically profitable. In this work a genetic algorithm (GA) is applied on order to find the most efficient array of membranes limited to six units and to eight possible membrane materials.

1.1. Carbon Dioxide Market

According to the United Nations Framework Convention on Climate Change, UNFCCC, the Kyoto Protocol agreed quotas on the maximum amount of greenhouse gases for developed and developing countries. In turn these countries set quotas on the emissions of local business installations and other organizations, generically termed 'operators'. The Nations have to manage this through their own national 'registries', which are required to be validated and monitored for compliance by the UNFCCC. Each operator has an allowance of credits. Each unit of credit gives the owner the right to emit one metric tonne of carbon dioxide or other equivalent greenhouse gas. Operators that have not used up their quotas can sell their unused allowances as carbon credits, while businesses that are about to exceed their quotas can buy the extra allowances as credits, privately or on the open market. As demand for energy grows over time, the total emissions must still stay within the cap, but it allows industry some flexibility and predictability in its planning to accommodate this.

By permitting allowances to be bought and sold, an operator can seek out the most cost-effective way of reducing its emissions, either by investing in cleaner technology and practices or by purchasing emissions from another operator who already has excess capacity.

For trading purposes, one allowance or Certified Emission Reductions, CER, is considered equivalent to one metric tonne of CO_2 emissions. These allowances can be sold privately or in the international market at the prevailing market price. These trade and settle internationally and hence permit allowances to be transferred between countries. Each international transfer is validated by the UNFCCC and transfers within the European Union are additionally validated by the European Commission.

Climate exchanges have been established to provide a spot market in allowances, as well as futures and options market to help discover a market price and maintain liquidity. Carbon prices are normally quoted in Euros per tonne of carbon dioxide or its equivalent. Other greenhouse gases can also be traded, but are quoted as standard multiples of carbon dioxide with respect to their global warming potential. These features reduce the quota's financial impact on business, while ensuring that the quotas are met at a national and international level.

There are two distinct types of Carbon Credits. Carbon Offset Credits COC's and Carbon Reduction Credits CRC's. Carbon Offset Credits consist of clean forms of energy production, wind, solar, hydro and biofuels. Carbon Reduction Credits consists of the collection and storage of Carbon from the atmosphere through reforestation, forestation, ocean and soil collection and storage efforts. Both approaches are recognized as effective ways to reduce the Global Carbon Emissions crises.

But selling carbon credits is not the only way of trade carbon dioxide; Pierantozzi, 2001, remarks that the Carbon dioxide is valuable as a chemical intermediate, a liquid refrigerant, and a source of inert gas. Numerous uses including food freezing, enhanced oil recovery, chemical manufacturing, refrigeration, and carbonation are possible uses for this gas.

The key point on CO_2 trading is the purity, many applications require a high purity level, e. g., for Enhanced Oil Recovery – EOR the CO_2 should be 94% pure or higher (in volume) for better miscibility condition on the oil reservoir, according to Iwasaki *et al.*, 2004.

2. FUNDAMENTALS

2.1. About the membrane separation process

The main parameters in a generic membrane are described in Fig. 1, where all the parameters named with the sub-index f are in reference to the feed stream, all with sub-index p are related to the permeated stream, and all with r are related to the retentate stream.

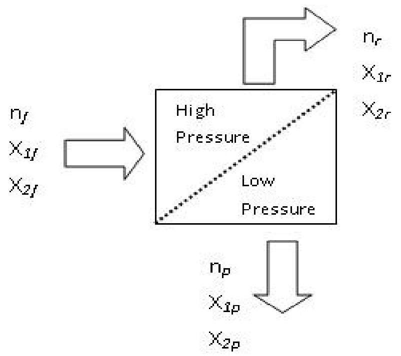

Fig. 1 – General scheme of membrane gas separation.

The molar flow rate n_i of a given species i across a membrane is expressed as

$$n_i = A\left(P/l\right)_i \Delta P_i \tag{1}$$

where A is the surface area (m^2), $(P/l)_i$ is the membrane permeability (mol µm kPa^{-1} m^{-2} s^{-1}) and ΔP_i is the pressure drop from the high pressure side (feed – retentate) to the low pressure side (permeate) for one component or species i (kPa).

Due to diffusion of different components or species in a relative low bulk average flow speed, diffusion is dominant and the entire path is submitted to the same concentration of a given species (Abdel-jawad *et al.*, 2007).

The pressure at the high level flow side, and therefore the species or component pressure drop ΔP_i (Tessendorf *et al.*, 1996) is:

$$\Delta P_i = x_r P_{high} - x_p P_{low} \tag{2}$$

and the conservation of molar flow rate and species are given by:

$$n_f = n_p + n_r \tag{3}$$

$$n_{if} = n_{ip} + n_{ir} \tag{4}$$

$$x_{1s} + x_{2s} = 1 \tag{5}$$

$$n_{is} = x_{is}.n_s \tag{6}$$

where *s* stands for each one of the flow streams. Combining the equations (2), (3) and (4), equations (7a) and (7b) are obtained,

$$x_{1p}n_p - A_i(\tfrac{P}{l})_1 P_{high} x_{1r} + A_i(\tfrac{P}{l})_1 P_{low} x_{1p} = 0 \tag{7a}$$

$$x_{2p}n_p - A_i(\tfrac{P}{l})_2 P_{high} x_{2r} + A_i(\tfrac{P}{l})_2 P_{low} x_{2p} = 0 \tag{7b}$$

for each component.

Applying molar flow rate conservation to each membrane is possible to obtain:

$$n_f x_{1f} - n_r x_{1r} - n_p x_{1p} = 0 \tag{8a}$$

$$n_f x_{2f} - n_r x_{2r} - n_p x_{2p} = 0 \tag{8b}$$

For resolving each membrane, it has to be mounted a system of six equations, equation (5), two times, one using the permeate stream and other using the retentate stream, equation (7a), equation (7b), equation (8a), equation (8b). This set of equations is a non linear system, this system particularly has a strong dependence on the initial guess. Thus a good choice of the initial guess reflects in a better accuracy of the result.

2.2. About the genetic algorithm

Brierley, 1998, describes the genetic algorithms as directed random search techniques used to look for parameters that provide a good solution to a problem. Essentially they are nothing more than educated guessing. The 'education' comes from knowing the suitability of previous candidate solutions and the 'guessing' comes from combining the fitter attempts in order to evolve an improved solution. Its working process comes from nature and the rule of survival of the fitter ones; this implies that these "most fitted" individuals are more likely to survive and have greater chance of passing their good features to the next generation. This is the process of evolution.

The GA used in this problem was developed by Brierley, 2008, is available on line and was modified for use in this particular case, coupling the code of membrane resolution to it.

The process involved in GA optimization problems is based on that of natural evolution and broadly works as follows for this case:

1. Randomly generate an initial population with surface area value and material characteristics;
2. Evaluate the suitability or 'fitness' of each solution by solving the membrane system and calculating the objective function;
3. Select two or more solutions based on fitness to form the next generation;
4. If the crossover probability is achieved, crossover the solutions at a random point on the string to produce two or more new solutions to increase the populations diversity;
5. If the mutation probability is achieved, mutate the new solutions, new and diverse individuals will appear, reducing the chance of achieving local minimum points;
6. Repeat the procedure until the stop criterion is achieved.

In the present work the GA randomly generates values of surface areas for each membrane considering the range between zero and 9000 m², with steps of 1000 m². The other randomly generated criterion is the membrane material, which is linked to permeability to CO_2, permselectivity and membrane cost per square meter, used by the GA to select the membrane material among eight possibilities.

The main parameters used in this algorithm are displayed in Tab. 1.

Table 1 - Parameters of the genetic algorithm.

Generations	20000
Population Size	40
Mutation Probability	1%
Crossover Probability	10%
Elite Individuals	3

The suitability criterion, or objective function, adopted on the genetic algorithm is given by economic profit function of the CO_2 permeate in the membranes:

$$\$_{CO2} = \$_{CO2\,market}^{x_{p1TOTAL}} \tag{9}$$

$$E_{profit} = \left(x_{1pTOTAL}\, n_{pTOTAL}\;\, m_{CO2}\, \$_{CO2}\, \Delta t\right) - \left\{x_{1pTOTAL}\, n_{pTOTAL}\;\, m_{CO2}\, \Delta h_{CO2}\, \$_{EE} - \left(1 - x_{1pTOTAL}\right) n_{pTOTAL}\;\, m_{N2}\, \Delta h_{N2}\, \$_{EE}\right\} - \left(\textstyle\sum_{i=1}^{6} A_i\, \$_{mat}\right) \tag{10}$$

where E_{profit} is the economic profit of the system. There are three main terms in the equation, in the first one the gains coming from the sale of the CO_2 are calculated considering that the market price concerns the CO_2 concentrate at 100%, thus adding a penalty to the cost related to the quantity of N_2 present in the permeate stream, and represented by $\$_{CO2}$, shown in equation (9), $x_{1pTOTAL}$ is the concentration of the total CO_2 permeated, n_{pTOTAL} is the total molar flow rate of the permeate, m_{CO2} is the molar mass of the CO_2, and Δt is the period of time in consideration. This first term is the only term that can assume a positive value. In the second term, the cost of compression of the permeated stream necessary to achieve a reasonable volume for transportation and storage was considered; in this term Δh_{CO2} is the enthalpy variation of CO_2 from 1 bar to 40 bar, $\$_{EE}$ is the cost of electric energy, m_{N2} is the molar mass of nitrogen, Δh_{N2} is the enthalpy variation of the N_2 from 1 bar to 40 bar. The last term consider the cost of each membrane itself, in this term A_i is the surface area of each membrane and $\$_{mat}$ is the estimated material cost for each membrane.

Note that the profit function takes into account all the main basic parameters necessary to carbon sequestration, but these are not the only costs involved in the process, costs of transport and storage where not considered.

3. CASE STUDY

The solving process applied in the solution of the proposed problem can be synthesized in the next steps:

1. Input of genetic algorithm basic parameters:
   1.1. Number of generations,
   1.2. Population size,
   1.3. String size,
   1.4. Number of contestants in every cross,
   1.5. Mutation probability,
   1.6. Crossover probability;
2. Random generation of the initial population, values of surface area and material will be randomly selected;
3. Repeat to the number of generations the calculation of the suitability of each individual in calcsuitability subroutine:
   3.1.1. Call the membrane subroutine, in which the membrane arrangement is simulated:
      3.1.1.1. Read the variables of CO2 market price and time,
      3.1.1.2. Read each material property (permeability, permselectivity, and cost) relating the material generated in 2 with the properties available for each material,
      3.1.1.3. Read the pre defined initial guesses for the IMSL library for each membrane,
      3.1.1.4. Read the stop criteria for the IMSL library (Relative Error and Maximum Iteration number),
      3.1.1.5. Read the feed stream of first membrane and the pressures of streams,
      3.1.1.6. Calculus of permeate and retentate molar flow flux,
      3.1.1.7. Retentate molar flow flux will be the feed stream in the next membrane,
      3.1.1.8. When all membranes where calculated is calculated the objective function,
      3.1.1.9. Return to calcsuitability subroutine;
   3.1.2. The objective function is the suitability value,
   3.1.3. Return to main program,
   3.2. Call breed subroutine in which the best parents are chosen:
      3.2.1. Select randomly the contestants for comparison,
      3.2.2. Choose the most suitable in the current generation,
      3.2.3. Apply crossover if a random number is less than the crossover probability,
      3.2.4. Apply mutation if a random number is less than the mutation probability,
      3.2.5. Choose three elite members randomly,
      3.2.6. End of subroutine breed;
4. Start over until stop criterion is achieved;
5. End program.

The chemical composition of the stream used for the simulation is obtained for the stoichiometric combustion of a generic fuel.

For sake of simplicity, it was considered that no NOx composite was formed in the reaction, and that all the water produced in the combustion was removed.

The feed stream of the membrane has the proportion of 15.038% for CO_2 and 84.962% for N_2, and is of 5000 mole per second.

The available materials for selection are in Tab. 2, with their respective characteristics.

Table 2 - Materials available for selection.

	Material	Permeability [mol µm m^{-2} Pa^{-1} s^{-1}]	Estimated Material Cost * [€/m²]	Permselectivity CO_2/N_2
1	Poly (amino imide) (Fuentes ET AL. – 1999)	1.1658×10^{-15}	1.0	20
2	BPDA - pP' ODA (Hayashi ET AL. – 1995)	1.1055E-13	2.5	30
3	BPDA / PPDA (Fuentes ET AL. 1999)	2.3800E-08	3.8	1.8
4	Phenolic Resin (Saufi ET AL. 2004)	5.4706E-14	1.5	6.4
5	Kapton (Suda ET AL. – 1997)	6.0970E-09	3.0	22.2
6	Phenol Formaldehyde (Wei ET AL. – 2002)	8.9998E-09	6.5	8.91
7	Polyimide (Okamoto ET AL. – 1999)	4.5560E-08	25.0	7
8	Polypirrolone (Kita ET AL. – 1997)	9.9495E-13	8.2	40

* The values presented in this column are estimated values and are not responsibility of any of the authors cited in the table.

The price of CO_2 used in this work is the average price of CO_2 as commodity between the months of January and April of 2009, according to the magazine Point of Carbon, its value is of 14.5 €/ton.

The price of the electrical energy was taken from the website of the "Companhia Estadual de Energia Elétrica – CEEE", the electricity supplier for Porto Alegre city, corresponding to April 2009 and converted to Euro using the average exchange rate between Real and Euro, provided by the Central Bank of Brazil, corresponding to the same month, giving the value of 0.04€/kWh.

4. RESULTS AND DISCUSSION

It is expected that the GA selects the optimal arrangement, once it was already tested in a previous work (Schmeda Lopez *et al.*, 2009). Note that the arrangement selected by the GA is composed by six membranes and the material selected is not the most permeable to CO_2. The arrangement described by the GA is shown in Figure 2 and Table 3.

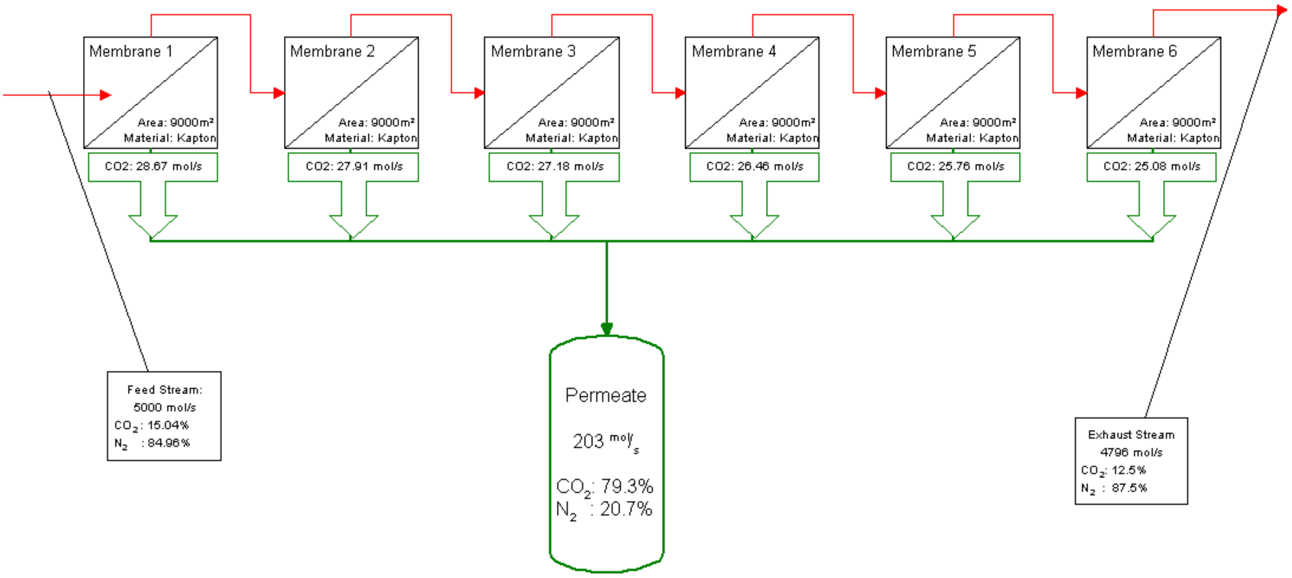

Figure 2 - Complete scheme of solution for the maximum value of the objective function.

Table 3 - Responses obtained by the GA.

Position	Surface Area	Material
1	9000 m²	Kapton
2	9000 m²	Kapton
3	9000 m²	Kapton
4	9000 m²	Kapton
5	9000 m²	Kapton
6	9000 m²	Kapton

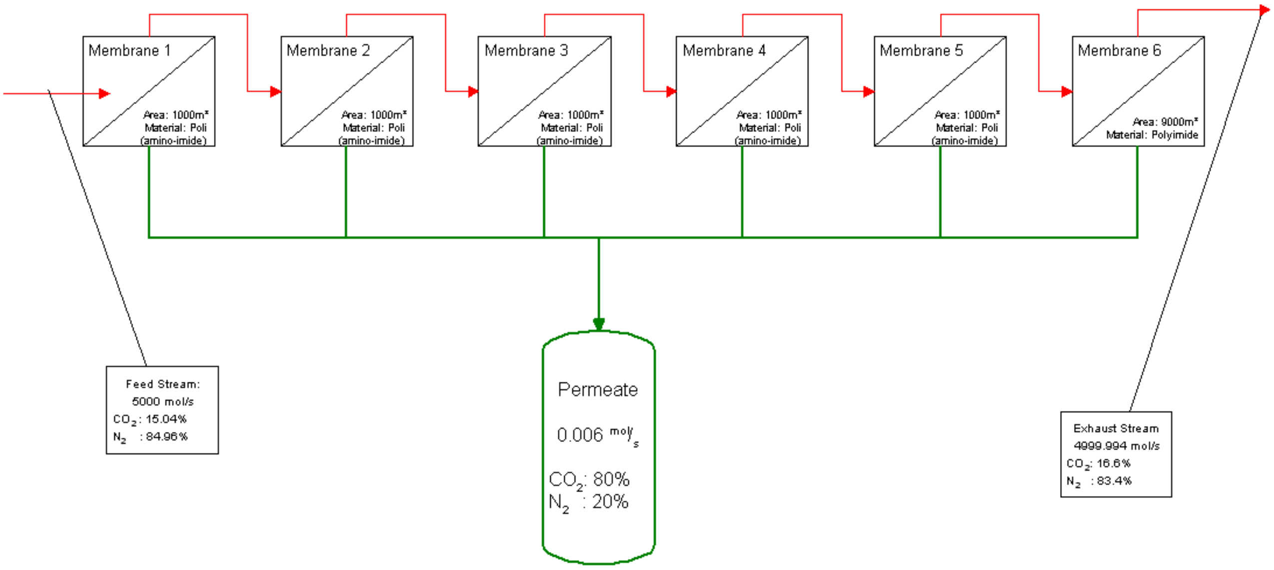

Figure 3 - Arrangement scheme for the maximal concentration.

The total permeate of CO_2 obtained from the best setup is 161.1 mol/s; the total N_2 permeated is 41.98 mol/s. The objective function (Eq. (9)), presented a value of 24,405.30 €/year of profit.

When an arrangement of five membranes is optimized the value of the objective function returns the value of 22,542.33 €/year of profit; however the concentration of the CO2 obtained is higher: 79.36%.

Another simulation was performed with a modification in the objective function in order to give the higher concentration, and the GA returned the value of 80% using the arrangement shown in Figure 3. In this case the economic value was -78,799.98 €/year and the molar flow rate of the permeate flow stream was of 0.006 mol/s.

In order to validate the result obtained using the GA, the exhaustive search method was employed. It took $(9x8)^6$ operations to generate the complete space of solution while it took only 4,800,000 operations using the GA. In this space of response the greater profit was achieved for the same membrane values obtained with the GA, thus validating the response and the application of the GA method.

5. CONCLUSIONS

The genetic algorithm could find an optimal solution for the proposed problem, allowing concluding that six membranes of 9000 m² of Kapton material is the optimal solution. The cost of the material plays a main role in the profit function; this was a strong argument in the suitability. The solution found by the GA concentrates the CO_2 to a point close to the maximum reachable at a higher molar flow rate.

The system of equations solved for each membrane is highly non linear and have a strong dependence on the initial guesses, which in the same way have a strong influence on the values presented in this work, different initial guesses can represent different final values for the same condition. A study of the best initial guesses should be done for every feed stream, once the selection of the appropriate initial guesses for all the possibilities is a difficulty of this part of the work. Nevertheless the results show that the algorithm is adequate to solve the set of equations.

The set of membranes proposed in this work do not produce high concentrated CO_2 stream at a viable cost, or molar rate. The cost of compression of the permeate stream is low in comparison to the cost of the membranes itself. The CO_2 permeated will not be useful as EOR agent, due to its concentration, but as well can be sold in the CRC market as avoided release, when consider the values adopted in this article. All the values concerning to the membrane materials where arbitrarily stipulated, as well as the profit function, which is stated as an exponential function of the CO_2 concentration. None of the tested membranes can reach the values recommended for EOR.

The objective function was proposed attending the need of an expression establishing a non linear correlation between the profit and the CO_2 concentration. Any profit function was found in the literature reviewed.

It is necessary to continue the study of the membranes arrangements for gas separation in power cycles. In next steps different arrangements of membranes must be studied, not only in series but also in parallel.

Another research issue will be the association of membranes with other gas separation technology, such as amine scrubbers, cryogenic separation, or pressure swing absorbers (PSA), in order to find a good combination of CO_2 removal with cost and technological feasibility.

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