

Thermodynamic Equipartition and Energy Efficient Membrane Networks*

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Abstract

This paper considers the relative merits of three optimization objective functions for the design of an energy efficient pervaporation membrane network for ethanol dehydration: the minimization of the standard deviation of the thermodynamic driving force, of the entropy generation, and of the power of separation. The resulting designs are compared with those of a standard numerical optimization minimizing the total exergy consumption of the compressors and heat exchangers. Results reveal that in terms of total exergy consumption, the equipartition of all three functions give results close to the reference case. However, in terms of the distribution of the membrane surface areas, the equipartition of the power of separation gives results closest to the reference case.

Keywords: *Thermodynamics, Equipartition, Pervaporation Membranes, Optimization.*

1. Introduction

In recent years, membrane separations have received increased attention by the chemical and process industries. In particular, pervaporation membrane networks have been successfully used to complement distillation columns for the separation of azeotropic mixtures (e.g. water-ethanol separation, MTBE production). In the pervaporation process, the membrane acts as a selective barrier between a liquid feed and a vapor permeate. These membranes have a high energy consumption relative to other membrane technologies. The present paper studies and compares equipartition based heuristics (Bedeaux et al., 1999) in the context of the design of energy efficient (serial) pervaporation networks.

According to Tondeur (1990), when a thermodynamic flux is a linear or a concave function of the driving force, the entropy generation rate of an energy optimal process has a uniform distribution along the space and/or time variables of the process. Kjelstrup et al. (1995) and Saour et al. (1996) illustrate that equipartition of driving forces (rather than equipartition of the entropy generation rate) should be aimed for when considering the optimal design of energy efficient separation processes, such as distillation. Both principles are derived from irreversible thermodynamics, which is built on the assumption of local equilibrium everywhere in the process. From a mathematical perspective, these heuristics boil down to minimizing the standard deviation of a given thermodynamic function (entropy generation rate or driving forces). Sorin and co-workers (2006, 2007) introduced the concept of power of separation in order to study separation processes. In the present context, it is natural to ask if equipartition of this function corresponds to processes with minimal total exergy consumption. Therefore, in the present paper, we compare the design of a serial pervaporation membrane network with minimal exergy consumption to serial pervaporation networks minimizing the standard

deviation of the following thermodynamic functions (respectively): mass transfer driving force, entropy generation, and power of separation. All these calculations are done for a fixed number of membrane units with a fixed total surface area.

2. Problem definition

The following two sections aim at describing the problem considered. In Section 2.1, the serial network of pervaporation membranes is briefly introduced. The notions of thermodynamic driving force and entropy production are then introduced. In Section 2.2, the optimization problems considered are defined.

2.1 Pervaporation Process for Ethanol Dehydration

Since a high temperature drop along a pervaporation membrane translates into an increasingly small permeate flow rate, a serial arrangement of membrane modules with reheating of the retentate is required (Fig. 1).

Figure 1 shows one example of the temperature profile of the retentate along the pervaporation network. As will be further demonstrated, the shape of this profile is the subject of our optimization. The model adopted to describe each of the membrane units is that of Bausa and Marquardt (2000). This model assumes one-dimensional flow in the membrane area coordinate (A). Note that " A " is linked to the spatial length coordinate of the membrane (z) through the relation $dA = w dz$, where " w " is a characteristic dimension of the membrane (Bausa and Marquardt, 2000).

Throughout this paper, the subscripts " i " and " j " represent (resp.) mixture components and the index of a membrane module. As a convention, the membrane modules are numbered from left to right (Fig. 1). Symbols f , p and r represent membrane feed, permeate and retentate streams (resp.), while P and T represent pressures and temperatures (resp.).

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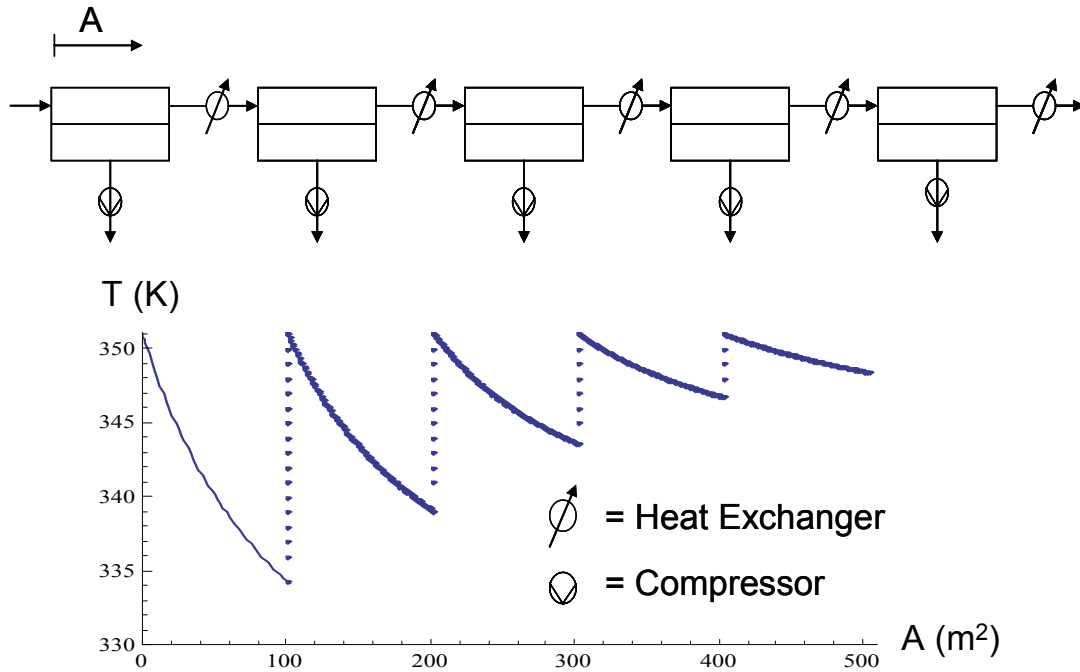


Figure 1. A serial pervaporation membrane network and its associated retentate side temperature (T) profile with respect to membrane area (A).

For the purpose of the present study, only the exergy losses caused by mass transfer within the membranes are considered. It is also assumed that the reheat between the stages is reversible, i.e. occurs without exergy losses. Consider a component “ i ” of the mixture and a cross-section at position “ A ” of membrane module “ j ”. For the diffusion based permeation process, the thermodynamic driving force ($X_{i,j}$) is defined as the difference between the ratios of the chemical potential and temperature at both sides of the membrane. According to the model assumptions, the temperatures of liquid and vapor are the same. Assuming ideal vapour phase, $X_{i,j}$ at the membrane cross-section is given by:

$$X_{i,j} = X_{i,j}(A)$$

$$= \frac{R_g T \ln(\gamma_i x_i) - R_g T \ln\left(\frac{P_p y_i}{P_i^{Sat}}\right) + V_i (P_{f,i} - P_{p,i})}{T} \quad (1)$$

where γ_i (resp. x_i) is the activity coefficient (resp. molar fraction) of component “ i ” in retentate side of the membrane, y_i is the molar fraction of component “ i ” in permeate side of the membrane, P_i^{Sat} is the saturated pressure of component “ i ” at temperature T , V_i is the liquid molar volume of component “ i ”, P_f (resp. P_p) is the feed (resp. permeate) side pressure and R_g is the universal gas constant.

The average driving force of component “ i ” over the whole membrane area of module “ j ” ($\bar{X}_{i,j}$) is given by:

$$\bar{X}_{i,j} = \frac{1}{A_j} \int_0^{A_j} X_{i,j} dA \quad (2)$$

where A_j indicates the membrane surface area of module “ j ”. The entropy generation of each module “ j ” (ΔS_j) is expressed as:

$$\Delta S_j = \sum_i \Delta S_{i,j} \quad (3)$$

$$\Delta S_{i,j} = \int_0^{A_j} J_i X_{i,j} dA \quad (4)$$

where $\Delta S_{i,j}$ represents the entropy generation of component “ i ” at module “ j ”, with associated component flux J_i per unit of membrane area. As defined by Ayotte-Sauvé et al. (2010), the power of separation of module “ j ” is given by:

$$P_{Sep,j} = R_g T_0 \left(\begin{array}{l} p_j \sum_i y_{p,i,j} \ln(y_{p,i,j}) + r_j \sum_i x_{r,i,j} \ln(x_{r,i,j}) \\ - f_j \sum_i x_{f,i,j} \ln(x_{f,i,j}) \end{array} \right) \quad (5)$$

Throughout the following numerical experiments, the vapour-liquid equilibrium and thermodynamic properties of the mixture are described by the NRTL model (Prausnitz et al., 1986).

2.2. Optimization Problems

Four optimization problems are considered. For each of these problems, a number of parameters are fixed: the number of membrane modules ($N = 5$); the total membrane area used in the network ($A_{Total} = 400.5 \text{ m}^2$) – the area of each module is allowed to vary but their sum is fixed; the feed flow rate to the membrane network ($F = 6 \text{ mol/s}$); the molar fraction of ethanol in the feed ($x_F = 0.84$); a target molar fraction of ethanol in the retentate output of the network ($x_R = 0.97$); the retentate-side pressure for each

membrane module (1 atm) and the efficiency of the compressors (85%).

It follows that there are 10 degrees of freedom for a serial pervaporation membrane network with parameters fixed as described above. To be more precise, fixing for each of the five modules the membrane surface area and the permeate-side pressure along with the aforementioned parameters determines the temperature profile of the retentate along the network and the properties of all input and output streams for all membrane units in the network.

The optimization problems are defined as follows.

Problem 1. Find the membrane surface area and the permeate-side pressure for each stage that minimize the total exergy consumption for compressors and heat exchangers, subject to the membrane model equations and the fixed parameters enumerated in the preceding paragraphs.

Problem 2. Find the membrane surface area and the permeate-side pressure for each stage that minimize the standard deviation of the driving force associated with water transfer subject to the same constraints as in problem 1.

Problem 3. Find the membrane surface area and the permeate-side pressure for each stage that minimize the standard deviation of the entropy generation subject to the same constraints as in problem 1.

Problem 4. Find the membrane surface area and the permeate-side pressure for each stage that minimize the standard deviation of the power of separation subject to the same constraints as in problem 1.

The objective functions for problems 2, 3 and 4 (resp.) are defined by:

$$\sigma(g) = \sqrt{\frac{1}{N} \sum_{j=1}^N (g_j - \text{mean}(g))^2} \quad (6)$$

where $\sigma(g)$ is the standard deviation of the function $g = \Delta S, \bar{X}_{\text{water}}$ or P_{sep} , N is the total number of membrane modules in the network, and $\text{mean}(g) = (1/N) \sum_{j=1}^N g_j$ is the mean value of the function g over the whole membrane network. Each of these problems is a non-linear programming problem (NLP) involving ordinary differential equations (i.e., the membrane model equations). These problems were treated using the general hill climbing method implemented in the Global Optimization package of Mathematica 6.0 (Wolfram, 2003).

The results of problem 1, which correspond to minimal total exergy consumption of the pervaporation network, will serve as a reference case to which the results of problems 2, 3 and 4 will be compared.

3. Numerical Results

The results of each problem yield the total exergy consumptions presented in Table 1 and Figure 2 shows the membrane surface area distribution within the pervaporation membrane network obtained for each problem.

As can be seen from Table 1, the equipartition of the entropy generation (problem 3) gives the closest results to the reference case (problem 1) in term of total exergy consumption, while the equipartition of the driving forces and of the power of separation give similar results. The Euclidean distance between the area distribution given in problem 2 (resp. 3 and 4) and the area distribution given in problem 1 is 109 (resp. 58 and 35). Recall that the Euclidean distance between two area distributions is obtained by summing the squares of differences in areas between each distribution and then taking the square root of this sum. This result can be interpreted by looking at Fig. 2 and noticing that by minimizing the standard deviation of power of separation (problem 4) one obtains a distribution of surface areas closest to that of the reference case (problem 1). Note that numerical optimization yielded the equipartition of each function for problems 2, 3 and 4. That is, the resulting solutions of these problems all have standard deviations smaller than 10^{-8} .

Since a pervaporation membrane module alone cannot admit increasingly large input flow rates while respecting a fixed retentate composition target, one has to consider membrane networks with modules in parallel (and in series). Equipartition for these networks is the subject of future work.

4. Discussion

There are many reasons why the power of separation merits special investigation as a design criterion for multi-step separation processes. As illustrated in the papers of Sorin et al. (2006, 2007) it characterizes both the quantity and quality of the production yield. An endoreversible model of a membrane separation process based on Finite Time Thermodynamics shows that a part of the exergy rate expended within a process is destroyed and the other part is transformed into power of separation. In the more recent work of Ayotte-Sauvé et al. (2010) it is shown rigorously that the power of separation is also geometrically related to the areas on the traditional McCabe-Thiele diagram for

Table 1. Total exergy consumption and area distributions for the results of each problem.

	Problem 1	Problem 2	Problem 3	Problem 4
Total exergy consumption (W)	14967	15699	15343	15689
Relative difference of exergy consumption with that of problem 1 (%)	0	4.9	2.5	4.8
Euclidean distance between area distribution and that of problem 1	0	109	58	35

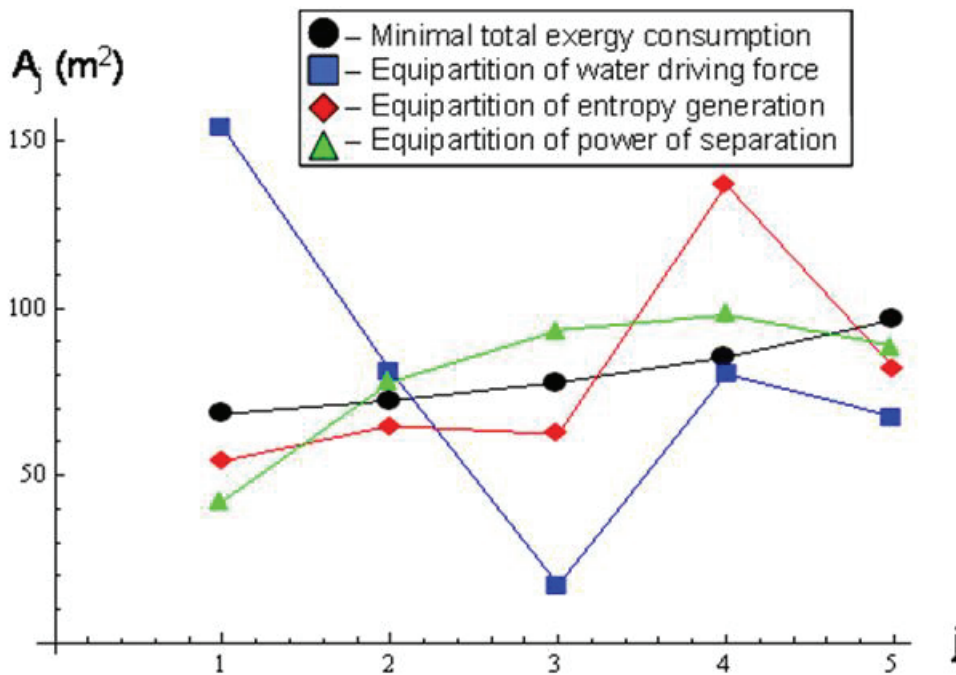


Figure 2. Distribution of membrane module surface areas for each problem.

binary distillation. Given that the diagram is applicable to membrane processes (Rautenbach, and Albrecht, 1989) the application of the power of separation to optimal structural design of membrane cascades is an important and challenging task. Finally as demonstrated by Ayotte-Sauvé et al. (2010), some mathematical properties of the power of separation (additivity, monotonic with exergy expenditure) allow the development of a new shortcut method for the energy efficient design of distillation/membrane hybrid processes. The method is both efficient and accurate when compared with the traditional optimization approach based on a superstructure.

5. Conclusions

The design strategies based on the equipartition of driving force for water permeation, the entropy generation due to the mass transfer, and the power of separation provide an approximation of the minimal exergy consumption close to the reference case. However, in terms of the optimal distribution of the surface areas among the membrane stages, the equipartition of the power of separation gives results closest to the reference case.

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Nomenclature

A	membrane surface area [m ²]
A_j	membrane surface area of module “j” [m ²]
A_{Total}	total membrane area [m ²]
f_j	feed flow rate in the module “j” [mol/s]
J_i	flux of component “i” [mol/s. m ²]
N	number of membrane module
p_j	Permeate flow rate in the module “j” [mol/s]

$P_{f,i}$	partial pressure of component “i” at the feed side [Pa]
p_i^{Sat}	saturated pressure of component “i” [Pa]
$P_{p,i}$	partial pressure of component “i” at the permeate side [Pa]
P_p	permeate pressure [Pa]
$P_{Sep,j}$	power separation of module “j” [W]
r_j	retentate flow rate in the module “j” [mol/s]
R_g	universal gas constant [N.m/mol.K]
T	temperature [K]
T_0	ambient temperature [K]
V_i	molar volume of component “i” [m ³ /mol]
x_i	molar fraction of component “i” in the retentate side
$X_{i,j}$	thermodynamic driving force of component “i” at module “j” [N.m/mol.k]
$\bar{X}_{i,j}$	average thermodynamic driving force of component “i” at module “j” [N.m/mol.k]
y_i	molar fraction of component “i” at the permeate side
γ_i	activity coefficient of component “i” at the retentate side
σ	standard deviation of the function

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