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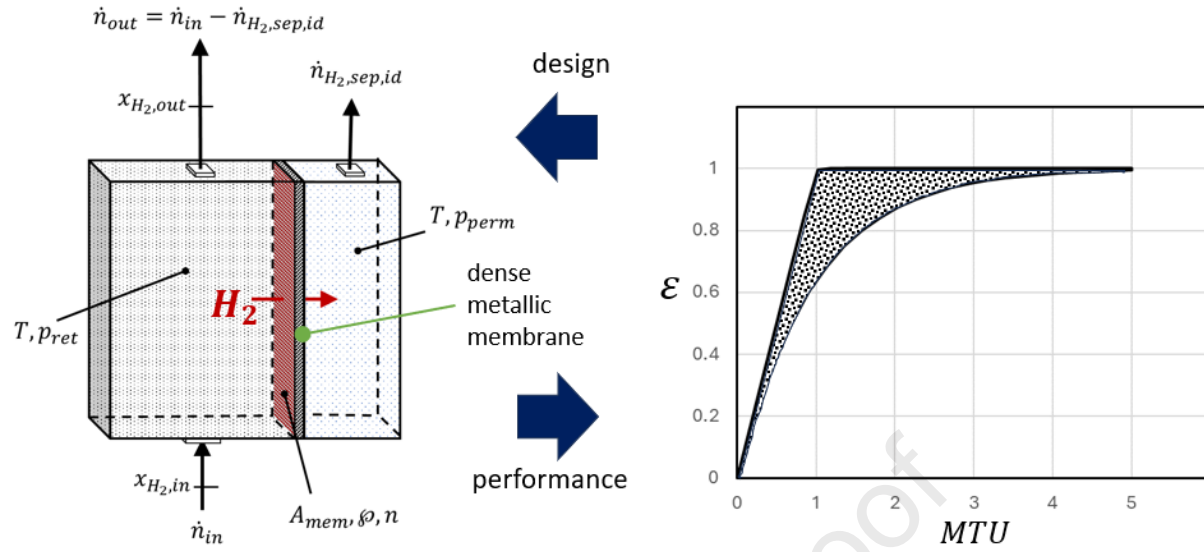
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Effectiveness-MTU modeling approach for hydrogen separation with dense metallic membranes

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Abstract

As hydrogen gains interest as energy vector, so it happens for its purification techniques. In particular, dense metallic membranes are a promising technology for many high-temperature applications. Modeling of hydrogen permeation is a fundamental support to their commercial development. Permeation through metallic membranes, in particular Pd-alloys, is regulated by a generalized form of the Richardson's equation, where driving force for permeation is due to the difference in hydrogen partial pressure at the membrane surfaces. From the flux expression it is possible to develop a model for a mass exchanger, in analogy with the mathematical description of heat exchangers. For the latter, a well-known method, called $\varepsilon - NTU$, is used to simplify heat transfer problem. The same approach applies to mass exchangers, where the $\varepsilon - MTU$ method had already been transferred to reverse osmosis. In this article, $\varepsilon - MTU$ method is applied to ideal mass exchangers for hydrogen separation. Effectiveness showed to be influenced by inlet hydrogen fraction, exponent n of partial pressures and pressure ratio. Moreover, a procedure to include concentration polarization losses is presented. A rule-of-thumb approach is proposed for an estimation of hydrogen recovery, validated to reproduced an experimental result with less than 7% relative error. $\varepsilon - MTU$ shows to be a fundamental support to membrane module design.

Keywords: modeling; membranes; hydrogen separation; mass exchanger; effectiveness-MTU.

1. Introduction

With the increasing attention that hydrogen is gaining today, due to its role as energy carrier in a low-carbon energy transition, also its purification techniques are receiving interest. Among the possibilities for hydrogen purification and separation, recently reviewed in literature [1]–[3], membrane separation, in particular using dense metallic membranes, is a particularly interesting option due to high purity, low costs and broad versatility. Hydrogen's ability to selectively permeate through certain metals is a physical phenomenon known from more than 150 years: it was firstly observed in 1863 through steel, platinum and iron [4], and later confirmed by observations of a high rate diffusion through heated palladium in experimental tests by Thomas Graham in 1866 [5], [6]. Already in 1914 it was claimed that, among metals, palladium had received the closest attention [7]; this is still true nowadays, where it represents the most studied material for the production of dense metallic membranes [8]. Palladium typically is not in pure form, but in several alloys (mainly silver, copper or gold), enhancing the stability in different environments, increasing the resistance to embrittlement [9] and reducing costs.

Pd-based membranes have nowadays achieved commercial level [8], due to their high flux and very high perm-selectivity towards hydrogen [10]. Among the commercially available solutions, reviewed in [8], tubular ceramic-supported thin-layer (<5 μm) Pd-Ag membranes have been developed by Tecnalia research centre and Eindhoven University of Technology [11] in the last decade, and specifically optimized for their integration in membrane reactors [12], [13]. These membranes are also equipped with a very thin (about 1 μm) ceramic coating layer on the top of the selective dense metallic layer to optimize their usage in fluidized bed reactors, in order to resist attrition of the floating particles [14], [15]. These membranes are currently scaled-up within the MACBETH project [16] in fluidized bed membrane reactors for steam reforming of biogas, where they shows potential techno-economic advantages at small scale [17], [18] compared to the conventional reforming route. The application of these membranes have been also recently investigated in a mass exchanger module (i.e. without chemical reactions), to separate hydrogen from syngas [19] and to recover hydrogen from the propane dehydrogenation reaction products [20], [21].

Mass exchangers based on Pd membranes are modules where, in a gas separation process, hydrogen is selectively removed from a gaseous mixture. The module is substantially a vessel containing the membranes, where the gaseous stream is progressively depleted from its hydrogen content. At least a mono-dimensional description of the problem is therefore necessary, since as hydrogen permeates its molar fraction, and then its partial pressure, decreases, lowering the driving force for permeation. Under some ideal assumptions, mass exchangers can be described in analogy with heat exchangers. In the latter, a heat transfer occurs between a hot stream and a cold stream, where the driving force for the heat exchange is the temperature difference. The temperature of the hot stream is progressively reduced, lowering the driving force for heat transfer, as it happens in the mass exchanger for hydrogen separation. In particular, when using dense metallic membranes, permeate side is typically pure hydrogen at atmospheric or vacuum pressure, constant along the membrane length. In this situation, analogy with heat exchangers is specific to the case of an evaporator, where the hot stream exchanges heat with a cold sink at constant temperature.

To design heat exchangers, a powerful technique was developed by Kays and London in a book, first edited in 1955 [22], named $\varepsilon - NTU$. Heat exchanger effectiveness ε , given by the ratio between the heat exchanged and the maximum amount of heat that could be ideally transferred, is expressed as a function of the Number of Thermal Units (NTU) and the ratio between the heat capacities of the two fluids. This method, that is substantially a dimensionless form of the equations that governs the heat exchange, is largely used to predict the performance of an existing heat exchanger (once its area is known) or to size a new one heat exchanger (once the effectiveness is selected). $\varepsilon - NTU$ relations are typically expressed analytically or in charts, that can be used especially when there are less claims on accuracy and there is more interest to have a whole picture of the exchanger behavior.

The same approach can be applied also to mass exchangers. In literature, it has already been successfully applied for membrane separation in pressure retarded osmosis [23] and in reverse osmosis [24] by the same authors. In these articles, the method is called, in analogy with heat exchangers, $\varepsilon - MTU$, where ε is the effectiveness and MTU are the Mass Transfer Units, that is an ad-hoc defined dimensionless number specific to the membrane process investigated. The influence of MTU and other dimensionless parameters was investigated and drawn in different charts. Linearized expressions were used for osmotic pressure in order to be able to find a closed-form of analytical solution, while including nonlinearities and concentration polarization by numerically solving the problem. In case of [24], also a comparison with experimental data resulted in an average error below 7.8%.

Beyond being used for reverse osmosis, to the knowledge of the authors the same concept have not been yet applied to other separation mechanisms. In this article, the $\varepsilon - MTU$ methodology is applied to a mass exchangers to separate pure hydrogen from a gaseous mixture, following the permeation law of dense metallic membranes, which, as stated, represents one of the most interesting solutions for hydrogen purification.

2. Hydrogen flux through dense metallic membranes

2.1 Generalities on hydrogen flux expression

The permeation mechanism of hydrogen through dense metallic membranes is the solution-diffusion, which is well-known. It was suggested firstly in 1894 by W. Ramsay [25] that, during its passage through Pd, hydrogen is in atomic form, and it was further verified in 1901 by A. Winkelmann, which showed that Ramsey hypothesis could explained why the diffusion rate (today named “flux”) of hydrogen varied as the squared root of the hydrogen gas pressure [26]; It is although reported he claimed the following year that the exponent 0.55 was a better fitting term than 0.5 [4]. Moreover, the fact that the diffusion of hydrogen trough metals should be preceded by a chemical dissociative adsorption and consecutive solution of atoms into the metal can be already found in the work of C. J. Smithells and C. E. Ransley in 1935 [27]. Dissociative chemisorption of hydrogen molecules on metallic surface followed by atoms diffusion through the lattice, and opposite recombination on the other side, is as the solution-diffusion mechanism is currently described [8].

Regarding the mathematical description of the permeation, in 1904, O. W. Richardson, J. Nicol and T. Parnell derived the flux \dot{J}_{H_2} equation from kinetic theory and thermodynamics [28], which is known since then as Richardson’s equation:

$$\dot{J}_{H_2} = \frac{k}{d} \cdot e^{-\frac{b}{T}} \cdot \sqrt{p_{ret}} \cdot \sqrt{T} \quad \left[\frac{mol}{s \cdot m^2} \right] \quad (1)$$

where p_{ret} is the gas pressure, T is the temperature, d the thickness of the metal and k and b specific constants for the gas-metal system; it was tested for nickel, iron, platinum, palladium and copper. Whether vacuum pressure is applied at the permeate side, the pressure dependance should be replaced by $\sqrt{p_{ret} - p_{perm}}$. Moreover, it turned out quite soon that the term \sqrt{T} was negligible and could be omitted for practical purposes. Equation (1) showed good agreement with temperature and thickness dependance – the latter until diffusion of hydrogen through the metal is the rate limiting step. However, the dependance on pressure had been already considered less satisfactory since the formulation of the equation [27]. As mentioned, the squared root dependance is related to the fact that hydrogen is dissolved in the metal in atomic form: the proportionality of solubility of diatomic gaseous molecules in metals to the squared root of the gas pressure has been verified by A. Sieverts in 1929 [29].

Deviations of the flux from square root dependance have been always observed at low pressures for all metals, which was attributed to an incompletely adsorbed layer at the metal surface [4]. R. M. Barrer, in 1940, gave an explanation of such deviations at low pressure claiming that if the adsorption and dissolution reactions from one side, or recombination and desorption on the other side, have a velocity lower than the diffusion though the metal, the equilibrium concentrations are prevented [30]. Beyond low-pressure deviations that happen for all metals, specifically for palladium a general flux dependance of the form $\dot{J}_{H_2} \propto p^n$, where n is bounded between 0.5 and 1, was already suggested in 1935 [27] also at higher pressures. A more recent discussion about the exponent is reported in the introduction of [31]. Still recently publications tried to explain the meaning of the pressure exponent. S. Hara et al., in 2009, claimed that the n exponent has no physical meaning, and therefore they tried to reproduce experiments, fitted with different n values using the square root ($n=0.5$) defining a permeability which was not constant, but a function of the pressure applied. In this sense, they generalized Sieverts’ law and permeability definition to explain the problem with a physical meaning, but limited to flat uniform membranes [32]. In the work of T. F. Fuerst et al in 2020, the authors reported that a $n=0.5$ indicates a diffusion-limited regime (where diffusion though the metal is the rate limiting step) and $n=1$ is the surface-limited regime (where dissociative-adsorption or associative-desorption are rate limiting steps). Between these extremes, there is the transition region, where the value of n can give an indication of the transition regime [33]. However, in 2010, T. B. Flanagan and D. Wang

tried to explain the meaning of n based on nonidealities of both solubility and diffusivity coefficients, meaning that Sieverts' law is not followed and Fick's law has a concentration-dependent diffusivity. They concluded that, if this dependency is not verified, it cannot be concluded that in case of $n > 0.5$ other steps other than diffusion are the slow steps [34]. M. Vadrucci *et al.* reported in 2013 that there are several reasons that can affect n : for example, in supported membranes, where a thin metal layer is deposited over a porous support, the mass transfer through the porous medium can be included in the permeation equation, leading to deviation of n from 0.5. In this way, the thin selective layer and the support can be modelled together and then do not require two different models, although the permeation mechanisms are quite different [35]. In the same year, A. Caravella *et al.* reported that, until a certain entity, the same equation applies where hydrogen is in mixture, and therefore also concentration polarization losses can be included in the value of n [36].

In conclusion, there is still no uniform interpretation of the meaning of n . What is worth mentioning is that the general dependence of the hydrogen flux from the partial pressure to the power of n , where n value is between 0.5 and 1, is valid in many different situations involving dense metallic membranes, regardless of the physical reason. In other words, the literature shows that, whether there is a variety of Pd-based membranes compositions and geometries, in most cases the flux can be represented by a generalized form of Richardson's equation, in which the pressure exponent n has to be experimentally determined for the specific application [31].

2.2 Definitions of flux and perm-selectivity

Hydrogen flux through dense metallic membranes can be described by the generalized form of Richardson's equation:

$$j_{H_2} = \frac{d\dot{n}_{H_2,sep}}{dA} = \wp \cdot (p_{ret,H_2,m}^n - p_{perm,H_2,m}^n) = \wp^0 \cdot e^{-\frac{E_a}{R \cdot T}} \cdot (p_{ret,H_2,m}^n - p_{perm,H_2,m}^n) \quad (2)$$

where $p_{ret,H_2,m}$ and $p_{perm,H_2,m}$ are the partial pressures of hydrogen gas at the membrane surface of the retentate side and of the permeate side respectively, that can be typically be related to the pressure and hydrogen molar fraction through the relation $p_{H_2} = p \cdot x_{H_2}$, strictly valid only for ideal mixture of ideal gases, but approximately valid in all the ranges of interest for metallic membranes [37]. \wp is the membrane permeance, that typically follows an Arrhenius-type dependence on temperature. Variables for flux definition are represented in Figure 1.

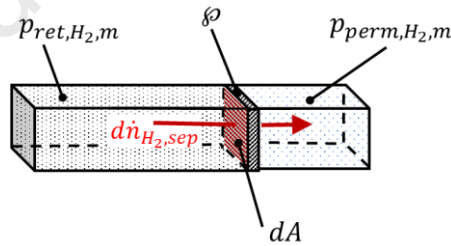


Figure 1: definition and representation of hydrogen flux

The total flow rate of hydrogen separated on a finite membrane area can then be found by integrating the flux over the membrane area, as in equation (3). Hydrogen flux through a dense metallic membrane is then typically fully described by the knowledge of three parameters (\wp^0 , E_a and n), and from the knowledge of the local thermodynamic conditions (pressure, temperature) and molar fractions along the membrane area:

$$\dot{n}_{H_2,sep} = \int_{A_{mem}} j_{H_2} \cdot dA \quad \left[\frac{mol}{s} \right] \quad (3)$$

Another important parameter in membranes characterization is the *perm-selectivity*. It is, in general, a function of temperature and pressures, and it is defined as the ratio between hydrogen and nitrogen fluxes, both measured as pure gas streams.

$$S_{H_2/N_2} = \left. \frac{j_{H_2}}{j_{N_2}} \right|_{T, p_{ret}, p_{perm}} \quad (4)$$

Values of selectivity have been reported recently in the range 20,000 - 143,000 at 3 bar and 400 °C [14], [38], corresponding to an hydrogen purity of 99.9950% - 99.9993%.

3. Mass exchanger mathematical model

3.1 Model assumptions

In the mass exchanger model, several idealities are assumed, regarding both the thermodynamic properties of the gaseous mixture and the membrane module configuration:

- the flow in the module has a plug-flow representation in steady-state, and it is isotherm and isobaric;
- the permeate side is maintained at a constant pressure and filled with only pure hydrogen (i.e. infinite perm-selectivity and no sweep gas used). Therefore, the second term of the driving force $p_{perm,H_2,m}$ is in all points equal to the pressure p_{perm} ;
- There are no concentration polarization losses;
- There is no competitive adsorption of chemical components (especially CO , but also CO_2 , C_2H_6 and C_3H_8 and Sulphur compounds), which typically leads to a decrease in hydrogen flux;
- Permeance pre-exponential factor \wp^0 , apparent activation energy E_a and partial pressure exponent n are constant.

Under these assumptions, the properties of a separator can generally be described in terms of a total inlet flow rate, which has a hydrogen molar fraction $x_{H_2,in}$. In other words, it can be assumed that, beyond hydrogen, there is an overall non-permeating component. All variables of interest, in this ideal case, are:

- the hydrogen molar fraction in the feed $x_{H_2,in}$
- the total feed inlet molar flow rate \dot{n}_{in}
- the operating temperature T and pressure p_{ret}
- the permeate-side pressure p_{perm}
- the membrane area A_{mem}
- membrane parameters \wp^0 , E_a and n

Under ideal conditions, hydrogen partial pressure at the membrane surface $p_{ret,H_2,m}$ is the same hydrogen partial pressure in the bulk of the phase p_{ret,H_2} . To underline that this is the ideal situation, the subscript *id* is added to the flux $\dot{J}_{H_2,id}$ and to the separated hydrogen flow rate $\dot{n}_{H_2,sep,id}$. Starting from equations (2) and (3):

$$\dot{n}_{H_2,sep,id} = \int_{A_{mem}} \dot{J}_{H_2,id} \cdot dA = \int_{A_{mem}} \wp \cdot (p_{ret,H_2}^n - p_{perm}^n) \cdot dA \quad (5)$$

Corresponding mass exchanger is represented in Figure 2, together with a qualitative representation of the hydrogen partial pressure reduction on the retentate side, due to its depletion, along the membrane. This trend corresponds to a reduction of the driving force, and thus of the hydrogen flux, as more hydrogen is separated.

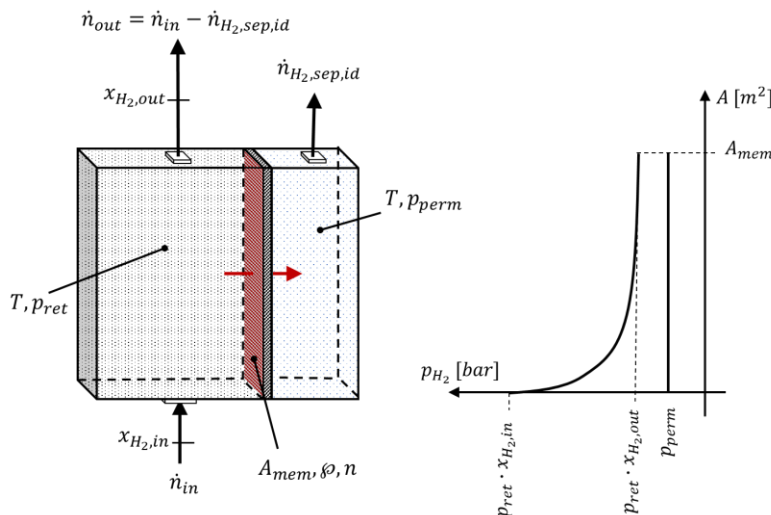


Figure 2: representation of mass exchanger module under ideal assumptions. On the right, qualitative representation of the

hydrogen partial pressures trends

3.2 Analytical model

The mathematical equations to calculate hydrogen separated are two first-order ODEs, one to compute the material balance of the retentate side and the other the one of the permeate side. For the retentate side, the ODEs Cauchy's problem is:

$$\begin{cases} \frac{d\dot{n}_{H_2,ret,id}}{dA} = -j_{H_2,id} \\ \dot{n}_{H_2,ret,id}^0 = \dot{n}_{in} \cdot x_{H_2,in} \end{cases} \quad (6)$$

On the permeate side, the ODE system is reported in equations system (7), and it is already solved once system (6) is solved.

$$\begin{cases} \frac{d\dot{n}_{H_2,sep,id}}{dA} = j_{H_2,id} = -\frac{d\dot{n}_{H_2,ret,id}}{dA} \\ \dot{n}_{H_2,sep,id}^0 = 0 \end{cases} \quad (7)$$

ODE of system (6), using the flux expression as in equation (5), can be expressed as:

$$\frac{d\dot{n}_{H_2,ret,id}}{dA} = -\wp \cdot \left((p_{ret} \cdot x_{H_2})^n - p_{perm}^n \right) = -\wp \cdot \left(p_{ret}^n \cdot \left(\frac{\dot{n}_{H_2,ret}}{\dot{n}_{ret}} \right)^n - p_{perm}^n \right) \quad (8)$$

where the denominator of hydrogen molar fraction $\dot{n}_{H_2,ret}$ is given by the sum of the local flow rate of hydrogen $\dot{n}_{H_2,ret}$ and the flow rate of all non-permeating compounds, which can be computed as $\dot{n}_{in} \cdot (1 - x_{H_2,in})$. Therefore, the final form of the ODE is:

$$\frac{d\dot{n}_{H_2,ret,id}}{dA} = -\wp \cdot \left(p_{ret}^n \cdot \left(\frac{\dot{n}_{H_2,ret,id}}{\dot{n}_{H_2,ret,id} + \dot{n}_{in} \cdot (1 - x_{H_2,in})} \right)^n - p_{perm}^n \right) \quad (9)$$

in which $\dot{n}_{H_2,ret}$ and $d\dot{n}_{H_2,ret}$ are functions of the membrane area, while all other terms are constants. Therefore, naming z the function to be found, only definite for positive values, and a, b, c, d the various positive constants, the ODE is in the form:

$$z' = -a \cdot \left(\left(\frac{z}{z+b} \right)^c - d \right) \quad (10)$$

which to the knowledge of the authors has no known analytical solution. The same can be expressed to find the variable $\dot{n}_{H_2,sep,id}$ by using the same expression (10) with a plus sign instead of a minus in front of the right term, and considering zero as initial value. These Cauchy's problems are typically solved with numerical methods. Although simple to achieve, the lack of an analytical solution makes it difficult to have an overview of the solutions behaviour, which calls for a method as the one presented in this work.

3.3 Recovery factor and effectiveness

The *recovery factor*, defined in equation (11), represents the ratio of hydrogen permeated through the membrane compared to the hydrogen fed to the separator.

$$RF = \frac{\dot{n}_{H_2,sep}}{\dot{n}_{H_2,in}} = \frac{\dot{n}_{H_2,sep}}{\dot{n}_{in} \cdot x_{H_2,in}} \quad (11)$$

Its value goes from zero, if no hydrogen is separated, up to a maximum value depending on the inlet and the permeate-side conditions. The expression for its maximum value (RF_{max}) can be found considering that

it is possible to separate hydrogen until its partial pressure on the retentate side equals the pressure on permeate side. This situation, where driving force reaches zero, corresponds to a hydrogen molar fraction ($x_{H_2,min}$) equal to the ratio between permeate and retentate side pressures:

$$(p_{ret} \cdot x_{H_2,min})^n - p_{perm}^n = 0 \quad \rightarrow \quad x_{H_2,min} = \frac{p_{perm}}{p_{ret}} \quad (12)$$

When this happens, from the global material balance of the mass exchanger it can be found the maximum hydrogen that can be separated, $\dot{n}_{H_2,sep,max}$:

$$\dot{n}_{H_2,sep,max} = \dot{n}_{in} \cdot \frac{p_{ret} \cdot x_{H_2,in} - p_{perm}}{p_{ret} - p_{perm}} \quad (13)$$

and, accordingly, the maximum recovery factor, RF_{max} :

$$RF_{max} = \frac{\dot{n}_{H_2,sep,max}}{\dot{n}_{H_2,in}} = \frac{1 - \frac{p_{perm}}{p_{ret} \cdot x_{H_2,in}}}{1 - \frac{p_{perm}}{p_{ret}}} \quad (14)$$

RF_{max} results a function of $x_{H_2,in}$, p_{ret} and p_{perm} only and can be plotted as a function of the variable p_{perm}/p_{ret} , using $x_{H_2,in}$ as a parameter. Results are displayed in Figure 3 and help to easily determine, for each value of the inlet hydrogen fraction, which is the minimum value of the ratio between permeate and retentate pressure to be adopted to guarantee a certain maximum recovery factor.

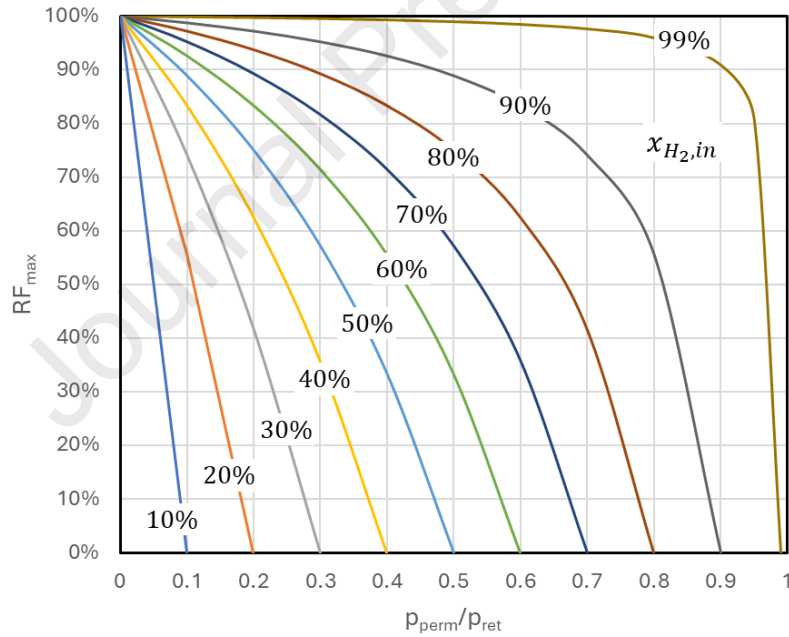


Figure 3: maximum recovery factor as a function of the ratio between permeate and retentate pressures, for different values of the inlet hydrogen molar fraction

The ratio between recovery factor and the maximum recovery factor is called *effectiveness* (ε). By definition, this is also the ratio between hydrogen separated and the maximum amount that can be separated.

$$\varepsilon = \frac{RF}{RF_{max}} = \frac{\dot{n}_{H_2,sep}}{\dot{n}_{H_2,sep,max}} \quad (15)$$

Whether hydrogen separated, at numerator of equation (11) and (15), is separated under ideal conditions listed above, it will be referred to as ideal recovery factor RF_{id} and ideal effectiveness ε_{id} .

4. ε -MTU method

As stated in the introduction, the approach is similar to the $\varepsilon - NTU$ method of heat exchangers, and in general it is a dimensionless form of the equation where the solution is determined by the value of a set of dimensionless parameters. Analytically, hydrogen permeated over a finite membrane area A_{mem} can be found by integrating equation (8) and referring to the permeate stream instead of to the retentate side:

$$\dot{n}_{H_2,sep,id} = \int_{A_{mem}} \wp \cdot \left((p_{ret} \cdot x_{H_2})^n - p_{perm}^n \right) \cdot dA = \wp \cdot A_{mem} \cdot \overline{DF}_{id} \quad (16)$$

where it has been defined an average ideal driving force \overline{DF}_{id} over the membrane length as in equation (17), where in the integral only hydrogen fraction x_{H_2} is a function of membrane area, while other parameters are constant.

$$\overline{DF}_{id} = \frac{1}{A_{mem}} \cdot \int_{A_{mem}} \left((p_{ret} \cdot x_{H_2})^n - p_{perm}^n \right) \cdot dA \quad (17)$$

To obtain a dimensionless form, both terms are divided for the maximum flow rate of hydrogen that can be separated (see equation (13)) and the right term is both multiplied and divided by the driving force value at the module inlet DF_{in} . In mathematical terms:

$$\frac{\dot{n}_{H_2,sep,id}}{\dot{n}_{H_2,sep,max}} = \frac{DF_{in}}{\dot{n}_{H_2,sep,max}} \cdot \frac{\wp \cdot A_{mem} \cdot \overline{DF}_{id}}{DF_{in}} \rightarrow \varepsilon_{id} = MTU \cdot \frac{\overline{DF}_{id}}{DF_{in}} \quad (18)$$

Equation (18) relates the ideal effectiveness to the MTU, that is defined as the ratio of the hydrogen that would be separated, in the same membrane area, maintaining the constant driving force as at its inlet value over the maximum hydrogen that can be separated. MTU definition is in equation (19):

$$MTU = \frac{\wp \cdot A_{mem} \cdot DF_{in}}{\dot{n}_{H_2,sep,max}} = \frac{\wp \cdot A_{mem}}{\dot{n}_{in}} \cdot \frac{(p_{ret} \cdot x_{H_2,in})^n - p_{perm}^n}{p_{ret} \cdot x_{H_2,in} - p_{perm}} \quad (19)$$

The numerator of MTU is not a physical value, and therefore it can increase to infinite as membrane area grows, while the denominator is a finite real value. Therefore, MTU can assume all values between 0 and infinite. Equation (18) cannot be solved analytically, but it is interesting to understand its numerical solutions for several values of the variables of interest. A sensitivity analysis has been performed, where variables have been freely varied in the ranges reported in Table 1.

Table 1: ranges of the variables of interest for the general sensitivity analysis

| Variable | Units | Set/Free/Calculated | Values/Range |
|----------------|--|---------------------|-----------------|
| $x_{H_2,in}$ | - | freely varied | (0; 1] |
| p_{ret} | bar | freely varied | (1; $+\infty$) |
| p_{perm} | bar | freely varied | [0; 1] |
| \dot{n}_{in} | mol/s | freely varied | (0; $+\infty$) |
| A_{mem} | m ² | freely varied | (0; $+\infty$) |
| \wp | mol/(m ² · s · bar ⁿ) | freely varied | (0; $+\infty$) |
| n | - | freely varied | [0.5; 1] |
| MTU | - | calculated | [0; 5] |

Numerical solutions of equation (18) are displayed in Figure 4. The upper limit represents pure hydrogen (i.e. $x_{H_2,in} = 1$) where driving force is always constant. In that case, when MTU is 1, all hydrogen that can be removed has been removed, and therefore no more recovery can be achieved. The lower limit is the effectiveness obtained when inlet driving force tends to zero, both because of a very low hydrogen molar fraction or because of a low pressure.

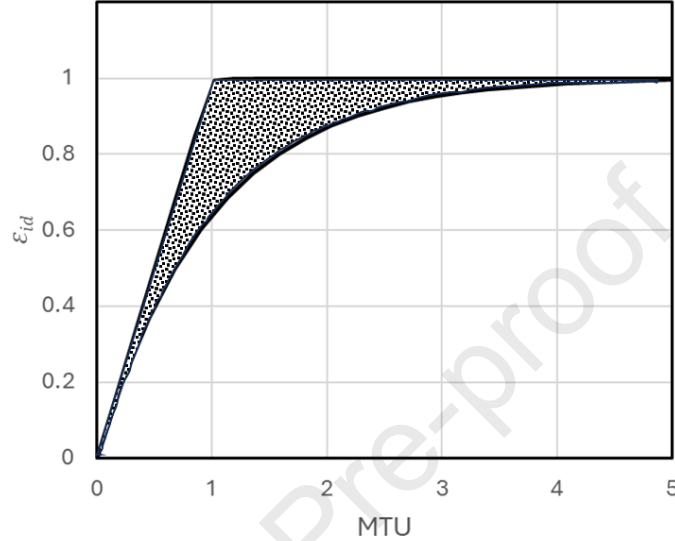


Figure 4: graphical plot of solutions of equation (18), where its variables change according to Table 1

Upper and lower limits are thus represented by the following mathematical expressions:

$$\varepsilon_{id}^{\max} = \begin{cases} MTU & \text{if } MTU < 1 \\ 1 & \text{if } MTU \geq 1 \end{cases} \quad (20)$$

$$\varepsilon_{id}^{\min} = 1 - e^{-MTU} \quad (21)$$

where in the mathematical expression for the minimum value it can be recognized the same relation that exists between ε and NTU for a heat exchangers, where the temperature of one of the two streams is uniform (as for example in a evaporator).

The region of solutions represented in Figure 4 already allows some preliminary conclusions. First, as it happens in $\varepsilon - NTU$ method for heat exchangers, it can be observed that for $MTU \ll 1$, all solutions collapse of the line $\varepsilon_{id} = MTU$. Mathematically, this happens because when MTU tends to zero means that the product $\varphi \cdot A_{mem} \cdot DF_{in}$ tends to zero, meaning that one or more factors are very small. This means a negligible hydrogen recovery, and therefore the average driving force is equal to the inlet driving force, leading to their unitary ratio in equation (18). The same holds when working with pure hydrogen. On the other side of the chart, another conclusion is that when $MTU > 5$, hydrogen is in all case fully recovered and there are no benefits from additional membrane area. Lastly, for all the values of interest ($0 < MTU \leq 5$), the conclusion that can be taken is that $\varepsilon_{id} - MTU$ region gives quite strict boundaries of the values of the effectiveness for each set MTU . As an example, the lowest ideal effectiveness at $MTU=0.68$ is 0.5, while upper value is 0.68. This means that, without any modeling calculation, it is already possible to determine a priori (since MTU is only based on inlet variables and membrane parameters) that ideal hydrogen separated will be bounded between 50% and 68% of the maximum amount that is possible to recover, that is known. At $MTU=1$ there is the maximum uncertainty: lower effectiveness is about 0.64 and upper value is 1. At $MTU=2.31$, the lower limit is 0.9; at $MTU=3$, lower effectiveness is 0.95.

Figure 4 shows the region of all solutions of equation (18). However, the discussion so far did not gather insight on how variables affect the value of the effectiveness within that range. To understand these effects,

another analysis has been conducted. In these calculations, the value of one variable is changed in set of discrete values, MTU is evaluated again in the range [0; 5] while the other variables are fixed. Preliminary results suggested that some variables can be grouped in parameters having the same effect on effectiveness. In particular:

- φ , A_{mem} and \dot{n}_{in} do not have any influence of effectiveness when MTU is fixed. So, for example, if area is doubled but also flow rate is doubled, MTU is the same and also effectiveness.
- for each value of MTU, effectiveness results the same when, freely varying p_{ret} and p_{perm} , the ratio p_{ret}/p_{perm} , hereafter called pressure ratio, was the same.
- The other two variables (hydrogen inlet molar fraction and exponent n) have a specific individual effect.

Based on these preliminary results, the effect of relevant variables, eventually grouped in parameters, is studied according to their values reported in Table 2. Parameter $(\varphi \cdot A_{mem})/\dot{n}_{in}$, having no influence on ε_{id} , has always been varied to end up with a distribution of MTU in the range [0;5].

Table 2: values of the variables/parameters to study their influence on effectiveness. Each variable is investigated in a discrete set of values, while all other variables had been fixed

| Variable | Units | Value when fixed | Values when investigated | Figure when investigated |
|--|------------------|------------------|-----------------------------|--------------------------|
| $x_{H_2,in}$ | - | 0.5 | 0.1 – 0.25 – 0.5 – 0.75 – 1 | 5a |
| p_{perm}/p_{ret} | - | 10 | 5 – 10 – 100 | 5b |
| n | - | 0.5 | 0.5 – 0.6 – 0.8 - 1 | 5c |
| $(\varphi \cdot A_{mem})/\dot{n}_{in}$ | $1/\text{bar}^n$ | Never fixed | To give MTU in range [0;5] | all |

Results of the sensitivity analysis are reported in Figure 5. In particular, in Figure 5a the effect of the inlet hydrogen molar fraction; in Figure 5b the effect of the pressure ratio; in Figure 5c the effect of the pressures exponent n . In general, it can be seen the strong influence of hydrogen inlet fraction on effectiveness, that results higher when $x_{H_2,in}$ grows. Similarly, an increase in pressure ratio also increases effectiveness, although this effect is milder than the benefits of a higher hydrogen fraction. Lastly, exponent n has an opposite effect, where line at lower n has the highest effectiveness. This last effect is however very limited on the overall performance.

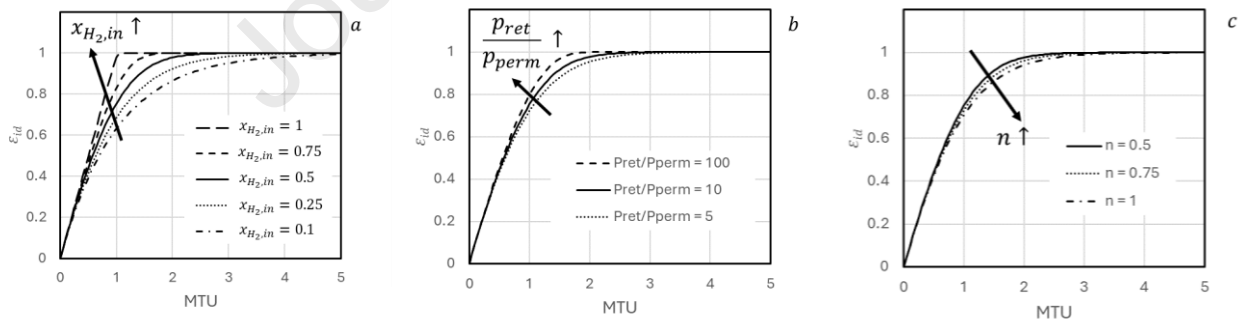


Figure 5: ideal effectiveness changing: a) inlet hydrogen molar fraction, b) pressure ratio, c) exponent n

For practical matters, it can be useful to draw some charts obtained for different combinations of the variables that have been investigated one-by-one before. Charts obtained by varying $x_{H_2,in}$ (0.1 – 0.25 – 0.5 – 0.75 – 0.9) and, for each value, investigating the effect of pressure ratios (5 – 10 – 100) for both $n=0.5$ and $n=1$ are reported in Appendix B.

It is also relevant to state that this ε -MTU method is general and have been developed to take into account as many variables as possible. However, in many situations it can happen to be bounded to particular constraints, as for example to have to treat a gas stream with a fixed composition, flow rate, temperature or so on. In these cases, the method could be in principle simplified. An example of this is given in Appendix A, where it is studied the case where both retentate and permeate pressures are fixed, as well as the inlet hydrogen molar fraction. Since these are also the parameters affecting the maximum recovery factor, having them fixed means to fix also RF_{max} , which simplifies strongly the analysis.

5. Concentration polarization losses

The advantage of ideal results is that they are general, meaning that they work for any geometry and stream composition. However, in reality, different losses may severely affect the performance of a mass exchanger. In particular, one major problem that always occurs with mixtures is the so-called concentration polarization (CP) phenomenon, where hydrogen partial pressure at the membrane surface is lower than its bulk value ($p_{ret,H_2,m} < p_{ret,H_2}$), due to the fact that the internal mass transfer takes some time to replace the hydrogen adsorbed on the membrane surface. CP losses have been widely studied in literature [39]–[41], but their description and the phenomenological correlations used for their description have been found to be often specific and not applicable to different geometries. Recently, [42] made available a large dataset of experimental points (423 different experiments) obtained with a cylindrical Pd-Ag thin-layer (4.3 μm) ceramic-supported membrane of 1.4 cm diameter, inserted in a cylindrical tube of 7.8 cm diameter. Three different membrane lengths were studied (46.7 cm, 30 cm and 15 cm), with the retentate at both 3 and 5 bar and the permeate always at atmospheric pressure. Experiments were run with different flow rates (from 2.8 to 25 NL/min), and therefore different velocities; different temperatures (350 °C, 400 °C, 450 °C); different hydrogen molar fraction at the inlet (from 22.5% to 97.5%), in a mixture with nitrogen. This database allows to study the influence of several variables on CP losses.

Experimental results, based on the measurement of hydrogen separated flow rate, have been compared with the numerical solution of equation (16) obtained under ideal conditions (i.e. no CP losses). Figure 6 reports the relation between experimental mass transfer units \overline{MTU} and the ideal MTU_{id} , meaning the MTU that is obtained by setting in the model the membrane area such that the hydrogen separated results the same as in the experiment. Experiments reproduced are the ones with inlet hydrogen fraction of 25%, 50%, 80% and 95%. In case of 80%, the points are displayed for three membrane lengths (46.7 cm, 30 cm and 15 cm) and they result to lie on a single exponential line. This is an important result, as it states that the entity of polarization losses depends, for a specific inlet hydrogen fraction, only on the value of MTU_{id} . As happens in the ideal case, performance are determined by membrane length in terms of how it contributes to MTU. Higher membrane areas while maintaining same MTU (for example increasing inlet flow rate) show the same entity of polarization losses.

For the other hydrogen fractions, only the points at 30 cm length are displayed, since it was proved for 80% that results at different lengths still lie on the same exponential line.

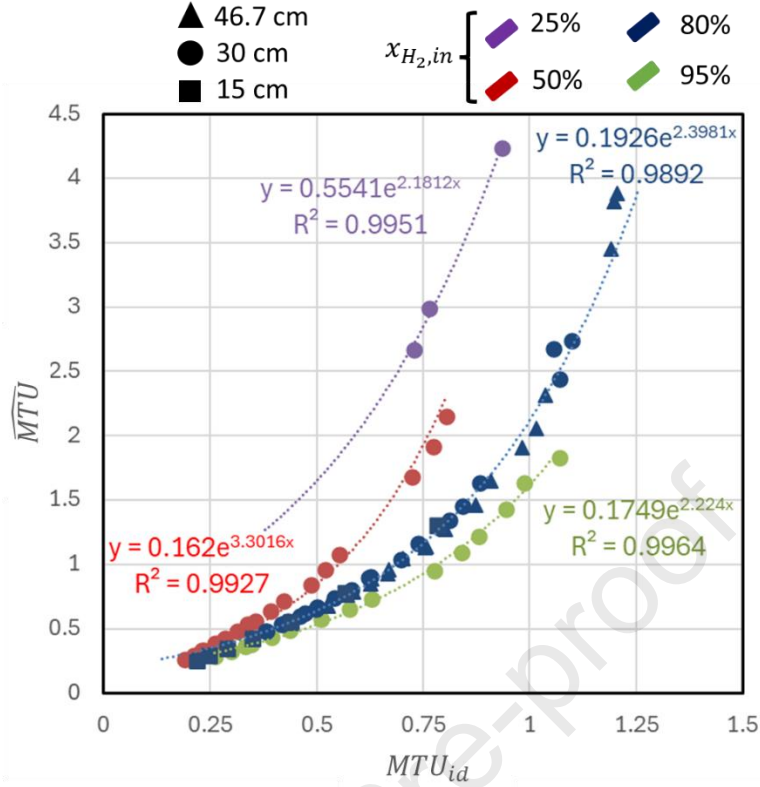


Figure 6: relation between real MTU and ideal MTU (without polarization) for different inlet hydrogen molar fractions for experiments at different temperatures (350, 400 and 450 °C), pressures (3 bar and 5 bar) and various flow rates (from 2.8 to 25 NL/min). Experimental values taken from [42]

It turned out that it is possible to fit accurately the points at different hydrogen inlet molar fractions with exponential relations, which can be used to evaluate the real membrane area based only on the ideal value, determined from the ε -MTU method. An example of this procedure is discussed in the next section.

6. Rule-of-thumb utilization of $\varepsilon - MTU$ method

To summarize, the ε -MTU method can be used for two design procedures: if the operating conditions and the membranes properties and area are set, then also MTU is set and the method can be used to predict the ideal effectiveness ε_{id} , hence to estimate the separator performance. On the other hand, it can be conversely used whether a desired effectiveness ε , that is the target to achieve, is set, and to estimate the ideal mass-transfer-units (MTU_{id}), and then – for given operating conditions and membrane properties - the membrane area necessary to reach the target. Moreover, if coupled with CP effect of Figure 6, the method becomes a powerful tool to estimate the real MTU (and then real membrane area) of the membrane separator. In this last paragraph, a rule-of-thumb method is proposed to illustrate the use of the method for an estimation of the membrane area, even without having the exact ε -MTU line (which depends on the values of n , p_{ret}/p_{perm} and $x_{H_2,in}$), but only using the general chart of Figure 4.

Supposing inlet conditions and operating parameters are known (total molar flow rate, hydrogen fraction, temperature, pressures, membrane permeance and exponent n), and a desired value of the hydrogen recovery is fixed (and then recovery factor, and then effectiveness). The problem is, in this case, to determine the membrane area necessary for this separation. Fixed ε , the ideal MTU can be bounded between a minimum and maximum value given by the inverse of equations (20) and (21):

$$MTU_{id}^{\min} = \varepsilon \quad (22)$$

$$MTU_{id}^{\max} = -\ln(1 - \varepsilon) \quad (23)$$

The rule-of-thumb consists in taking as MTU_{id} the value, between minimum and maximum, at the same distance in percentage as it is the complement-to-one of the inlet hydrogen fraction. So, for example, in case inlet hydrogen fraction is 50%, the value of MTU assumed is halfway between minimum and maximum. In case of an inlet hydrogen fraction of 25%, MTU is the value at $\frac{3}{4}$ of the distance between the minimum and the maximum. In formula:

$$MTU_{id}^{\text{RoT}} = \varepsilon + (1 - x_{H_2, \text{in}}) \cdot (-\ln(1 - \varepsilon) - \varepsilon) \quad (24)$$

This procedure gives an estimation of the ideal area. Including polarization, the area would be higher, following the exponential trends of Figure 6. Real MTU can be calculated from the ideal ones, as:

$$MTU^{25\%} = 0.554 \cdot e^{2.1812 \cdot MTU_{id}} \quad \text{for } x_{H_2, \text{in}} = 25\% \quad (25)$$

$$MTU^{50\%} = 0.162 \cdot e^{3.3016 \cdot MTU_{id}} \quad \text{for } x_{H_2, \text{in}} = 50\% \quad (26)$$

$$MTU^{80\%} = 0.193 \cdot e^{2.3981 \cdot MTU_{id}} \quad \text{for } x_{H_2, \text{in}} = 80\% \quad (27)$$

$$MTU^{95\%} = 0.175 \cdot e^{2.2240 \cdot MTU_{id}} \quad \text{for } x_{H_2, \text{in}} = 95\% \quad (28)$$

For the values of hydrogen fraction in between the values experimentally detected, the value of MTU is linearly interpolated between the two adjacent values. The same holds for values below 25%, where the value of MTU is linearly interpolated between 0 and the one determined from equation (25).

The rule-of-thumb is illustrated through a practical example, taken from the same database of experiments [42]. With a feed flow rate of 8 NL/min ($5.95 \cdot 10^{-3}$ mol/s) with 75% of hydrogen, using the 30 cm long membrane, at 400 °C and with 4 bar of pressure, the aim is to reach an effectiveness of 65% (i.e. to separate 65% of the hydrogen that can be theoretically separated). In the database, this result is achieved with the 30 cm long membrane, and then a membrane area of 0.013195 m². The experimental \overline{MTU} results then 1.214, where the cap indicates it is an experimental determined value. To estimate this value with the rule-of-thumb, from the target effectiveness it can be calculated the ideal rule-of-thumb MTU from equation (24), being $x_{H_2, \text{in}} = 75\%$ and $\varepsilon = 0.65$. It results $MTU_{id}^{\text{RoT}} = 0.75$. From the ideal value, the real one is calculated taking into account polarization losses. To estimate the value at 75% of hydrogen fraction, values at 50% and 80% are linearly interpolated. It results, from equations (26) a value of 1.927 and from equation (27) a value of 1.166; by linearly interpolating, at 75% the value results $MTU^{75\%} = 1.293$. Accordingly, membrane area results 0.01405 m² and, accordingly, a length of 32 cm. Relative difference in membrane area evaluated with the rule-of-thumb and the experimental value is 6.5%. Values and calculations are summarized in Table 3.

Table 3: values of membrane parameters and operating conditions of the experiment which results are estimated using a rule-of-thumb approach based on the $\varepsilon - MTU$ method

| Variable | Units | Specification | Value |
|-----------------------------|---|---------------|---------|
| membrane | | | |
| ϕ^0 | $\frac{\text{mol}}{\text{s} \cdot \text{m}^2 \cdot \text{bar}^{0.581}}$ | property | 2.145 |
| E_a | kJ/mol | property | 9.262 |
| n | - | property | 0.581 |
| Operating conditions | | | |
| \dot{n}_{in} | mol/s | set | 0.00595 |
| $x_{H_2, \text{in}}$ | - | set | 0.75 |
| p_{ret} | bar | set | 4 |
| p_{perm} | bar | set | 1 |
| T | °C | set | 400 |

| Relevant parameters | | | |
|---|---|---|----------------|
| \wp | $\frac{mol}{s \cdot m^2 \cdot bar^{0.581}}$ | $\wp = \wp^0 \cdot e^{-\frac{E_a}{R \cdot T}}$ | 0.410 |
| RF_{max} | - | $RF_{max} = \frac{1 - \frac{p_{perm}}{p_{ret} \cdot x_{H_2,in}}}{1 - \frac{p_{perm}}{p_{ret}}}$ | 88.6% |
| $\dot{n}_{H_2,sep,max}$ | mol/s | $\dot{n}_{H_2,sep,max} = RF_{max} \cdot \dot{n}_{in} \cdot x_{H_2,in}$ | 0.00395 |
| Target | | | |
| ε | - | Target set | 0.65 |
| $\dot{n}_{H_2,sep}$ | mol/s | $\dot{n}_{H_2,sep} = \varepsilon \cdot \dot{n}_{H_2,sep,max}$ | 0.00257 |
| RF | - | $RF = \frac{\dot{n}_{H_2,sep}}{\dot{n}_{in} \cdot x_{H_2,in}}$ | 57.6% |
| Experimental results | | | |
| \hat{A}_{mem} | m^2 | Experimentally determined | 0.0132 |
| \widehat{MTU} | - | $\widehat{MTU} = \frac{\wp \cdot \hat{A}_{mem} \cdot (p_{ret} \cdot x_{H_2,in})^n - p_{perm}^n}{\dot{n}_{in} \cdot \frac{p_{ret} \cdot x_{H_2,in} - p_{perm}}{p_{ret} - p_{perm}}}$ | 1.214 |
| $\hat{J}_{H_2,average}$ | $mol/(s \cdot m^2)$ | $\hat{J}_{H_2,average} = \frac{\dot{n}_{H_2,sep}}{\hat{A}_{mem}}$ | 0.1947 |
| Rule of thumb based on $\varepsilon - MTU$ method | | | |
| MTU_{id}^{RoT} | - | $MTU_{id}^{RoT} = \varepsilon + (1 - x_{H_2,in}) \cdot (-\ln(1 - \varepsilon) - \varepsilon)$ | 0.75 |
| $MTU^{50\%}$ | - | $MTU^{50\%} = 0.162 \cdot e^{3.3016 \cdot MTU_{id}}$ | 1.927 |
| $MTU^{80\%}$ | - | $MTU^{80\%} = 0.193 \cdot e^{2.3981 \cdot MTU_{id}}$ | 1.166 |
| $MTU^{75\%}$ | - | $MTU^{75\%} = MTU^{80\%} + \frac{MTU^{80\%} - MTU^{50\%}}{0.8 - 0.5} \cdot (0.75 - 0.8)$ | 1.293 |
| A_{mem} | m^2 | $A_{mem} = \frac{\dot{n}_{in}}{\wp \cdot MTU^{75\%}} \cdot \frac{p_{ret} \cdot x_{H_2,in} - p_{perm}}{(p_{ret} \cdot x_{H_2,in})^n - p_{perm}^n}$ | 0.01405 |
| Relative difference | - | $\frac{A_{mem} - \hat{A}_{mem}}{\hat{A}_{mem}}$ | 6.5% |

This detailed example showed how to utilize the rule-of-thumb estimation of the membrane area based on a target separation. Rule-of-thumb has been validated on the available experiments at 50% and 95% inlet hydrogen fraction obtained with the 15 cm and the 46.7 cm membranes. Indeed, these values had not been used in the fitting process of Figure 6. Moreover, in the validation also one experimental point at inlet hydrogen fraction of 66.7% and one at 70% have been included, both obtained with the 15 cm membrane. Value of the experimental \widehat{MTU} are compared with the value predicted MTU^{RoT} . Parity plot is show in Figure 6.

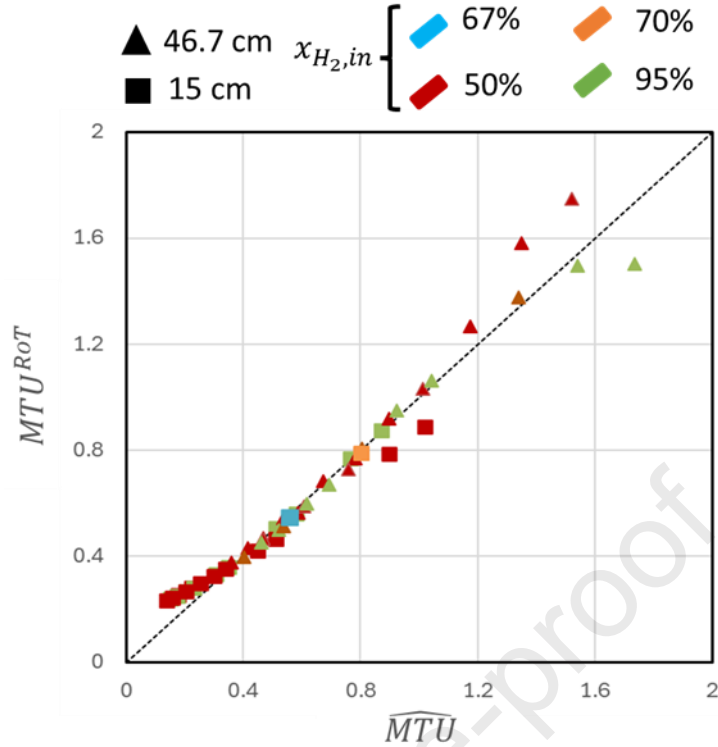


Figure 7: parity plot between the value of MTU in the experiments and the MTU estimated with the rule-of-thumbs. Experiment at 70% was run at 450 °C and 3 bar, with 4.7 NL/min of feed. Experiment at 66.7% at 400 °C and 3 bar, with 6 NL/min of feed. Experiments at 50% and 80% were run at both 450, 400 and 350 °C, 5 or 3 bar and with different flow rates between 4 and 26 NL/min.

As most of the data available are for hydrogen fractions higher than 50%, it could be verified the accuracy of the method that region. For lower fractions, few data are available for both fitting and validation, therefore the conclusion is that more data are needed to obtain robust results as for higher fractions. Rule-of-thumb can still however be used for a first guess estimation.

7. Conclusions

The design of a membrane separator to recover pure hydrogen from a gaseous mixture is influenced by several variables, both related to the properties and the area of the membrane used and to the operating conditions. Although the solutions of the characteristic ODE, to calculate the amount of hydrogen permeated, can be quite easily computed numerically, it may remain unclear the effect of some variables or parameters in hydrogen recovery. In this article, an $\varepsilon - MTU$ approach (as for the heat exchangers there is the well-known $\varepsilon - NTU$ method) has been developed to assess the relevant dimensionless groups and facilitate the mass exchanger design (see section 4).

This method is based on the definition of effectiveness (i.e. ratio between hydrogen separated and maximum amount that can be separated) as a function of a dimensionless parameter MTU, that can be calculated based only on inlet conditions and membrane properties. As MTU goes close to zero, it tends to be equal to the effectiveness. If $MTU > 5$, in all cases ideal effectiveness is 1, so membrane area is always overestimated for that problem (or flow rate is underestimated). For any value in between of MTU, effectiveness varies into a narrow range, depending on three dimensionless parameter: inlet hydrogen molar fraction, exponent n in flux expression and the ratio between retentate-side and permeate-side pressures. Among these, inlet hydrogen fraction showed to have the strongest influence (see Figure 5).

Since concentration polarization phenomena can severely affect the real performance compared to an ideal situation, a correlation between real and ideal MTU has been found based on an available database on experiments of H_2/N_2 mixtures fed to a Pd-Ag cylindrical membrane (see section 5). For any value of inlet hydrogen fraction, it turned out to exist an exponential relation between ideal and real membrane area required for a given separation. The procedure proposed should be extended and validated for lower values of hydrogen fraction, whenever new set of experimental results fraction are made available.

Finally, a rule-of-thumb analytical procedure has been proposed to estimate the ideal MTU (i.e. obtained without concentration polarization losses), taking as value in the overall $\varepsilon - MTU$ chart results the value, between minimum and maximum MTU, at the range percentage given by the inlet hydrogen fraction (see section 6).

The rule-of-thumb proposed, coupled with the CP correlations, is shown in detail applied to an experimental result, where prediction of membrane area compared resulted with a relative error below 7% (see Table 3). The rule-of-thumb results have been also validated by reproducing experimental results at 50%, 66.7%, 70% and 95% of inlet hydrogen fraction with good accuracy.

In the sub-case that pressures and inlet hydrogen fraction are fixed, the problem can be simplified since the maximum hydrogen recovery is always constant. In this case, a more simple method have been proposed, where recovery factor (i.e. hydrogen separated over hydrogen fed) results a function of the parameter $(\varphi \cdot A_{mem})/\dot{n}_{in}$ (see appendix A). In this sub-case, only exponent n affects the recovery factor, while when n is determined, all the solutions lies on a line in the RF – $(\varphi \cdot A_{mem})/\dot{n}_{in}$ chart (see Figure 8).

Due to the utility that $\varepsilon - MTU$ charts may have in the design of experimental setups and mass exchanger modules in general, ideal results for different values of inlet hydrogen molar fraction, exponent n and pressure ratio have been provided in Appendix B. Effectiveness values can be then reconducted to real values (including CP losses) by studying the phenomena in the module of interest or by using the correlation provided in this article (see Figure 6) if the latter is found to be applicable on the system of interest.

To conclude, the article provided an in-depth analysis of the parameters affecting hydrogen separation in dense metallic membrane, both in the ideal situation and including real effect of polarization losses, providing a valid support for the mass exchanger design. A rule-of-thumb based on analytical relations is also proposed to have a simple method for modules design.

CRedit authorship contribution statement

Michele Ongis: Conceptualization, Validation, Investigation, Writing – original draft. **Gioele Di Marcoberardino:** Validation, Writing – review and editing. **Fausto Gallucci:** Validation, Writing – review and editing. **Marco Binotti:** Conceptualization, Validation, Writing – review and editing.

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Nomenclature

| | |
|-----------------|---|
| A | Variable for membrane area, m^2 |
| A_{mem} | Membrane area, m^2 |
| b | Parameter in original Richardson equation, K |
| d | Membrane thickness in original Richardson equation, m |
| \overline{DF} | Average value of the driving force, bar^n |
| DF_{in} | Driving force at mass exchanger inlet, bar^n |
| E_a | Apparent activation energy in permeance equation, J/mol |
| \dot{J}_{H_2} | Hydrogen flux through the membrane, $mol/(s \cdot m^2)$ |

| | |
|----------------------|--|
| k | Permeability in original Richardson equation, $mol/(m \cdot s \cdot bar^{0.5})$ |
| MTU | Mass transfer units, – |
| n | Partial pressures exponent in generalized Richardson equation, – |
| \dot{n}_{in} | Molar flow rate of total gas inlet in the mass exchanger, mol/s |
| $\dot{n}_{H_2,sep}$ | Molar flow rate of hydrogen separated through the membranes, mol/s |
| $\dot{n}_{H_2,ret}$ | Molar flow of hydrogen gas in retentate side along the membrane, mol/s |
| \dot{n}_{ret} | Molar flow rate of gas in the retentate side along the membrane, mol/s |
| \wp | Hydrogen permeance, $mol/(m^2 \cdot s \cdot bar^n)$ |
| \wp^0 | Hydrogen permeance pre-exponential factor, $mol/(m^2 \cdot s \cdot bar^n)$ |
| p_{perm} | Pressure of the gaseous stream at the retentate side on the membrane, bar |
| p_{ret} | Pressure of the gaseous stream at the retentate side on the membrane, bar |
| R | Universal gas constant, J/mol |
| RF | Recovery factor, – |
| T | Temperature, K |
| $x_{H_2,in}$ | Hydrogen inlet molar fraction, – |
| <i>Greek symbols</i> | |
| ε | Effectiveness, – |
| <i>Subscripts</i> | |
| H_2 | Relative to hydrogen |
| N_2 | Relative to nitrogen |
| id | Relative to ideal conditions (i.e. no CP losses, no competitive adsorption, plug flow, ideal gases). |
| in | Relative to the conditions at the mass exchanger inlet |
| m | Relative to the proximity of membrane surface |
| max | Maximum value that can be achieved |
| $perm$ | Relative to permeate-side of the membrane |
| ret | Relative to retentate-side of the membrane |
| sep | Relative to the hydrogen passing through the membrane |
| <i>Superscripts</i> | |
| 0 | Relative to mass exchanger inlet (initial condition of Cauchy's problems) |
| max | Maximum value that can be achieved |
| min | Maximum value that can be achieved |
| \wedge | Value determined experimentally |
| <i>Abbreviations</i> | |
| CP | Concentration polarization |
| ODE | Ordinary differential equation |

Appendix A: Hydrogen recovery, set the pressures and inlet H₂ fraction

The behavior of RF_{max} allows a distinction among the variables affecting the hydrogen separation. They can be divided in two classes based of the following criteria:

- variables which affect the maximum hydrogen that can be recovered (and therefore RF_{max});
- variables which don't.

In particular, it turns out that \dot{n}_{in} , A_{mem} , T and membranes parameters (\wp^0 , E_a and n) do not affect the maximum recovery factor (while they can certainly affect the recovery factor), while $x_{H_2,in}$, p_{ret} and p_{perm} do affect it. As a consequence, it is possible to define a sub-set of solutions of the problem to determine hydrogen permeation, that is to map the solutions when $x_{H_2,in}$, p_{ret} and p_{perm} are fixed and, according to equation (14), also RF_{max} is fixed.

In this appendix, the solution to this problem will be addressed. This family of problems correspond to the situation where a gas stream is available at a certain pressure and composition, and a membrane separator should be designed with a fixed permeate pressure. When this is the case, both pressures and hydrogen inlet molar fraction are determined, while the membrane type and area installed have to be determined.

The approach proposed in this work is to define a dimensionless form of equation (16). The idea is to divide both sides for the flow rate of hydrogen fed. At the left side can then be recognized the ideal recovery factor.

$$\frac{\dot{n}_{H_2,sep,id}}{\dot{n}_{H_2,in}} = \frac{\wp \cdot A_{mem} \cdot \overline{DF}_{id}}{\dot{n}_{in} \cdot x_{H_2,in}} \rightarrow RF_{id} = \frac{\wp \cdot A_{mem}}{\dot{n}_{in}} \cdot \frac{\overline{DF}_{id}}{x_{H_2,in}} \quad (29)$$

Recovery factor results given by the product of the term $(\wp \cdot A_{mem})/\dot{n}_{in}$, where all the variables that can be changed by the mass exchanger designer are reported (i.e. inlet flow rate, membrane permeance, depending on the type of membrane and system temperature, and total membrane area), and the term $\overline{DF}_{id}/x_{H_2,in}$, where all the variables assumed fixed (pressures and inlet hydrogen flow rate) appear, together with the solution of integral (17). In the second factor it appears also the exponent n , which value depends on membrane selection.

Equation (29) does not have an analytical solution, but can be solved numerically. The idea is to set defined values for the fixed variables $x_{H_2,in}$, p_{ret} , p_{perm} and a range for the other variables, while n , being in general bounded between 0.5 and 1, it will be considered as a parameter with 3 values: 0.5, 0.75 and 1.

$x_{H_2,in}$, p_{ret} , p_{perm} have been assumed to be 50%, 5 bar and 1 bar respectively. The ratio p_{ret}/p_{perm} is 0.2, and accordingly to Figure 3, it can be derived that RF_{max} results 75%. In the case assumed, therefore, selection of membrane permeance and area is free, but even with an infinite membrane area or an infinite permeance, no more than 75% of the hydrogen fed can be separated. Table 4 reports values and ranges for the variables of interest used in the numerical resolution of the problem.

Table 4: ranges of the variables of interest for sensitivity analysis at fixed pressures and hydrogen fraction

| variable | Units | Set/Free/Calculated | Values/Range |
|------------------------------------|--|---------------------|----------------|
| $x_{H_2,in}$ | - | set | 0.5 |
| p_{ret} | bar | set | 5 |
| p_{perm} | bar | set | 1 |
| \dot{n}_{in} | mol/s | freely variated | (0; +∞) |
| A_{mem} | m ² | freely variated | [0; +∞) |
| \wp | mol/(m ² · s · bar ⁿ) | freely variated | [0; +∞) |
| n | - | set | 0.5 – 0.75 – 1 |
| $(\wp \cdot A_{mem})/\dot{n}_{in}$ | 1/bar ⁿ | calculated | [0; 2.5] |

Results of the sensitivity analysis are reported in Figure 8: for each fixed value of n , the recovery factor is only a function of the parameter $(\wp \cdot A_{mem})/\dot{n}_{in}$. As this parameter increases, the RF increases until it reaches the maximum value. The slope of the RF_{id} curve is higher as n increases.

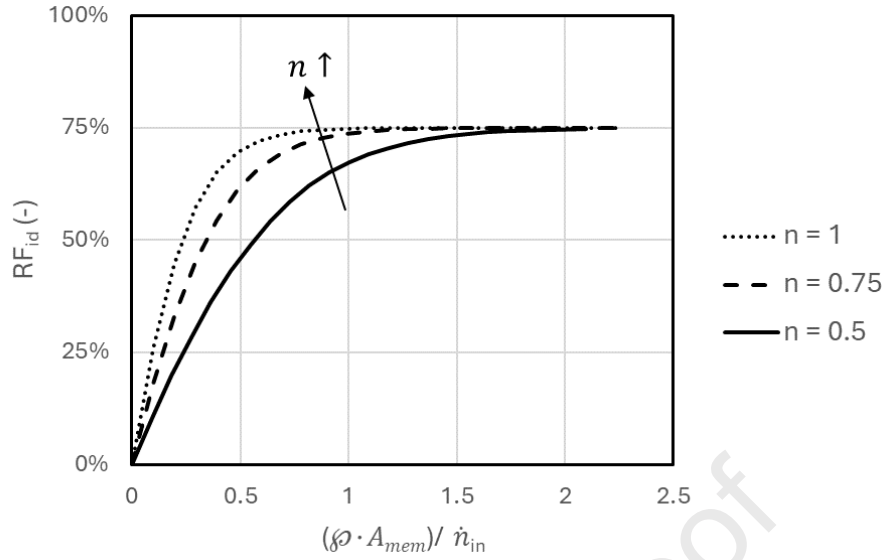
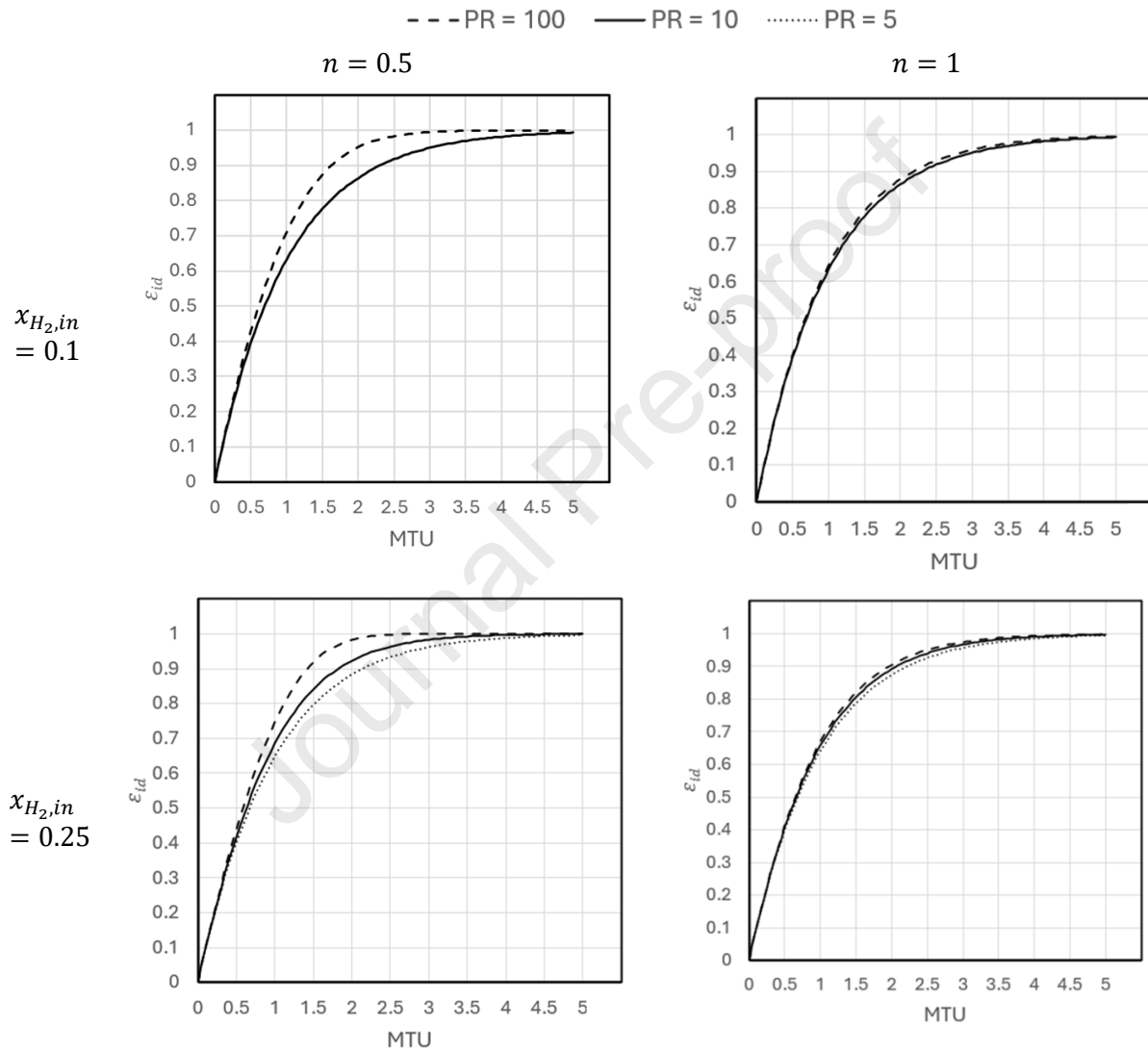


Figure 8: solutions of equation (29) for variables defined in Table 4

Results obtained in Figure 8 are strictly valid for the set of values selected for $x_{H_2,in}$, p_{ret} and p_{perm} . However, the concept can be applied in general. For each set of $x_{H_2,in}$, p_{ret} , p_{perm} , and once determined the exponent n , ideal recovery factor is determined by the values of the parameter $(\varphi \cdot A_{mem})/\dot{n}_{in}$, regardless of the values of each factor. In other words, it makes no difference to work (ideally) with a very permeable membrane (φ), with a certain membrane area (A_{mem}) or treating more or less gas (\dot{n}_{in}), until the value of the parameter $(\varphi \cdot A_{mem})/\dot{n}_{in}$ is the same. This also means that these variables have the same effect on recovery factor. As an example, it has the same effect, in the ideal case, to use a membrane with double permeance, to double the number of membranes (i.e. membrane area) or to halve the inlet flow rate.

Appendix B: $\varepsilon - MTU$ curves for mass exchanger design

As stated in the article, $\varepsilon - MTU$ charts can be a valid support for the design of a membrane module, as a mass exchanger to separate high-purity hydrogen from a gaseous mixture. Beyond many un-idealities that may occur and that should be taken into account, the starting point is always the ideal sizing. In this sense, it may be useful to have charts representing potential ranges for hydrogen molar fraction and pressure ratios. These charts are provided in Figure 9, for both 0.5 and 1 as values for exponent n . Charts obtained by varying $x_{H_2,in}$ (0.1 – 0.25 – 0.5 – 0.75 – 0.9) and, for each value, investigating the effect of pressure ratios (5 – 10 – 100). Values in between can be found, as first guess, by interpolating the values in figure.



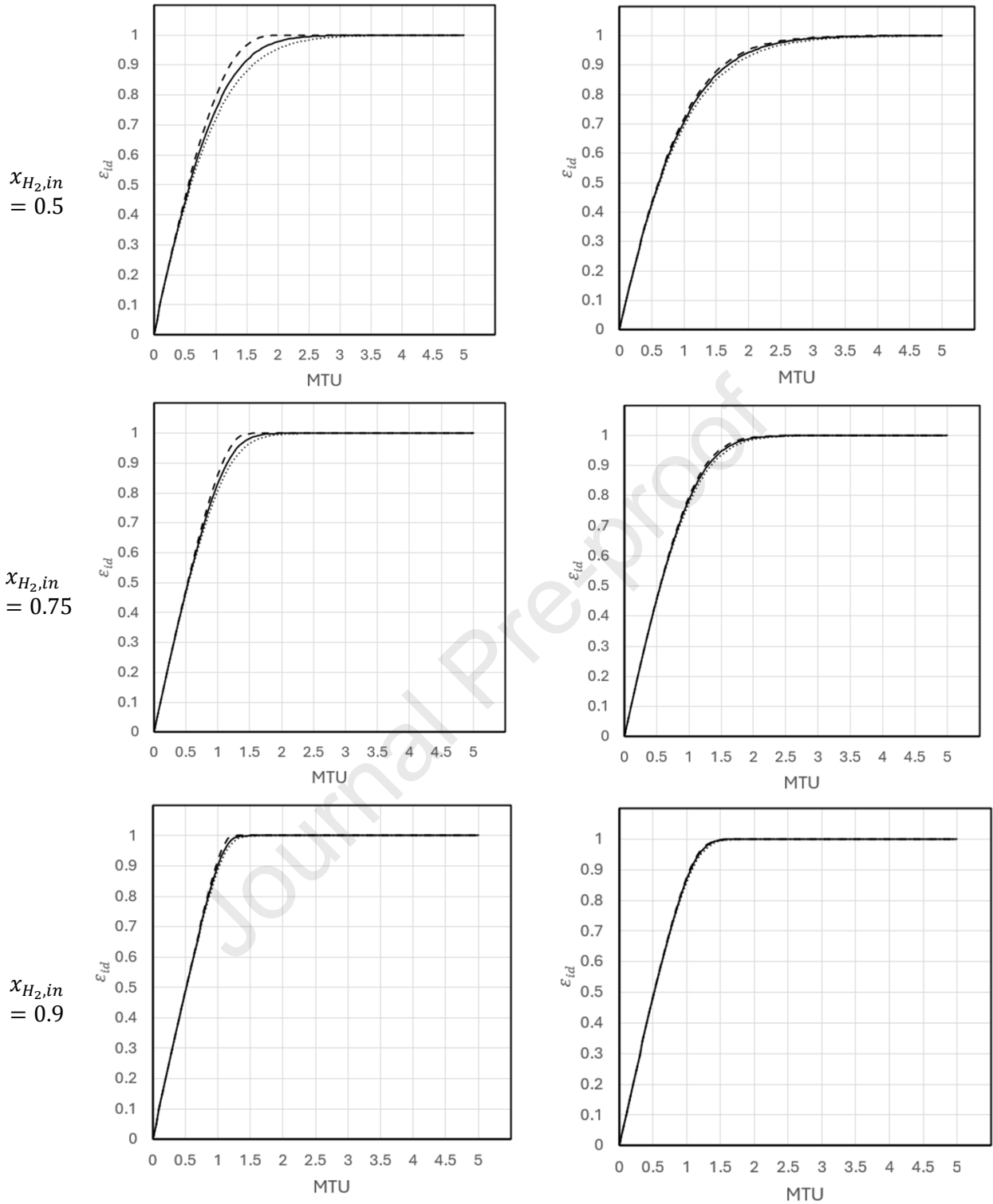


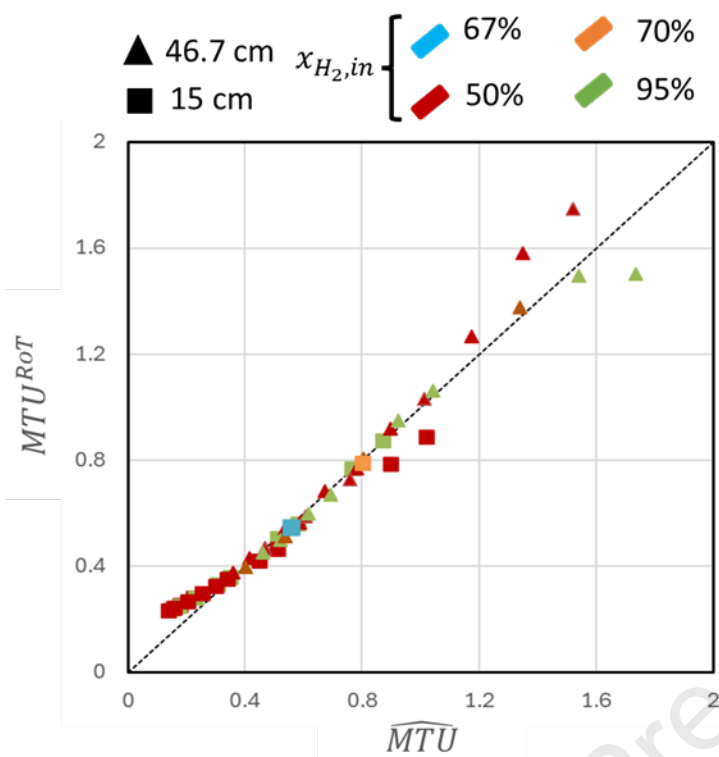
Figure 9: $\varepsilon - MTU$ charts for different values of inlet hydrogen molar fraction (0.1, 0.25, 0.5, 0.75, 0.9) and pressure ratio (5, 10, 100), for n exponent values 0.5 and 1

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- An ϵ -MTU method (as ϵ -NTU for heat exchangers) developed for mass exchangers
- Method is applied to hydrogen separation using dense metallic membranes
- Separation is influenced by 3 parameters: H₂ fraction, exponent n , pressure ratio
- A rule-of-thumb is proposed to estimate total area, including polarization losses

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Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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