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## ASPECTOS CLAVE EN LA METODOLOGÍA DEL ANÁLISIS EXERGÉTICO. APLICACIÓN A PROCESOS DE DESALACIÓN Y A CICLOS DE REFRIGERACIÓN POR ABSORCIÓN.

## *KEY ASPECTS IN THE METHODOLOGY OF EXERGETIC ANALYSIS. APPLICATION TO DESALINATION PROCESSES AND ABSORPTION REFRIGERATION CYCLES.*

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# OUTLINE

# RESUMEN

En este trabajo se presenta una profundización en algunos aspectos conceptuales de los análisis exergéticos que aparecen confusos en la bibliografía, lo que dificulta su aplicación práctica y las comparaciones entre diferentes autores.

Por una parte, se realizan algunos planteamientos teóricos en los que se intenta contestar a las preguntas:

a) ¿Cómo definir convenientemente el estado muerto de un sistema confinado? En los análisis exergéticos, se dice que el sistema se encuentra en el estado muerto cuando se alcanzan las condiciones del ambiente, normalmente consideradas como $T_0$ = 20-25 °C y $p_0$= 1 atm. Pero, en determinadas situaciones prácticas, como puede ser un sistema confinado, donde nunca se va a alcanzar el equilibrio mecánico con el ambiente, tomar como presión del estado muerto la del ambiente puede no ser la mejor opción. Otras posibles soluciones son analizadas aquí.

b) ¿Tiene sentido un valor negativo de la exergía física? En teoría, no tiene sentido un valor de exergía negativa, pero no es raro encontrar en la bibliografía valores de exergía física negativa, sobre todo cuando la presión del sistema es inicialmente inferior a la del ambiente. Aun así, este resultado numérico parece contradecir lo que el "*sentido común"* define como exergía: la energía disponible. En este trabajo se analiza esta situación y se aportan explicaciones alternativas.

c) ¿Es correcto seguir definiendo la exergía como "*máximo trabajo útil teórico...*"? en los trabajos originales de Gibbs, aparece la expresión "*energía disponible*". Posteriormente, la definición se ha concretado hacia "*máximo trabajo útil teórico …*". Pero, los razonamientos que aquí se presentan, nos permiten afirmar que la exergía no sólo representa el "*máximo trabajo útil teórico…*" sino que se podría representar también con el "*máximo calor útil teórico…*", más en concordancia con la definición original de "*energía disponible*".

d) ¿Cuál es la forma más correcta de plantear la eficiencia exergética de un proceso? En la definición de eficiencia energética de un proceso todos los investigadores coinciden. Sin embargo, en la definición de eficiencia exergética esto no es así. Si se guardara una similitud con la eficiencia energética, la eficiencia exergética podría definirse como "*el producto obtenido dividido entre los recursos utilizados*". Sin embargo, la definición de "*entrada-salida*": lo que sale dividido entre lo que entra, está ganando acepción. En este trabajo se analizan las implicaciones de una y otra definición en procesos industriales concretos.

Además, en esta Tesis se abordan dos casos prácticos. En el primero de ellos se lleva a cabo un análisis exergético completo de una planta de desalación de agua de mar por ósmosis inversa en operación. La estructura de la planta es en cierto modo compleja, por las sucesivas modificaciones que ha sufrido a lo largo de los años. Sin embargo, esto permite realizar interesantes comparaciones entre las eficiencias exergéticas de dispositivos similares. También se pueden dar orientaciones, a los operadores de la planta, sobre los dispositivos sobre los que convendría actuar, a corto plazo, para mejorar su eficiencia. También se razona sobre la definición de la eficiencia exergética en las

membranas de ósmosis inversa, teniendo en cuenta su misión, que es transformar la energía mecánica en energía química. Y se realiza una amplia y exhaustiva comparación con la literatura.

El segundo caso de estudio tiene relación al análisis exergético de un sistema de refrigeración por absorción, utilizando la mezcla $H_2O$/LiBr. El sistema tiene una sola etapa y está refrigerado por agua, pero la metodología sería igualmente aplicable a sistemas múltiples con diferentes opciones tanto de refrigeración como de absorción de energía. Se considera la elección de un estado muerto para sistemas confinados, que no tienen por qué alcanzar el equilibrio mecánico ni químico con el ambiente, y donde, aun así, la exergía química juega un papel importante. El estudio se completa con una comparación bibliográfica profunda.

Los resultados obtenidos confirman que hay algunos aspectos clave en los análisis exergéticos sobre los que se debería poner más cuidado y atención a la hora de aplicar esta metodología sobre procesos y sistemas industriales concretos: la correcta elección del estado muerto, las ecuaciones utilizadas para el cálculo de las propiedades termodinámicas de las sustancias, incluida la exergía física y química, y la definición de eficiencia exergética, de modo que los estudios realizados por diferentes autores puedan ser conveniente y cabalmente comparados.

# ABSTRACT

This work presents an in-depth study of some conceptual aspects of exergy analysis that appear confusing in the literature, which makes their practical application and comparisons between different authors difficult.

On the one hand, some theoretical approaches are performed in which an attempt is made to answer the questions:

a) How to conveniently define the dead state of a confined system? In exergy analysis, the system is said to be in the dead state when the ambient conditions, normally considered as $T_0$ = 20-25 °C and $p_0$= 1 atm, are reached. However, in certain practical situations, such as a confined system, where mechanical equilibrium with the environment will never be reached, taking the ambient pressure as the dead state pressure may not be the best option. Other possible solutions are analyzed here.

b) Does a negative value of the physical exergy make sense? In theory, a negative exergy value does not make sense, but it is not uncommon to find negative physical exergy values in the literature, especially when the system pressure is initially lower than the ambient pressure. Even so, this numerical result seems to contradict what "*common sense*" defines as exergy: the available energy. This work analyzes this situation and provides alternative explanations.

c) Is it correct to keep on presenting exergy only as "*maximum theoretical useful work output...*"? In Gibbs' original works, the expression "*available energy*" appears. Subsequently, the definition has been specified as "*maximum theoretical useful work output ...*". But the reasoning presented here allows us to affirm that the exergy not only represents the "*maximum theoretical useful work output...*" but could also be represented by the "*maximum theoretical useful heat output...*", more in agreement with the original definition of "*available energy*".

d) What is the most correct way to state the exergy efficiency of a process? All researchers agree on the definition of the energy efficiency of a process. However, in the definition of exergy efficiency this is not the case. If it were similar to energy efficiency, exergy efficiency could be defined as "*the exergy output divided by the exergy resources*". However, "*input-output*" formulation (exergy output divided by exergy input), has gained acceptance. This work discusses the implications and suitability of both formulations for specific industrial processes.

On the other hand, this Thesis deals with two practical case studies. In the first one, a complete exergy analysis of a seawater reverse osmosis desalination plant in operation is carried out. The structure of the plant is somewhat complex, due to the successive modifications it has undergone over the years. However, this allows interesting comparisons to be made between the exergy efficiencies of similar devices. Guidance can also be given to plant operators on the devices on which short-term actions should be undertaken to improve their efficiency. The definition of exergy efficiency in reverse osmosis membranes is also discussed, taking into account their purpose, namely, the transformation of mechanical energy into chemical energy. And an extensive and comprehensive comparison with the literature is made.

The second case study is related to the exergy analysis of an absorption refrigeration system, using the $H_2O$/LiBr mixture. The system has a single stage and is water-cooled, but the methodology would be equally applicable to multiple stage systems with different heating and refrigeration operation options. Selection of a dead state for confined systems, which need neither to reach mechanical nor chemical

equilibrium with the environment, and where, even so, chemical exergy plays an important role, is considered. The study is completed with an in-depth literature comparison.

The results obtained confirm that there are some key aspects in the exergy analysis on which more care and attention should be paid when applying this methodology on specific industrial processes and systems: the correct choice of the dead state, the equations used for the calculation of the thermodynamic properties of the substances, including physical and chemical exergy, and the definition of exergy efficiency, so that the studies carried out by different authors can be conveniently and thoroughly compared.

# NOMENCLATURE

| | |
|---|---|
| $ex$ | Specific exergy, kJ/kg |
| $Ex$ | Exergy, kJ |
| $\dot{Ex}$ | Exergy flow rate, kW |
| $h$ | Specific enthalpy, kJ/kg |
| $\dot{m}$ | Mass flow rate, kg/s |
| $p$ | Pressure |
| $\dot{Q}$ | Heat power, kW |
| $s$ | Specific entropy, kJ/kg·K |
| $t$ | time, s |
| $T$ | Temperature, K |
| $V$ | Volume, m$^3$ |
| $v$ | specific volume, m$^3$/kg |
| $\dot{W}$ | Electric power, kW |

*Greek letters*

| | |
|---|---|
| $\chi$ | molar fraction |
| $\varepsilon$ | Fuel- product Exergetic efficiency |
| $\mu$ | Chemical potential |
| $\eta$ | Inlet-outlet Exergetic efficiency |

*Subscripts and superscripts*

| | |
|---|---|
| $0$ | Dead state |
| $D$ | Destruction |
| $e$ | Exit |
| $ex$ | Exergetic |

| | |
|---|---|
| *F* | Fuel |
| *i* | i-th material stream / inlet |
| *j* | Instantaneous value |
| *k* | k-th component |
| *L* | Loss |
| *P* | Product |
| *PH* | Physical |
| *q* | Related to heat |
| *tot* | Total |
| *VC* | Control volume |
| *w* | Related to work |
| * | At chemical equilibrium with the environment |

*Abbreviations*

| | |
|---|---|
| ERI | Pressure exchanger from Energy Recovery Inc. |
| G | Generator |
| HPP | High pressure pump |
| JCR | Journal of citations report |
| M | Motor |
| RO | Reverse osmosis |
| SCIE | Science Citation Index Expanded |
| SPECO | Specific Exergy Costing |

# LIST OF FIGURES

# 1. INTRODUCTION

## 1.1. BACKGROUND

This Thesis can be considered as the result of a process of logical evolution and scientific thought development of the PhD student in the field of the exergy method, as a tool of analysis in the assessment of energy processes. Each of the publications presented here is part of this evolutionary process, and their genesis is briefly explained in this introduction.

*First publication: The exergetic efficiency as a performance evaluation tool in reverse osmosis desalination plants in operation.*

A long-term stay (2 years) in Berlin, in the team of Professor George Tsatsaronis at the *Institut für Energietechnik* of the *Technische Universität Berlin*, led the PhD student to become familiar with the methodology of exergy analysis. Exergy analysis provides a powerful tool for assessing the quality and quantity of a resource. An exergy analysis identifies the location, magnitude and sources of thermodynamic inefficiencies in an energy conversion system. During her stay in Berlin, the PhD student collaborated with Prof. Tsatsaronis' team in performing exergy analyses of theoretical energy intensive processes, as the *Exergoeconomic estimates for a novel zero-emission process generating hydrogen and electric power*. But, upon her return to the University of Las Palmas de Gran Canaria, she considered the application of the method in real industrial processes in the island's local environment. Specifically, the possibility of collaborating with the operators of a reverse osmosis desalination plant arose. It should not be forgotten that the Canary Islands is a pioneering region in Europe and in the World in the field of desalination. The first desalination plant was built on the island of Lanzarote in the 1960s, a distillation plant, which was the predominant technology until the 1980s. Subsequently, distillation plants were replaced by reverse osmosis systems, a more efficient technology from a productive and economic point of view. Reverse osmosis is the current technology in almost all the plants located in the Canary Islands. The plant under study is a large seawater reverse osmosis desalination plant that currently supplies the capital of the island of Gran Canaria and some other municipalities. It was put into operation in 1988 with an initial capacity of 24,000 $m^3/d$ and 7 production lines. Since then, several expansions have been carried out, counting at present with ten reverse osmosis lines with a total nominal production of 82,000 $m^3/d$. Throughout the successive expansions of the plant, the line configurations have been substantially modified in terms of energy recovery components (Pelton turbines or pressure exchange devices), number of reverse osmosis stages, filtration and collection technologies or components involved in feed water pressurization (high pressure pumps, pressure exchangers, booster pumps).

Due to its special configuration, with ten desalinated water production lines, similar but with different characteristics, the plant represents a unique model to assess the energy efficiency as a tool for evaluating the performance of operating reverse osmosis desalination plants. Exergy efficiency assesses the thermodynamic performance of a component, plant or industry, relative to the performance of similar components, plants or industries: comparing the exergy efficiencies of different devices (a turbine with a pump, for example) is usually not meaningful. In this study, similar devices, but with different operating configurations, are compared in terms of their exergy efficiency. Thus, exergy efficiency identifies and quantifies thermodynamic inefficiencies, and locates the most inefficient components (the most inefficient pump among pumps, or the most inefficient reverse osmosis unit among reverse osmosis units, for example). Therefore, this parameter can be successfully used to control and improve plant performance. This study represents a novelty because no reference related to exergy analysis of reverse osmosis desalination plants has been found in the literature presenting this use of exergy efficiency. Previous works are limited to give the second law efficiency of the total desalination plant and the devices involved. Some of them also try to compare the exergy efficiency of the different devices, but, as already mentioned, this comparison is not really meaningful.

As a result, important recommendations were proposed to the operators of this plant. This way, exergetic efficiency has been successfully used to improve the operation of the plant.

*Second publication: "A critical review of definitions for exergetic efficiency in reverse osmosis desalination plants".*

Exergy analyses are very useful tools in the design, optimization and assessment of energy processes (Bejan et al., 1996). However, far from existing an agreement among researchers, there are several key conceptual points of the analysis in which there is a disparity of opinions. This leads, on the one hand, to uncertainty about the validity of the studies found in the literature and, on the other hand, to difficult or insignificant comparisons with the literature.

The comparison between the results of our first work (*The exergetic efficiency as a performance evaluation tool in reverse osmosis desalination plants in operation*) and those of the literature, gave us a surprise. Figure 1 shows the comparison between the values of exergetic efficiency obtained in our work and those extracted from the literature for a reverse osmosis desalination plant and for the core components of the process.

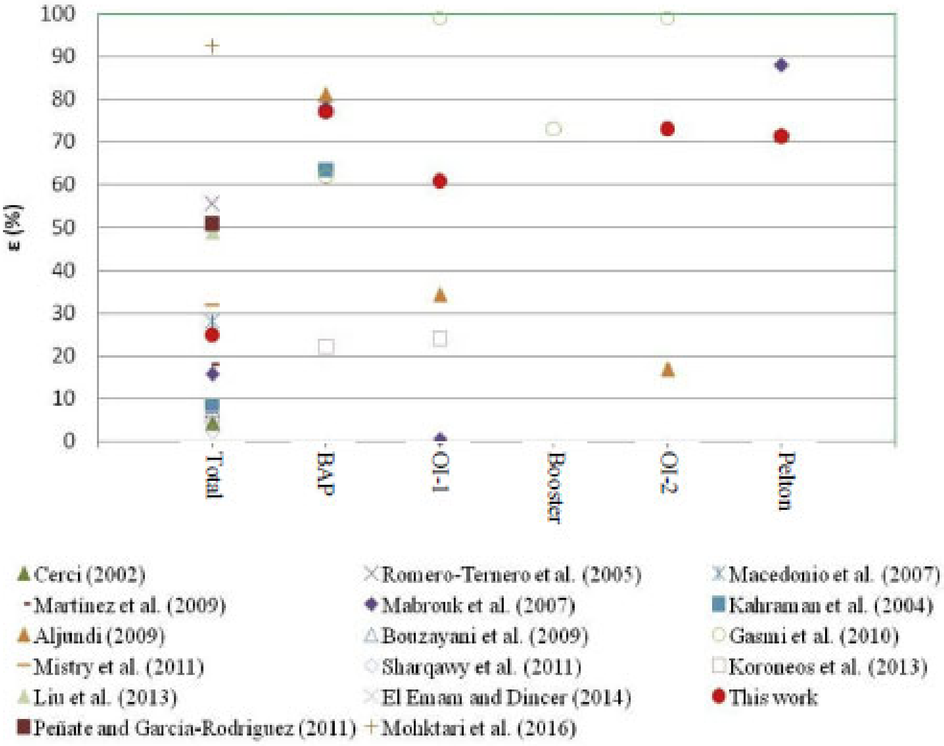

Figure 1.1.Total exergetic efficiency of reverse osmosis desalination plants and exergetic efficiency of the core components. Data from Literature. For references, see Publication 1.

In this figure, very dissimilar values are observed. For example, with respect to the exergetic efficiency of the total plant, the values vary from < 2% (Sharqawy et al., 2011), 4.3% (Cerci, 2002) to 48.91 % (Liu et al., 2013). In our first work, for similar conditions, we obtained, an exergy efficiency of 24.6 %. In high pressure pumps, the values of the exergy efficiency range from 20 % of (Koroneos et al., 2013) to 81 % of (Aljundi, 2009), with a value of 78 % in our work. And, in reverse osmosis membranes, the disparity is even greater, from 25 % of (Koroneos et al., 2013) to 99 % of (Gasmi et al., 2010), where our value was around 60 %.

Although the reverse osmosis processes presented by each article are not exactly the same, these enormous deviations can only be due to different conceptual definitions. On the one hand, the very definition of exergy efficiency differs from one author to another. In effect (Cerci, 2002; Sharqawy et al., 2011), defined the exergetic efficiency as the ratio of all exergy outflows to inflows. Other authors used the so-called rational or fuel-product exergy efficiency (Peñate & García-Rodríguez Lourdes, 2011; Romero-Ternero et al., 2005); But, in addition, within the definition of fuel-productg efficiency, a key factor is the identification of the fuel exergy value (the resources used) and the product exergy value (what is finally obtained). And we noted that some authors gave incorrect definitions to fuel and product exergy (Liu et al., 2013).

Moreover, in reverse osmosis modules, for example, where chemical separation takes place, chemical exergy plays an important role. And not all researchers take into account the variation of the chemical exergy of seawater as it passes through the reverse osmosis membrane. Another key issue is the thermodynamic model used in the calculation of thermodynamic properties. It has been observed in the literature that inadequate thermodynamic models and incorrect definitions of exergy efficiency lead to confusing and contradictory results: negative values of chemical exergy, exergy production in pumps, or higher irreversibilities in membranes than in pumps.

In order to clarify these contradictions, we set out to provide a precise and unambiguous definition of exergy efficiency in reverse osmosis desalination plant devices and to carry out a critical comparison of the results obtained with our definitions with what was found in the literature.

*Third publication: "Key issues on the exergetic analysis of $H_2O$/LiBr absorption cooling systems".*

Exergy efficiency is not the only concept on which there is a disparity of approaches among researchers when applying exergy analysis to a process: the identification of the dead state and the subsequent calculation of the exergy of a material stream are other important issues.

The dead state is understood as the final state after the considered interaction of the system and the environment towards equilibrium. For an open system, where energy and mass transfers can occur, the logical dead state of the system is characterized by the ambient pressure, the ambient temperature, and chemical equilibrium between the components of the system and the environment. Though, for a closed system, where there can be no mass transfer, chemical equilibrium will certainly not be attained. And, if the system is rigid, mechanical equilibrium does not have to be reached either.

A careful study of Prof. Richard Gaggioli´s writtings, a pioneer and world-wide recognized expert in exergy analysis, led us to an interesting approach that could be easily applied to refrigeration systems, for example (R.A. Gaggioli, 1983). This author, for a simple compression refrigeration machine proposes that the dead state pressure could be taken as the pressure that would be reached if the machine is turned off and the system is let to reach thermal equilibrium with the environment. This pressure would correspond to the saturation pressure of the coolant at room temperature.

We found it interesting to apply this idea to $H_2O$/LiBr absorption cooling systems, where the composition of the mixture changes as it passes through some devices, so that the change in chemical exergy can also play an important role. An in-deep literature review on papers related to the exergy analysis of single $H_2O$/LiBr absorption cooling systems revealed a disparity of methodologies. Most of the articles took the ambient pressure or similar values (1 bar, 1 atm) as the dead state pressure. But, other authors did not mention this parameter and in the work of (Salhi et al., 2018), the value of 0.01 bar was considered without justification. The reference temperature also adopted different values around 20, 25, 30 °C, or the ambient temperature. But (Jernqvist et al., 1992), considered that $T_0$ "may be chosen at a level where heat energy is considered worthless for an actual application" and they took the temperature of the medium on the heating side of the evaporator.

Another point of divergence was the inclusion or not of the chemical exergy of the streams in the analysis. (Misra et al., 2003), calculated the chemical exergy of the refrigerant (water) but did not consider the chemical exergy of the solution, because there is no chemical reaction in the process. Some authors were of a similar opinion. (Agarwal et al., 2019), pointed out that kinetic, potential and chemical exergy are negligible for a flowing stream in control volume, though they are not. (Gomri, 2009), argued that "because there is no departure of chemical substances from the cycle to the environment, the chemical exergy is zero". Other authors did not calculate it because they did not need it for the analysis, and some authors simply did not even mention it. In contrast, some articles carried out a detailed calculation of the chemical exergy of all substances and streams, but using different approaches (Cimsit et al., 2015; de Oliveira (Jr) & Le Goff, 1994; Koehler et al., 1988; Palacios-Bereche et al., 2012).

The definition of the exergetic efficiency in absorption cooling systems is, again, another controversial point regarding exergy analysis. The exergetic efficiency of the different components of the system is usually calculated in the literature, but the comparison of the results becomes difficult or complex due to the lack of uniformity in the methodology, as already pointed out.

In summary, from the literature review, three key points were identified in the exergy analysis of $H_2O$/LiBr absorption cooling systems:

a) the definition of the dead state,

b) the calculation of the exergy of the material streams, and

c) the definition of the exergy efficiency of the devices and of the overall system.

The third paper takes a detailed look at all these key aspects from the point of view of the methodology and the concepts: controversial and diverging hypothesis are cleared up and a comprehensive, coherent and consistent approach is proposed. The comparison with the literature presenting a complete and original method of the exergetic calculation of the absorption machine, is performed.

*Further methodological formulation: key aspects and common misconceptions in exergy analysis.*

The in-deep study of Prof. Richard Gaggioli´s writings led us to other additional key issues of the exergy analysis, where misconceptions can be found in the literature. In this work we have compiled the most significant aspects, from a conceptual point of view, and we have proposed reformulations of the concept. The method for this elaboration has consisted of:

a) Critical analysis of the concepts or definitions present in the literature.
b) Search in the sources: what do the pioneers of exergy analysis say about the subject?
c) Adoption of solutions consistent with the basic concepts.

In this work we have counted on the valuable contributions of Professor Gaggioli during the PhD student's stays, first at S. Diego State University (2017), and, subsequently, at Marquette University in Milwaukee (Wisconsin, USA), years 2018, 2019, 2021 and 2022.

The key points are as follows:

- Exergy is commonly defined as "*the maximum theoretical useful work (shaft work or electrical work) obtainable as the system interacts with the environment towards equilibrium, heat transfer occurring with the environment only*" (Bejan et al., 1996). - However, Gibbs originally referred to the concept of "available energy" in a wider sense (Gibbs, 1875). In discussions with Gaggioli, the idea of defining exergy not only in terms of the maximum useful work output, but also, why not, in terms of the maximum useful heat output, came up. And this idea is embodied in this work.
- The environment is usually modeled as a "*simple compressible system, large in extent, and uniform in temperature, $T_0$, and pressure, $p_0$*" (Bejan et al., 1996). And, for simplicity, typical environment conditions, such as $p_0$=101,3 kPa, $T_0$= 20-25 ºC are taken. The environment is also normally considered as composed of "*common substances existing in abundance within the Earth´s atmosphere, oceans, and crust*" (Bejan et al., 1996). However, in specific cases, these conventions may not be entirely correct and there is a danger of performing an exergy calculation that does not fit the practical circumstances (already pointed out with the example of the $H_2O$/LiBr absorption refrigeration system).
- Everyone recognizes that exergy cannot be negative. The limit case, of zero exergy, occurs when a system comes into equilibrium with the environment "spontaneously", without providing work. In this case, the initial capacity of the system to develop work is completely wasted. (Bejan et al., 1996). However, it is not uncommon to find negative physical exergy values in the literature. The authors justify this on the grounds that such

cases are those of systems that are initially at a pressure lower than that of the environment. As they evolve towards equilibrium, it is as if the environment has to do work on the system. This is somewhat incomprehensible, considering that exergy is "available energy". At least, the questions arise:  Is it really possible a negative value of exergy? And, in that case, what does it mean?

The theoretical formulation of the solutions, consistent with the basic concepts, is detailed in section 3.2. of this work. This part of the work has not been published yet. A fourth article covering all these ideas is under preparation.

## 1.2. THESIS LAYOUT

This Thesis is structured in five chapters (see Table 1.1.). The motivation and background of the research, along with the justification of the thematic unity of the Thesis, its organization and structure, are briefly introduced in chapter 1. The hypotheses and objectives are described in Chapter 2. The methodological principles for performing an exergy analysis, and the key aspects and common misconceptions in exergy analysis are identified and addressed in chapter 3. Two case studies are considered in the present study: the first one is a real system that includes a reverse osmosis desalination plant in operation. The second one is a theoretical system that includes a $H_2O$/LiBr absorption cooling system. The publications showing the results of the case studies are presented in chapter 4. Conclusions of the present research, together with the suggestions for future research work, are presented in Chapter 5. The contents of the Thesis are completed with an initial summary (both in Spanish and English) and the final presentation of the bibliographical references.

Table 1.1. Layout of the Thesis.

| | |
|---|---|
| Summary | Both in Spanish and English. |
| Chapter 1 | Motivation and background of the research. Justification of the thematic unity of the Thesis, its organization and structure. |
| Chapter 2 | Hypotheses and objectives. |
| Chapter 3 | Methodological principles for performing an exergy analysis, and key aspects and common misconceptions in exergy analysis. |
| Chapter 4 | Publications on the applications of the methodological principles and the identification of key aspects and misconceptions in the exergy analysis of two case studies: a real reverse osmosis desalination plant in operation and a $H_2O$/LiBr absorption cooling system. |
| Chapter 5 | Conclusions of the current study and suggestions for future work. |
| References | Final presentation of the bibliographical references. |

# 2. HYPOTHESES AND OBJECTIVES

**HYPOTHESIS 1:**

*Energy efficiency can be used to identify and quantify the thermodynamic inefficiencies of a process and to locate the most inefficient devices.*

A reverse osmosis desalination plant in operation is presented, with several similar operating lines, but with different configurations depending on the energy recovery components (Pelton turbines or pressure exchange devices), the number of reverse osmosis stages, the filtration and intake technologies or the components involved in feed water pressurization (high pressure pumps, pressure exchangers, booster pumps), located on the Atlantic coast of the island of Gran Canaria.

**Objective 1:**

Comparing, in terms of their exergy efficiency, similar devices, but with different operating configurations. In this way, the exergy efficiency will allow to identify and locate the most inefficient components (the most inefficient pump among the pumps, or the most inefficient reverse osmosis unit among the reverse osmosis units, for example). As a final objective, this parameter can be used to control and improve plant performance.

This goal is addressed by the publication: *"The exergetic efficiency as a performance evaluation tool in reverse osmosis desalination plants in operation." Desalination 413 (2017) 19–28.*

**HYPOTHESIS 2:**

*High deviations found in the literature in the values of the exergetic efficiency of reverse osmosis desalination plants, and core devices, can only be due to different conceptual definitions.*

The definition of exergy efficiency differs from one author to another. In addition, a key factor is the definition of the fuel exergy value (the resources used) and the product exergy value (what is finally obtained) for the correct definition of the so-called rational or fuel-product exergy efficiency. Moreover, in reverse osmosis modules, for example, where chemical separation takes place, chemical exergy plays an important role. Another key issue is the thermodynamic model used in the calculation of thermodynamic properties. It has been observed in the literature that inadequate thermodynamic models and incorrect definitions of exergy efficiency lead to confusing and contradictory results.

**Objective 2:**

Providing a precise and unambiguous definition of exergy efficiency in reverse osmosis desalination plant devices. Proposing the use of correct models for the calculation of the thermodynamic properties. And making critical comparisons of the results obtained with our definitions with what is found in the literature.

These goals are addressed by the publication: *"A critical review of definitions for exergetic efficiency in reverse osmosis desalination plants". Energy 137 (2017) 752-760.*

**HYPOTHESIS 3:**

*From a literature review, three key points in exergy analysis are identified:*
*a) the definition of the dead state,*
*b) the calculation of the exergy of the material streams, and*
*c) the definition of the exergy efficiency of the devices and of the overall system.*

As a case study, the single effect $H_2O$/LiBr absorption refrigeration system is used. The literature review shows a large discrepancy in the conceptual formulation of the exergy analysis of the absorption refrigeration cycle by various authors. This raises a problem when carrying out validations and formulating comparisons.

**Objective 3:**

Clearing up controversial and diverging hypothesis related to the exergy analysis of a single effect $H_2O$/LiBr absorption refrigeration system. Formulating a comprehensive, coherent and consistent approach. Presenting a complete and original method of the exergetic calculation of the absorption machine. Comparing the results with those of the literature.

These goals are addressed by the publication: *"Key issues on the exergetic analysis of $H_2O$/LiBr absorption cooling systems". Case Studies in Thermal Engineering 28 (2021) 101568.*

**HYPOTHESIS 4:**

*Avoiding common misconceptions:*

- *Exergy is certainly the maximum useful work output, but it could also be considered as the maximum useful heat output.*
- *Definitions of the dead state not in line with practical circumstances.*

- *Does a negative physical exergy value make sense?*

**Objective 4:**

To critically analyze the definitions, present in the literature. Looking at the sources: what do the pioneers of exergy analysis have to say about the subject? Adoption of solutions consistent with the basic concepts.

These goals are addressed by section 3.2.: *KEY ASPECTS AND COMMON MISCONCEPTIONS IN EXERGY ANALYSIS.*

# 3. METHODOLOGY

Exergy represents the available energy of a system. It can be defined as the maximum useful amount of energy that could be get when the system interacts with the environment towards equilibrium. Following, the methodological principles for performing an exergy analysis are presented below (section 3.1). Also, key aspects and common misconceptions in exergy analysis are identified and addressed (section 3.2).

### 3.1. EXERGY ANALYSIS

An exergy balance at steady state conditions for a control volume can be formulated as:

$$\frac{dEx_{VC}}{dt} = \sum_{i}\left(1-\frac{T_0}{T_j}\right)\cdot \dot{Q}_j - \left(\dot{W}_{VC} - p_0\frac{dV_{VC}}{dt}\right) + \sum_{i}\dot{m}_i ex_i - \sum_{e}\dot{m}_e ex_e - \dot{E}x_D \quad (1)$$

where,

$\frac{dEx_{VC}}{dt}$ is the time rate of change in the exergy of the control volume.

$$\dot{E}x_{q,j} = \left(1-\frac{T_0}{T_j}\right)\cdot \dot{Q}_j \quad (2)$$

Is the exergy transfer associated with the time rate of heat transfer, $\dot{Q}_j$,at the location on the boundary of the control volume where the instantaneous temperature is $T_j$.

$\dot{W}_{VC}$ accounts for the time rate of exergy transfer by work other than flow work. The associated exergy transfer is given by:

$$\dot{E}x_w = \dot{W}_{VC} - p_0\frac{dV_{VC}}{dt} \quad (3)$$

$\frac{dV_{VC}}{dt}$ represents the time rate of change of volume of the control volume itself.

$\dot{m}_e ex_e$ and $\dot{m}_i ex_i$ are the time rate of exergy transfer at the outlet and inlet, respectively.

$\dot{E}x_D$ is the time rate of exergy destruction due to irreversibilities within the control volume.

At steady state, $\frac{dEx_{VC}}{dt} = 0$ and $\frac{dV_{VC}}{dt} = 0$, so, the exergy balance reduces to:

$$0 = \sum_{j}\left(1-\frac{T_0}{T_j}\right)\cdot \dot{Q}_j - \dot{W}_{VC} + \sum_{i}\dot{m}_i ex_i - \sum_{e}\dot{m}_e ex_e - \dot{E}x_D \quad (4)$$

In this equation can be seen that the rate at which exergy is transferred into the control volume exceeds the rate at which exergy is transferred out in the rate at which exergy is destroyed within the control volume due to irreversibilities. Simplified, it becomes:

$$0 = \sum_j \dot{E}x_{q,j} - \dot{W}_{VC} + \sum_i \dot{E}x_i - \sum_e \dot{E}x_e - \dot{E}x_D \tag{5}$$

where: $\dot{E}x_e = \dot{m}_e ex_e$ and $\dot{E}x_i = \dot{m}_i ex_i$ are the exergy transfer rates at outlet and inlet, respectively.

### *3.1.1. Estimation of the exergy of the working fluids*

The exergy of the working fluid at different points of the process has to be calculated. The exergy of a fluid, in the absence of electrical, magnetic, nuclear or surface tension effects, consists of four components: kinetic, potential, physical and chemical. And, when the kinetic and potential effects are negligible, it is enough to obtain the physical and chemical components of the exergy. Moreover, when the scope of the exergy analysis is limited to obtaining the destroyed exergy, the application of the Gouy- Stodola equation is sufficient and it is not necessary to calculate the chemical exergy of the working fluid. Similarly, if in a process there is no change in the composition of the fluid, no chemical reaction, and no separation of its components, the calculation of chemical exergy is not required since its value does not change.

The physical component of the exergy of a stream of matter per unit mass, $ex^{PH}$, is given by (Hatsopoulous & Keenan, 1965):

$$ex^{PH} = (h - h_0) - T_0(s - s_0) \tag{6}$$

where $h$ and $s$ are the specific enthalpy and entropy values of the fluid at the operating pressure and temperature, respectively. The subscript "*0*" indicates that the value of the properties is obtained at the dead state pressure and temperature conditions ($p_0$ and $T_0$).

Chemical exergy is "*the maximum work that can be achieved when a substance is driven from its equilibrium state at the environment pressure and temperature (dead restricted state) to the equilibrium state of equal chemical potentials (dead unrestricted state) by means of processes that involve heat, work and mass transfers with the environment*" (Palacios-Bereche et al., 2012). For a mixture or solution, it is obtained, at the pressure and temperature conditions of the dead state ($p_0$ and $T_0$), by means of (Ahrendts, 1977):

$$ex^{CH} = \sum_i \chi_i \left(\mu_{i,0} - \mu_{i,0}^{*}\right) \tag{7}$$

where $\mu_{i,0}$ (kJ/kg) is the chemical potential of "*i*", at $p_0$ and $T_0$, when the composition is that of the state under consideration, $\mu_{i,0}^{*}$ (kJ/kg) is the chemical potential of "*i*" when, at $p_0$ and $T_0$, the system reaches chemical equilibrium with the environment, $\chi_i$ is the mass fraction of component "*i*".

As it follows from equations (6) and (7), for the calculation of exergy, it is essential to accurately obtain the thermodynamic properties of the fluid: enthalpy, entropy and chemical potential.

### *3.1.2.* Definition of Exergetic efficiency.

The exergetic efficiency of a device or process is a parameter whose calculation can be ambiguous and confusing due to the lack of uniformity that appears in the literature. In this Doctoral Thesis work, special interest is placed on applying the concept correctly and generating relationships that can be unequivocally applied by researchers, facilitating the bibliographic comparison.

In the early days of the development of the exergy method (period 1940-1980 approx.) there was broad consensus among researchers to use the concept of exergy efficiency as rational exergy efficiency or "*fuel-product*" efficiency, $\varepsilon$. This definition considers the relationship between the exergy of the desired product, $\dot{E}x_P$, and the exergy resources used to generate it, or fuel exergy, $\dot{E}x_F$, (Hatsopoulous & Keenan, 1965; Pettit & Gaggioli, 1980; Tsatsaronis, 1993):

$$\varepsilon = \frac{\dot{E}x_P}{\dot{E}x_F} \tag{8}$$

The *fuel-product* expression is consistent with the conventional definition of energy efficiency, which relates energy produced to energy consumed. It presents the difficulty of defining fuel and product, which depend on the operating purpose.

Lazzareto and Tsatsaronis (Lazzaretto & Tsatsaronis, 2006) define in detail, for a given device, which exergy terms are to be considered as part of the fuel or as part of the product:

*"The product is defined to be equal to the sum of*

- *all the exergy values to be considered at the outlet (including the exergy of energy streams generated in the component) plus*
- *all the exergy increases between inlet and outlet (i.e. the exergy additions to the respective material streams) that are in accord with the purpose of the component.*

*Similarly, the fuel is defined to be equal to.*

- *all the exergy values to be considered at the inlet (including the exergy of energy streams supplied to the component) plus*

- *all the exergy decreases between inlet and outlet (i.e. the exergy removals from the respective material streams) minus*

- *all the exergy increases (between inlet and outlet) that are not in accord with the purpose of the component."*

Exergy increases and decreases refer mainly to increments or reductions in the exergy of a mass flow, associated with a change either of the physical exergy or of the chemical exergy.

After introducing the exergy of the fuel and product, the exergy balance for the *k-th* component becomes:

$$\dot{E}x_{F,k} = \dot{E}x_{P,k} + \dot{E}x_{D,k} + \dot{E}x_{L,k} \tag{9}$$

where $\dot{E}x_{F,k}$represents the exergy of the fuel, i.e, the resources expended to generate the product, $\dot{E}x_{P,k}$. $\dot{E}x_{D,k}$is the exergy destructed within the component and $\dot{E}x_{L,k}$stands for the exergy losses.

Regarding to a single component, exergy losses are due to heat losses or to material stream losses. When the temperature of the system boundaries is set to the temperature of the reference environment, $T_0$, heat losses are not considered.

The exergy balance for the total system is, then:

$$\dot{E}x_{F,tot} = \dot{E}x_{P,tot} + \sum_{k} \dot{E}x_{D,k} + \dot{E}x_{L,tot} \tag{10}$$

where global inputs and outputs of the system are considered.

As the application of exergy analysis became more widespread, a second definition appeared, for some cases where it could be difficult or impossible to find a "*product*". It is the so-called "*input-output*" exergy efficiency, $\eta_{ex}$, where the exergy of the outflows is divided by the inflows (Lior & Zhang, 2007; Marmolejo-Correa & Gundersen, 2012; Moran, 1989):

$$\eta_{ex} = \frac{\sum Exergy\ out}{\sum Exergy\ in} \tag{11}$$

Lior and Zhang, 2007, suggest the use of this expression for processes where most of the outputs are useful. Moran, 1989, indicates its use also in dissipative elements, such as throttling valves.

In our opinion, this second definition is not free of conceptual conflict, such as the lack of sense that the calculation of an exergy efficiency in an expansion valve may have, just as an energy efficiency could not be defined, because its mission is to dissipate energy, not to produce it.

Moreover, the appearance of this definition of "*input-output*" coincided with the massive, exponential extension of the application of exergy analysis to all types of processes, which led to great confusion. Many researchers began to use "*input-output*" exergy efficiency without discrimination and without adequately reasoning the existence of a fuel and a product in their devices or processes.

*Dissipative components*

It could be argued that for some elements, such as expansion valves, it is not possible to obtain a "*fuel-product*" exergy efficiency value, since they are merely dissipative elements, without a product. But the fact is that it is not possible to define an energy efficiency for them either, precisely because their mission is to dissipate energy, not to produce it. Therefore, it may not make much sense to speak, in general, of exergy efficiency in these devices. One approach to addressing the inclusion of these elements in the exergy analysis and in the calculation of an exergy efficiency is proposed by Tsatsaronis (Tsatsaronis, 1993). This author indicates that, since expansion valves serve other devices, when formulating exergy efficiency, the valve and the device they serve should be considered together.

## 3.2. KEY ASPECTS AND COMMON MISCONCEPTIONS IN EXERGY ANALYSIS.

Although the theoretical foundations of exergy analysis were already formulated before the 1970s, their practical application has led to the emergence of numerous procedures that are not free of controversy and disparity (Sciubba & Wall, 2007; Tsatsaronis, 2007). The exponential growth, since 2000, of publications applying these methodologies, often without sufficient critical reflection, has only generated greater ambiguity in exergy analysis, such that, today, not all published articles follow a rigorous and reliable conceptual method.

There are several concepts that are confused in the bibliography, on which we have elaborated here what could be called a body of knowledge or thought. The method for this elaboration has consisted of:

a) Critical analysis of the concepts or definitions present in the literature.

b) Looking to the sources: what do the pioneers of exergy analysis have to say about the subject?

c) Adoption of solutions consistent with the basic concepts.

This work has been enriched by the contributions of Professor Gaggioli (pioneer in this type of studies) during the PhD student's stays at Marquette University in Milwaukee (Wisconsin, USA), years 2018, 2019, 2021 and 2022.

The key points on which the articles already published and others pending publication have been elaborated are presented here.

### *3.2.1. Exergy as useful work and useful heat.*

In any more or less recent book on thermodynamics (since 1980), and in the scientific works being published since then, exergy is understood as the maximum conceivable production of useful work, when a system interacts with the environment until equilibrium between the two is reached.

This suggests that exergy certainly *represents* the maximum useful work output, but it will be shown herein that it also *represents* the maximum useful heat output. This will be illustrated graphically in Figures 3.1 and 3.2.

Figure 3.1 shows a system consisting of air at a given pressure and temperature, ($p_1$, $T_1$) both higher than the ambient, ($p_0$, $T_0$). In order to calculate the maximum useful work that this system could release while interacting with the environment towards equilibrium, the following reversible process could be employed: the system evolves first isentropically down to $T_0$, and then isothermally down to $p_0$. The work delivered in the process is the area under curve 1→0 and the

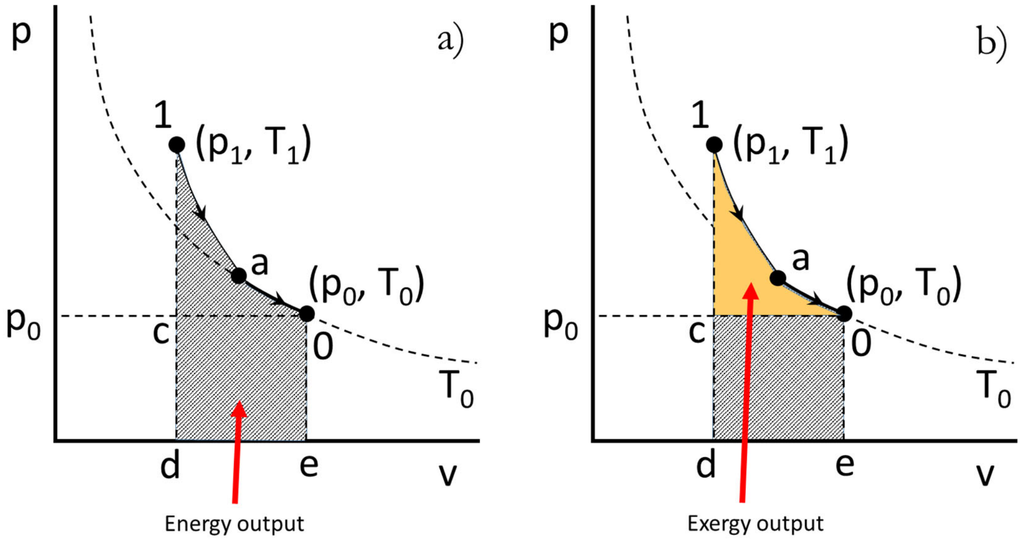

Figure 3.1 Graphical representation of the work exchanged in the process 1→a→0, where air evolves towards equilibrium with the environment.

x-axis in Figure 3.1-a), $\int pdv$, area (1-d-e-0-1). However, not all of that work is *useful* work, since some of that work is absorbed by the environment, area (c-d-e-0-c). The useful work is just the orange area in Figure 3.1-b), area (1-c-0-1). And this useful work is equal to exergy. So exergy represents not the maximum work output but the maximum *useful* work output.

But, similarly, we can argue using Figure 3.2, which represents the heat exchanged when the same system evolves from the state ($p_1$, $T_1$) to reach equilibrium with the environment, ($p_0$, $T_0$). In this example, the system evolves first at constant volume down to $p_0$, and then at constant pressure, down to $T_0$.

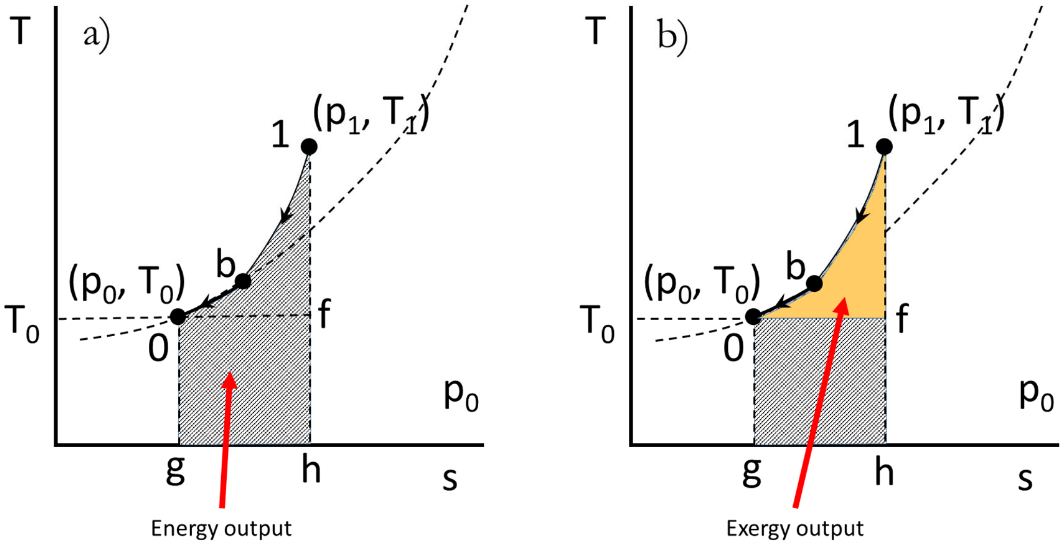

Figure 3.2. Graphical representation of the heat exchanged in the process 1→b→0, where air evolves towards equilibrium with the environment.

The heat given up corresponds to the area under the curve 1→0 and the x-axis in diagram 3.2-a), area (1-0-g-h-1), If this heat were applied to a heat pump, for example, the heat deliverable corresponds to the yellow area (1-0-f-1) in Figure 3.2-b), since part of the heat will be uselessly absorbed by the environment. And this useful energy corresponds, once again, to exergy.

But exergy of state 1 is fix, and so is exergy of state 0 (null). It means that the energy useful output of both processes must be the same, the yellow areas of both figures must be the same (when drawn to scale). In every representation of the exergy, whether on the Ts diagram or pv diagram, the area representing the exergy is bounded by lines of constant $v$, constant $p_0$, constant $T_0$ and constant $s$.

Thus, it is demonstrated that the exergy is not simply the maximum useful work output, but also the maximum useful heat output. That is, heat could also be used to quantify exergy. Therefore, a more coherent definition of exergy might be: the maximum net energy transfer that can be attained from the system and the environment, until equilibrium is reached. This reasoning does not appear, to date, in any book or article and is part of the content of an article currently in preparation.

### *3.2.2. The dead state.*

When the pressure, temperature, composition, velocity or level at which a system is found is different from that of the environment, there is a possibility that the system will develop work by interacting with the environment. As the properties of the system approach those of the environment, this possibility decreases, disappearing completely when the equilibrium is reached. This state of the system is called the *dead state*. In this state the system possesses an energy, but its exergy is zero, since it cannot interact with the environment because it is in equilibrium with it.

Exergy is a measure of the deviation of the state of a system from the state under the conditions of the environment, therefore, it is an attribute of both together: of the system and of the environment. Hence the importance of the correct definition of the environment when calculating the exergy of a system.

Conventionally, almost all authors take as dead state conditions the pressure and temperature of a reference environment, as a rule: $p_0$=101,3 kPa, $T_0$= 20-25 ºC. For the calculation of chemical exergy, more or less complex formulations have been developed in which a reference environment is defined, consisting of a set of conveniently selected substances. (Ahrendts, 1977; Diedrichsen, 1991; Szargut et al., 1988). However, in specific cases, these conventions may not be entirely correct and there is a danger of making an exergy calculation that is not in line with practical circumstances. For example:

- In air-conditioning processes, subject to outside air inlets of changing conditions, it may not make much sense to take as ambient conditions a fixed value of $p_0$=101,3 kPa, $T_0$= 20-25 ºC. Instead, it seems more logical to take, at least for the temperature, the value of the outside air at any given time, as the dead state condition (Blanco-Marigorta et al., 2021). Something similar happens in desalination processes, with respect to the input of salt water from the environment.

- Some systems may be conveniently divided into subsystems, and consider different dead state conditions depending on the subsystem in question. This is especially practical in refrigeration systems, where the cooling fluid is confined. No matter how much it evolves, it will never be able to reach a mechanical or chemical equilibrium with the environment, only thermal equilibrium will be possible (Richard A. Gaggioli, 1983). This author, for a simple compression refrigeration machine proposes that the dead state temperature is taken as the ambient temperature, but as pressure, the pressure that would be reached if the machine is turned off and let the system reach thermal equilibrium with the environment. This pressure would correspond to the saturation pressure of the coolant at room temperature. Although logical, it has not been found that any article in the subsequent literature uses this approximation.

  Something similar happens in absorption refrigeration machines, Figure 3.3. An extensive literature review has shown that there is no article in the literature that uses as dead state conditions for the solution circulating inside the machine, a pressure other than that of the environment. However, this does not seem to be very well founded, since the interior fluid, no matter how much it evolves until it reaches equilibrium with the environment, will never be able to achieve mechanical equilibrium. In this dissertation work, the dead state pressure is proposed as the pressure that would be reached when the machine stops and reaches the ambient temperature. (Value that the dynamic study of absorption refrigeration machines by (Viswanathan et al., 2012), has shown to be close to the low cycle pressure).

  Similarly, it does not seem to be very well founded, for the calculation of the chemical exergy of the solution circulating inside the machine, to choose as the composition of the dead state, that of a reference environment taken by convention, which, on the other hand, is what always appears in the literature, since that fluid, being confined, will never reach chemical equilibrium with the environment. In this work, the composition of the dead state of the solution is proposed as that corresponding to the chemical equilibrium between the solution and the coolant at the ambient temperature. This also constitutes a novel contribution of this dissertation.

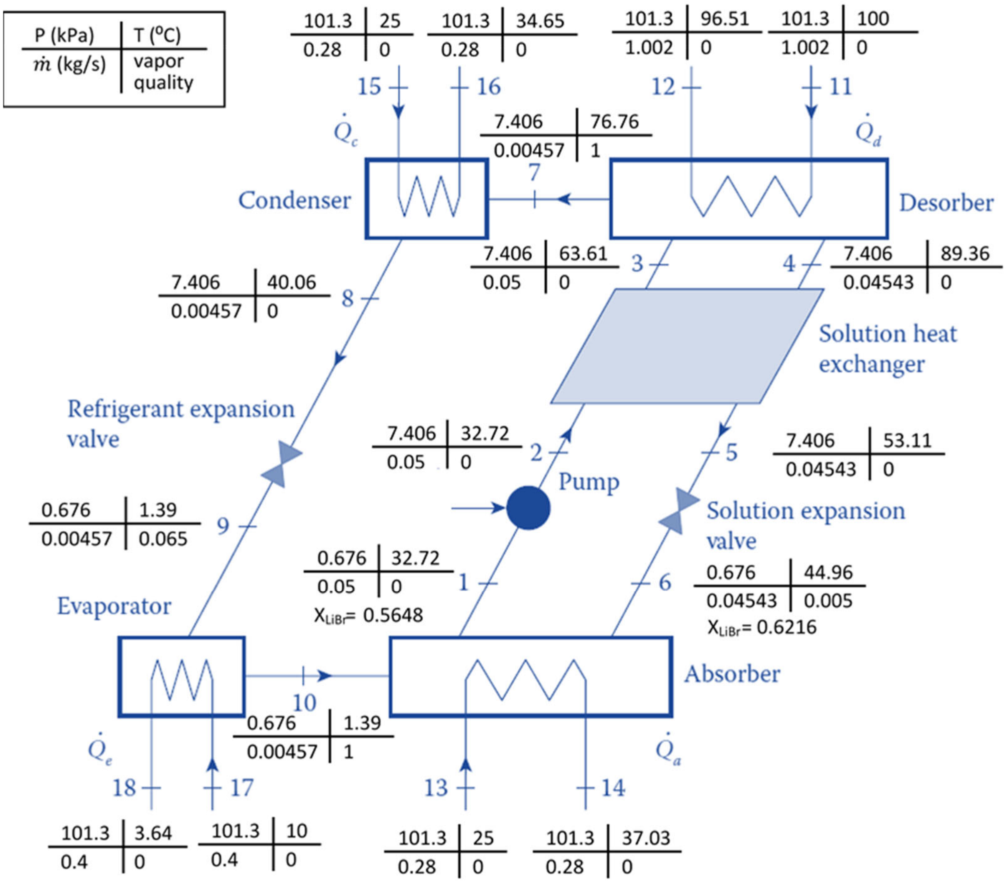

Figure 3.3. Schematic and operation conditions for the simple absorption $H_2O$/LiBr refrigeration cycle (Herold et al., 2016).

### 3.2.3. *Does a negative physical exergy value make sense?*

As everyone recognizes, exergy can be destroyed and is generally not conserved. The limiting case occurs when exergy is completely destroyed, which would occur if a system were brought to equilibrium with the environment "spontaneously" without providing work. In that case, the capacity to develop work that exists initially is completely wasted. Since no work has to be provided for a spontaneous process to take place, we can say that the value of exergy is at least zero and therefore cannot be negative, (Bejan et al., 1996).

However, it is not uncommon to find negative physical exergy values in the literature. The authors justify this on the grounds that such cases are those of systems that are initially at a pressure lower than that of the environment. As they evolve towards equilibrium, it is as if the environment has to do work on the system. This is somewhat incomprehensible, considering that exergy is "available energy". At least, the questions arise: What is the sense of a negative available energy? Could it be that the conditions of the chosen dead state are wrong?

In discussions with Gaggioli, referred to above, it has been concluded that it is not that physical exergy can be negative, but that sometimes exergy follows a direction opposite to the flow of matter, which gives it a negative value, from the quantitative point of view.

This can be illustrated by the example in Figure 3.4. A tank, initially filled with air, is connected to a vacuum pump, in order to extract air from the tank and obtain a vacuum pressure in the tank. In the final state, the tank will certainly have no air, but will it have exergy? It can be shown that it does. Suppose that the engine, G, were reversible, and that the pump were reversible, so that it could work as a turbine Figure 3.5.

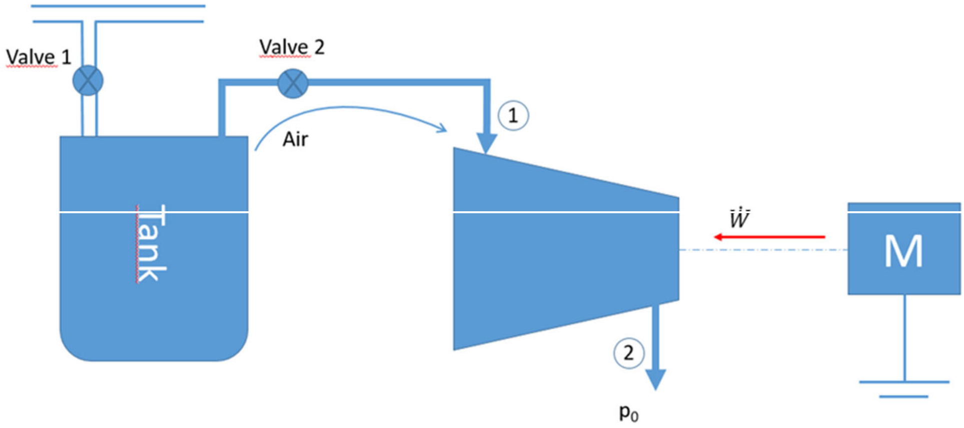

Figure 3.4. Tank filled with air connected to a vacuum pump.

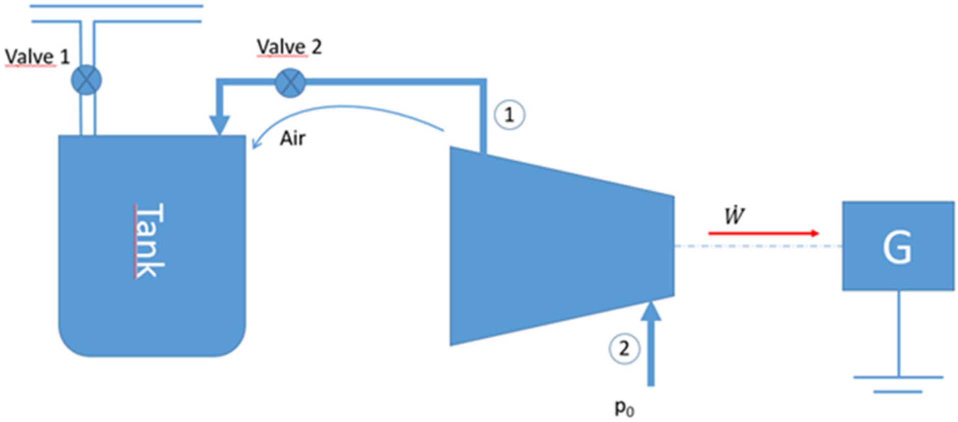

Figure 3.5. Vacuum tank connected to a turbine.

If valve 2 is opened, air flows into the tank, moving the turbine and supplying power to the generator. But where does this exergy come from? It cannot come from the environment, since the exergy of the environment is zero. It must come from the tank. This means that the air flows into the tank, but the exergy flows in the opposite direction, towards the generator (Figure 3.6.-a).

While creating the vacuum, the air was flowing out of the tank, but the exergy was flowing into the tank (Figure 3.6-b).

Therefore, here we have two processes in which, clearly, the exergy follows a direction opposite to the flow of matter.

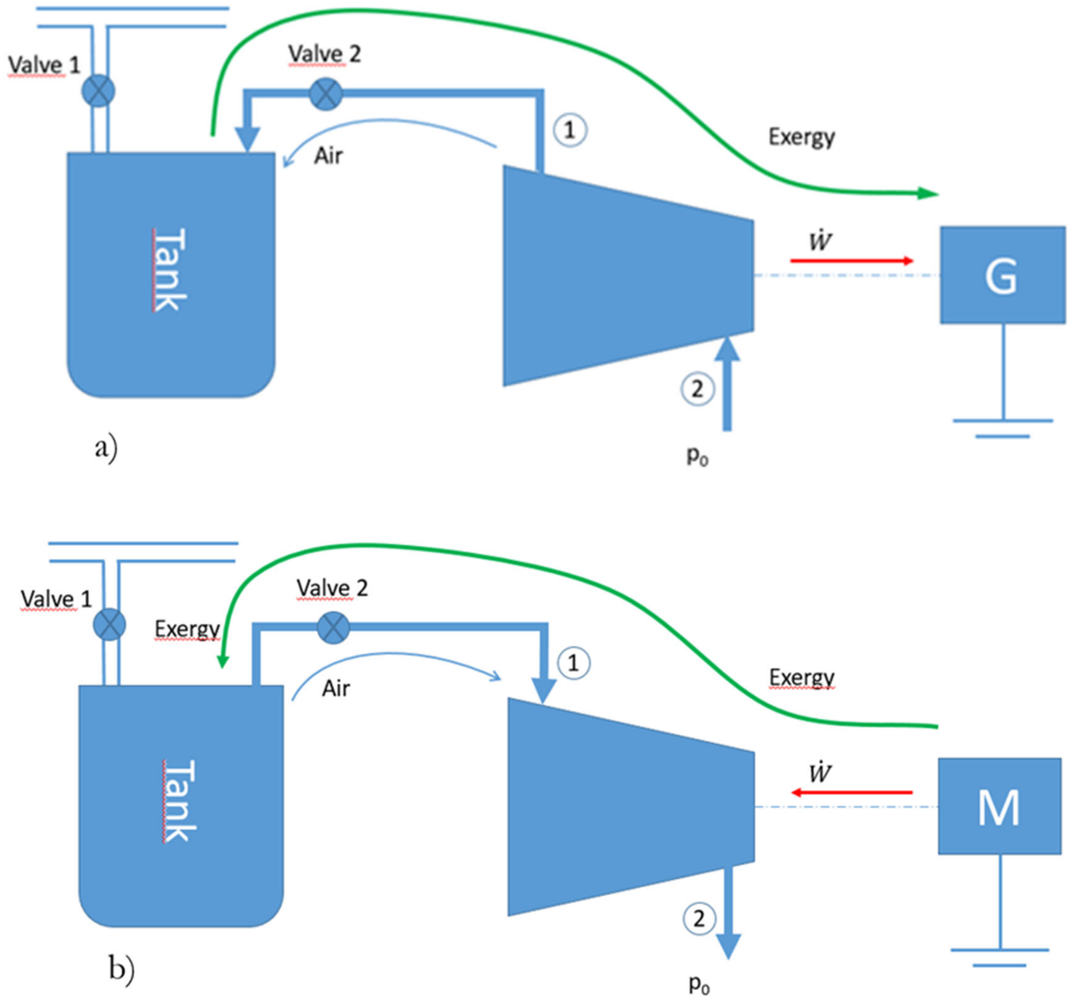

Figure 3.6. Exergy flowing in the opposite direction to air. a) Air flowing through the turbine to the tank, b) creating a vacuum in a tank through a pump.

This reasoning is also a clear contribution of this dissertation to the body of knowledge on exergy analysis, which cannot be found anywhere else, and which will be published shortly, in collaboration with Prof. Gaggioli.

# 4. PUBLICATIONS

## 4.1. The exergetic efficiency as a performance evaluation tool in reverse osmosis desalination plants in operation.

*Article:* The exergetic efficiency as a performance evaluation tool in reverse osmosis desalination plants in operation.

*Authors:* A.M. Blanco-Marigorta, A. Lozano-Medina, J.D. Marcos.

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*Position:* 2/90.
*Category:* Water Resources.

### Abstract

Exergetic efficiency characterizes the performance of a system or a system component from the second-law of Thermodynamics viewpoint. Although this parameter can be used in the comparison of the operation of similar components working under similar conditions, there are not many articles in the literature dealing with this purpose. In this paper, a desalination plant located in Gran Canaria (Canary Islands, Spain) is considered. Different configurations are possible in the ten reverse osmosis production lines of the plant, depending on the procedure used for the energy recovery, the number of reverse osmosis stages, the technologies applied to the intake and filtration processes, or the components involved in feed water pressurization. Using real data, the exergetic efficiency is assessed as a performance evaluation tool. Through the comparison of the exergetic efficiency of similar devices, though different production lines, the components with operation defects that should be repaired are identified: the most inefficient pelton turbines, intake pumps, high pressure pumps, booster pumps, reverse osmosis membrane modules, and pressure exchanger modules. This way, exergetic efficiency can be successfully used to control and to improve the operation of the plant.

### Summary of the PhD student's contributions

The work has been entirely prepared by the PhD student. She is responsible for the conceptualization, methodology, data treatment, analysis of results, conclusions and preparation of both the draft and the final paper. In the design of the process, she has had the collaboration of an engineer of the plant (A. Lozano-Medina). The supervision of the whole work has been in charge of the director of the Thesis, J. Daniel Marcos.

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# The exergetic efficiency as a performance evaluation tool in reverse osmosis desalination plants in operation

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ABSTRACT

Exergetic efficiency characterizes the performance of a system or a system component from the second-law of Thermodynamics viewpoint. Although this parameter can be used in the comparison of the operation of similar components working under similar conditions, there are not many articles in the literature dealing with this purpose. In this paper, a desalination plant located in Gran Canaria (Canary Islands, Spain) is considered. Different configurations are possible in the ten reverse osmosis production lines of the plant, depending on the procedure used for the energy recovery, the number of reverse osmosis stages, the technologies applied to the intake and filtration processes, or the components involved in feed water pressurization. Using real data, the exergetic efficiency is assessed as a performance evaluation tool. Through the comparison of the exergetic efficiency of similar devices, though different production lines, the components with operation defects that should be repaired are identified: the most inefficient pelton turbines, intake pumps, high pressure pumps, booster pumps, reverse osmosis membrane modules, and pressure exchanger modules. This way, exergetic efficiency can be successfully used to control and to improve the operation of the plant.

## 1. Introduction

Freshwater is not evenly distributed across the globe, and it is not available in sufficient quantity, where and when needed. Therefore, desalination of sea water and brackish water, are essential to provide freshwater to a large number of populations and communities around the world. There are countries like Qatar and Kuwait which are 100% supplied with desalinated water [1]. Also, some islands of the Caribbean or the Mediterranean rely heavily on desalination for drinking water, for agriculture or for industrial processes [2]. In the Canary Islands (Spain), the uneven distribution of rainfall and the population increase have made necessary the development of desalination systems since the 60s.

Water and energy are closely linked. According to Olsson [3], water and energy should take a parallel planning. The production and treatment of water require energy, and the conversion of primary energy requires water. With regard to desalination, energy needs vary considerably depending on the process and technology. In general, thermal processes require more energy than membrane-based processes, such as reverse osmosis (RO) or nanofiltration.

The first desalination plants in the Canary Island were distillation plants, and this was the predominant technology well into the 80s [4]. Then, distillation plants gave way to reverse osmosis systems, which is a more efficient technology from a productive and economic point of view. Reverse osmosis is the current technology in almost all of the plants located in the Canary Islands.

Energy optimization of desalination processes has led to significant reductions in energy consumption. Related to reverse osmosis processes, energy consumption has dropped from 20 $kWh/m^3$ in the 70s to $<2$ $kWh/m^3$ nowadays [5]. Several factors can be given for these significant achievements: membrane developments, pump efficiency improvements, the use of variable-frequency drives, or the implementation of energy recovery devices, such as hydraulic turbines or pressure exchangers, in order to recover the energy of the brine.

Exergy analysis is a widely accepted methodology for the characterization and optimization of energy systems. This second law analysis identifies thermodynamic inefficiencies in a process and their locations. One interesting parameter that characterizes the performance of an energy system from the thermodynamic viewpoint is the exergetic efficiency. The difference between the actual value of the exergetic efficiency –as percentage- and 100% represents the exergy provided to a system that has been wasted in this system as exergy destruction and exergy losses.

The application of exergy analysis to desalination plants date back to the 1960s: In 1963 Tribus and Evans [6] presented a wide report with the thermoeconomics of sea-water conversion. Later on, in 1970, El

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**Nomenclature**

| | |
|---|---|
| BP | Booster pump |
| DWEER | *Dual Work Exchanger Energy Recovery* |
| ERI | Pressure exchanger from *Energy Recovery Inc.* |
| HPP | High pressure pump |
| PES | Pressure exchanger |
| RO | Reverse osmosis |
| $e$ | Specific exergy, kJ/kg |
| $\dot{E}$ | Exergy flow rate, kW |
| $\varepsilon$ | Exergetic efficiency |
| $h$ | Specific enthalpy, kJ/kg |
| *in* | Inlet |
| $\dot{m}$ | Mass flow rate, kg/s |
| *out* | Outlet |
| $p$ | Pressure |
| $s$ | Specific entropy, kJ/kg·K |
| $T$ | Temperature, K |
| $\dot{V}$ | Volumetric flow, $m^3/s$ |
| $\dot{W}$ | Electric power, kW |
| $y^*$ | Exergy ratio |

*Subscripts and superscripts*

| | |
|---|---|
| *0* | Dead state |
| CH | Chemical |
| *D* | Destruction |
| *F* | Fuel |
| *i* | *i*-th material stream |
| *k* | *k*-th component |
| *L* | Loss |
| *P* | Product |
| PH | Physical |
| RO | Reverse osmosis |
| *tot* | Total |

Sayed and Aplenc [7] analyzed and optimized a vapor-compression desalination process by the application of a thermoeconomic approach. Since then, many related papers have been published.

Just concerning reverse osmosis desalination plants in operation, first exergy analysis was performed by Cerci [8] on a brackish water plant, which had a production of 7250 $m^3/d$. The process had just one RO stage, and the brine flowed through throttling valves directly into the ocean. In their results, the membrane modules were responsible for the greater exergy destruction of the system. The exergetic efficiency of the whole plant was reported as 4.3%. The introduction of a pressure exchanger on the brine stream increased this value to 4.9%. Kahraman et al. [9] presented also an exergy analysis of a brackish water RO desalination plant in operation. They calculated the exergy destruction within all the components. The largest exergy destruction occurred in separation units and in the pumps. The total RO unit presented an exergetic efficiency of 8.0%. They proposed that the cost of desalination could be significantly reduced with the use of variable frequency drives and high-efficiency pumps. Romero-Ternero et al. [10] applied an exergy analysis to a seawater RO desalination plant in operation with a production capacity of 21,000 $m^3/d$ placed in Tenerife (Canary Islands). The RO process had just one stage, but it operated already with Pelton turbines. They found that 80% of the exergy destruction occurred in main components (high-pressure pumps, regulation valves, RO modules, and energy recovery devices); 48% of this amount corresponded to the high-pressure pump and the Pelton turbine. Mabrouk et al. [11] presented an exergoeconomic analysis of several desalination plants in operation located in the Suez Gulf region, including a RO plant. Aljundi [12] analyzed thermodynamically the brackish water RO plant of Al-Hussein using actual plant data. In their calculations, the throttle valves were responsible for the highest exergy destruction followed by the two-stage RO units. The exergetic efficiency of the plant was only 4.1%. They proposed the use of high-efficiency pump/motor set-up with a variable frequency drive, and the replacement of the traditional throttling valves with energy recovery devices. Gasmi et al. [13] optimized the energy consumption of a RO desalination plant in operation using exergy analysis and exergetic efficiency. The plant had a capacity of 30,00 $m^3/d$ and four double stage RO lines, but they did not performed a comparison between similar devices in the different lines. They just indicated the percentage of exergy destroyed in each device with and without several design improvements, like the use of booster interstage pumps, Pelton turbines or pressure exchangers. Peñate and García-Rodríguez [14] analyzed the reduction of specific energy consumption in seawater reverse osmosis desalination plants in operation using energy recovery devices instead of Pelton turbines. Their study was technically and thermoecono-mically justified. Also related with energy recovery devices is the work of Al-Zahrani et al. [15]. They showed the variation of some indicators (specific energy consumption and recovery ratio) with salinity, temperature, and pressure. They summed up the relevance of energy recovery devices when salinity of feed water is high. Sharqawy et al. [16] proposed a new formulation for the calculation of seawater thermodynamic properties, exergy among others. They demonstated the deficiencies of previous ideal mixture models in calculation of the flow exergy and the exergetic efficiency. Nevertheless, they still obtained a very low second law efficiency for a reverse osmosis desalination plant (<2%), even when energy recovery devices were used. Therefore, they suggested the pressure retarded osmotic method as energy recovery technology. With it, an exergetic efficiency of 20% and an input power reduction of 38% were obtained. Mistry et al. [17] calculated the total entropy generation in various desalination systems, including RO. They concluded that the definition of the useful exergy output of the system is crucial to set out the Second Law efficiency. For desalination systems, this is the minimum least work of separation required to extract a unit of water from a feed stream of a given salinity. El-Emam and Dincer [18] used Thermoeconomic analysis to obtain the performance of a RO plant as a function of salinity. The exergy analysis showed that the largest irreversibilities occurred in the RO module and the high-pressure pump. A second law efficiency of 5.82% was obtained for the base case. An actual 127 ton/h two pass RO desalination plant was studied by Eshoul et al. [19] with the seawater solution treated as a real mixture and not an ideal mixture. The exergy efficiency of the RO desalination was improved by 49% using an energy recovery turbine, and by 77% with a pressure exchanger. Qureshi and Zubair [20] discussed the correct definition of exergetic efficiency for RO desalination systems. They saw a clear connection between specific energy consumption and the chosen efficiency definition. They studied the effect of salinity, mass ratio, and turbine and pump efficiency. In all case, the reverse osmosis unit had the best efficiency when a pressure exchanger was used as an energy recovery device. Later on, the same authors [21] utilized operational data to perform an exergy analysis of a brackish water desalination plant located in California. The reverse osmosis unit of the plant presented a second law efficiency of 0,066%. In order to justify this low value, they compared it with the value obtained by Cerci [8] (4.3%). Qureshi and Zubair concluded that their low value of the exergetic efficiency was not completely unexpected taking into account that: a) the use of accurate seawater properties resulted in an exergetic efficiency that was 2.85 times lower than the originally reported by Cerci [8]; and that b) Cerci considered the brine in the definition of exergetic efficiency of the total plant, but they considered it as a lost. In a recent work, Eveloy et al. [22] evaluated the exergetic efficiency of a complex system (including a reverse osmosis unit) for the production of electricity and freshwater. They obtained a second law efficiency of 29% in the RO unit.

This article presents an exergetic analysis of a large reverse osmosis desalination plant in operation. The plant is located on the Atlantic island of Gran Canaria (Canary Islands, Spain). It was brought into operation in 1898 with an initial capacity of 24,000 $m^3$/d and 7 production lines. Since then, several extensions have been performed, and it has nowadays ten reverse osmosis lines with a total nominal production of 82,000 $m^3$/d. Throughout the consecutive extensions of the plant, different lines have been built with different configurations, depending on the energy recovery components (Pelton turbines or pressure exchange devices), the number of reverse osmosis stages, the filtration and intake technologies or the components involved in feed water pressurization (high pressure pumps, pressure exchangers, booster pumps).

With its special configuration, with ten similar lines, the plant represents a unique model in order to assess the exergetic efficiency as a performance evaluation tool in reverse osmosis desalination plants in operation. Exergetic efficiency asses the thermodynamic performance of a component, plant, or industry, relative to the performance of similar components, plants, or industries: the comparison of exergetic efficiencies of dissimilar devices is generally not meaningful. By this means, the performance of a pump or a reverse osmosis unit, for instance, can be gauged relative to the typical present-day performance level of pumps or reverse osmosis units, but the comparison of exergetic efficiency for pumps and reverse osmosis units does not make much sense [23]. In this study, similar devices, but with different operation settings are compared based on their exergetic efficiency. In this way, the exergetic efficiency identifies and quantifies the thermodynamic inefficiencies, and it locates the most inefficient components (the most inefficient pump among pumps, or the most inefficient RO unit among RO units, for instance). Therefore, this parameter can be successfully used in order to control and to improve the operation of the plant. This study represents a novelty because none of the above-mentioned references present this use of exergetic efficiency. Previous literature papers just give the second law efficiency of the total desalination plant and the devices involved. Some of them also try to compare the exergetic efficiency of the different devices, but, as already mentioned, this comparison is not really meaningful.

## 2. Methodology

An exergy balance at steady state conditions can be formulated for the $k$-th component as:

$$\dot{E}_{F,k} = \dot{E}_{P,k} + \dot{E}_{D,k} + \dot{E}_{L,k} \tag{1}$$

Regarding to a single component, exergy losses are due to heat losses or to material stream losses. Heat losses are not considered in this work because the temperature of the system boundaries is set to the temperature of the reference environment, $T_0$. Material losses in desalination processes are due to the brine, and they are considered here just at the level of the total plant, as stated below.

The exergy balance for the total system is:

$$\dot{E}_{F,tot} = \dot{E}_{P,tot} + \sum_k \dot{E}_{D,k} + \dot{E}_{L,tot} \tag{2}$$

The thermodynamic evaluation of a system component carried on this paper is based on:

- The rate of exergy destruction: $\dot{E}_{D,k}$.
- The exergetic efficiency, $\varepsilon_k$, or second law efficiency:

$$\varepsilon_k = \frac{\dot{E}_{P,k}}{\dot{E}_{F,k}} = 1 - \frac{\dot{E}_{D,k}}{\dot{E}_{F,k}} \tag{3}$$

- The exergy destruction ratio, $y^*_{D,k}$, defined as:

$$y^*_{D,k} = \frac{\dot{E}_{D,k}}{\dot{E}_{D,tot}} \tag{4}$$

An acceptable exergy efficiency definition requires the correct formulation of fuel and product exergy. The exergy of the fuel is the exergy consumed in the component in order to obtain a desired product. The exergy of the product is obtained taking into account the desired result. In this study, definitions given in [24] have been used, with the separate consideration of the chemical and physical flow exergies.

Thus, for the RO desalination plant components:

$$\varepsilon_{pump} = \frac{\dot{E}_{out} - \dot{E}_{in}}{\dot{W}} \tag{5}$$

$$\varepsilon_{turbine} = \frac{\dot{W}}{\dot{E}_{in} - \dot{E}_{out}} \tag{6}$$

$$\varepsilon_{\text{pressure exchanger}} = \frac{\dot{E}_{seawater\ \ out} - \dot{E}_{seawater\ \ in}}{\dot{E}_{brine\ \ in} - \dot{E}_{brine\ \ out}} \tag{7}$$

In the reverse osmosis membranes the separation of the salt occurs. As a result, the inlet and outlet streams do not have the same chemical composition. Therefore, not only the physical exergies, but also the chemical exergies of the outlet material streams differ from the respective values of the inlet streams.

Fig. 1 shows a schematic of a general reverse osmosis device:

Taking into account that the purpose of the RO membranes is the chemical separation of salt, leading to an increase in the chemical exergy between inlet and outlet, and to a decrease in the physical exergy within the same streams, the exergetic efficiency of the RO membranes can be unambiguously defined as:

$$\varepsilon_{RO} = \frac{\left(\dot{E}_2^{CH} + \dot{E}_3^{CH}\right) - \dot{E}_1^{PH}}{\dot{E}_1^{PH} - \left(\dot{E}_2^{PH} + \dot{E}_3^{PH}\right)} \tag{8}$$

This definition is in agreement with the formulation of Sorin et al. [25], who emphasized that "the thermodynamic analysis of the RO process throws a conversion of mechanical exergy into chemical exergy which generates two purified streams from a raw feed stream". In this way, for a reverse osmosis device, at the level of the component, both permeate and brine are considered part of the product. In our formulation, we do not take just the permeate as the product and the brine as a lost, because the purpose of the membrane is the chemical separation of the salt. Permeate and brine are two outlet streams: one with a high concentration of salt and the other with a low concentration of salt.

For the total process, however, two situations can be taken into account:

- The only product of the plant is the permeate:

$$\varepsilon_{tot} = \frac{\dot{E}_{P,tot}}{\dot{E}_{F,tot}} = \frac{\dot{m}_{permeate}\, e^{CH}_{permeate}}{\dot{W}_{pumps} - \dot{W}_{turbines} + \dot{m}_{permeate}\left(e^{PH}_{\text{seawater}} - e^{PH}_{\text{permeate}}\right)} \tag{9}$$

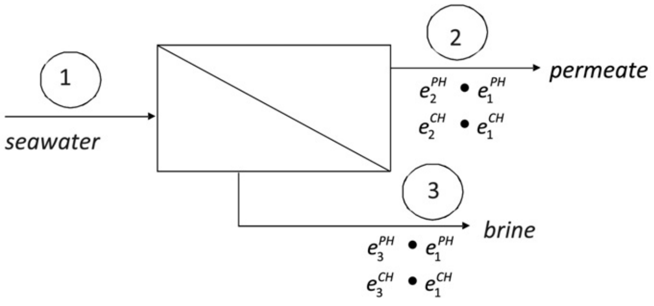

**Fig. 1.** Schematic of a general reverse osmosis device.

and the brine is a lost (according to [17,21]):

$$\dot{E}_{L,tot} = \dot{m}_{brine}\left(e^{PH}_{brine} + e^{CH}_{brine} - e^{PH}_{\mathrm{seawater}}\right) \tag{10}$$

- Both permeate and brine streams are valued to take advantage of their exergetic potential [1,19]:

$$\dot{E}_{P,tot} = \dot{m}_{permeate}\, e^{CH}_{permeate} + \dot{m}_{brine}\left(e^{PH}_{brine} + e^{CH}_{brine} - e^{PH}_{\mathrm{seawater}}\right) \tag{11}$$

An exergy analysis requires the proper calculation of the thermodynamic properties involved in it. In our desalination plant, the working fluids are seawater, with a salt concentration of 37,000 ppm, permeate, within 150–400 ppm of salt concentration, and brine, within 72,000–90,000 ppm. Other chemicals are not considered because this plant does not use chemical products in the pre-treatment phase.

Seawater is an electrolytic compound that consists of water and sodium chloride. Most of the articles found in literature do not take this characteristic into account; they just consider seawater as an ideal mixture, and they do not calculate the chemical exergy term [8–10,12,15]. As a result, erroneous values are obtained in the calculation of the exergy destruction or the exergetic efficiency. Just the work of Fitzsimons et al. [5] showed the significance of calculating the chemical exergy term in desalination processes, and that considerable care must be taken to select a suitable approach. In this work, the updated Sharqawy seawater functions [16] have been used.

The formulation applied in [26] has been used in this paper to obtain the exergy flows. For physical exergy values:

$$e^{PH} = (h - h_0) - T_0(s - s_0) \tag{12}$$

where dead state conditions, $T_0 = 21.5$ °C, $p_0 = 1$ bar, and a salinity of 37,000 ppm are represented by subscript 0. Thermodynamic properties, enthalpy, $h$, entropy, $s$, and chemical exergy, $e^{CH}$, of seawater, brine, and permeate were calculated from Sharqawy et al. functions [16].

In order to validate our calculations of the thermodynamic properties, we have compared the results generated by our computer algorithm with those obtained by Sharquawy et al. [16]. Table 1 shows both results in the range of 10–35 °C. It can be checked that the deviation is always negligible.

## 3. Case study: reverse osmosis desalination plant in Gran Canaria

As a case study, a real desalination plant in operation has been chosen. The plant is located in Gran Canaria, the Canary Islands, and it supplies the main city and the surroundings with freshwater. It was brought into service in October 1989, with an initial capacity of 24,000 m$^3$/d and 7 production lines. Since then, it has undergone several extensions and modifications in order to meet the drinking water needs of the region, and to improve and optimize the reverse osmosis industrial process. Thus, in 2001 an eighth line was installed, and, later on, in 2007, two new lines were put into operation. With these extensions, the freshwater nominal production reaches nowadays 82,000 m$^3$/d, when the ten lines are working. A detailed description of the plant has already been published in [27]. Here, just the main differences between the ten lines are emphasized. A schematic of the plant is shown in Fig. 2.

Seawater with an annual mean salinity of 37,000 ppm is pumped from a dew pond. The temperature of seawater in the pond varies during the year between 19 °C and 26 °C. For the calculations, a mean temperature of 21 °C has been taken in this work.

In the filtration procedure, consecutive sand, precoat, and cartridge filters are used with pressure losses within 2.3% and 4%. An antifouling/antiscaling agent (Hypersperse MDC220) is added between the precoat and cartridge filters, but just occasionally. The first seven lines (A, B, C, E, F, G and H) share intake and filtration procedures. The seawater is first pumped to pressure and sand filters, and then collected in a pool. From there, the water is led to precoat and cartridge filters. After the filtration procedure, the water is split into seven parallel lines, where a high pressure pump (HPP) brings the inlet water to an operating pressure higher than 60 bar. Lines F and G share the HPP. The other lines have their own HPP each of them.

Line 8 (I) has its own seawater pumps and filtration components. A first filtration is performed through pressure filters, and no collection tank is used. For Lines 9 and 10 (K and L) filtration procedure is similar to that of Line 8. K and L share the intake, filtration, and pressurization components. During the reverse osmosis and energy recovery processes they operate in parallel.

A two-stages reverse osmosis desalination process takes place in all ten lines with a booster inter-stage pump (BP). In Line B the booster pump is not in operation. A regulation tank collects the permeate from both stages. The brine from the second stage feeds an energy recovery device: a Pelton turbine in Lines B, C, I, K, and L (Fig. 3); a pressure exchanger from Energy Recovery Inc. (ERI) in Lines E, F, G, and H (Fig. 4); a Dual work exchange energy recovery (DWEER) in Line A (Fig. 5). Brine is then returned to the sea and freshwater is pumped to the municipal storage tanks after a common re-mineralization and pH adjustment post-treatment with calcite and CO$_2$.

## 4. Results and discussion

### 4.1. Energetic evaluation

Table 2 presents some parameters and results for the operation of the ten lines: seawater inlet flow rate ($\dot{V}$), inlet pressure for reverse osmosis membranes (stage 1, $p_1$, and stage 2, $p_2$), flow rate of permeate (stage 1, $\dot{V}_{per,1}$, stage 2, $\dot{V}_{per,2}$, and total, $\dot{V}_{per,tot}\dot{V}_{\mathrm{pertot}}$), purity of total permeate flow $TDS_{\mathrm{per\ tot}}$, conversion factor of membranes, (stage 1, $Cf_1$, stage 1, $Cf_2$, and total, $Cf_{\mathrm{tot}}$) and specific energetic consumption, $c$, defined as energy consumption per m$^3$ of permeate.

In specific energy calculation, only the mechanical energy consumption of the pumps has been taken into account. Other aspects, such as economical details, capital investment, maintenance, equipment

**Table 1**
Seawater thermodynamic properties.

| $T$ (°C) | $v \cdot 10^6$ ($m^3$/kg) | | $h$ (kJ/kg) | | $s$ (kJ/kg K) | | $\mu_w$ (kJ/kg) | | $\mu_w$ (kJ/kg) | | e PH (kJ/kg) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | a | b | a | b | a | b | a | b | a | b | a | b |
| 10 | 974 | 974 | 40,1 | 40,1 | 0,144 | 0,144 | −3,2 | −3,2 | 68,9 | 69,0 | 1,71 | 1,71 |
| 15 | 975 | 975 | 59,9 | 59,9 | 0,214 | 0,214 | −4,2 | −4,2 | 69,1 | 69,1 | 0,77 | 0,77 |
| 20 | 976 | 976 | 79,8 | 79,8 | 0,282 | 0,282 | −5,6 | −5,6 | 69,7 | 69,9 | 0,20 | 0,20 |
| 25 | 977 | 977 | 99,8 | 99,8 | 0,350 | 0,350 | −7,3 | −7,3 | 70,9 | 71,1 | 0,00 | 0,00 |
| 30 | 978 | 979 | 119,7 | 119,7 | 0,416 | 0,416 | −9,3 | −9,3 | 72,4 | 72,8 | 0,14 | 0,14 |
| 35 | 980 | 980 | 139,7 | 139,7 | 0,482 | 0,482 | −11,7 | −11,7 | 74,2 | 74,8 | 0,62 | 0,62 |

a Sharquawy et al. [[16].]
b This work.

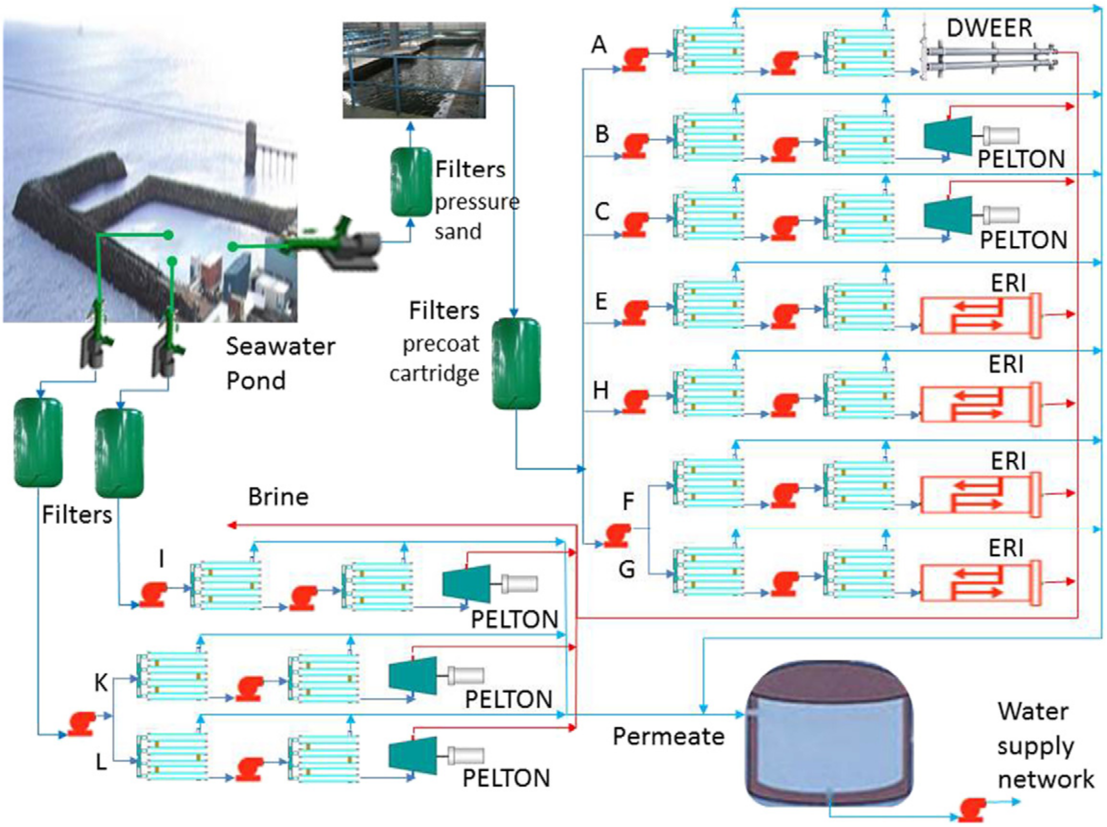

**Fig. 2.** Schematic of the reverse osmosis desalination plant.

replacement, accessories, etc., have not been considered here because it is not the purpose of this work to carry out a complete economic evaluation, but just to compare the thermodynamic performance of the different devices and lines.

It is not feasible to perform an accurate comparison regarding the energetic efficiency of the different lines and to obtain general conclusions, because the operating conditions of the lines are not always the same. A first approach to the results displayed in Table 2 and other calculations are shown as follows:

- Specific energy consumption in the whole plant has a value of 3.55 kWh/m$^3$.
- As expected, lines using pressure exchanger devices as energy recovery systems present lower values of specific energy consumption, *c*, than lines using Pelton turbines. For example, energy consumption, *c*, in Line E (operated by ERI devices) is 15% lower than the corresponding magnitude in Line C (operated by a Pelton turbine). The same magnitude, *c*, in Lines F–G (operated by ERI devices) is 23% lower than in Lines K–L (operated by Pelton turbines). The value of the specific exergy consumption in Line A stands out. This line is operated by a DWEER device with the configuration represented in Fig. 5. The introduction of the DWEER has improved the total specific energy consumption by 4.82%. The use of a pressure exchanger device saves, on average, 23.5% electricity by reducing the high pressure pumps requirements of power.
- Sea water inlet pumping represents a specific energy consumption of 0.62 kWh/m$^3$. Last pumping of permeate to regulator tank has a specific energy consumption of 0.66 kWh/m$^3$. Both processes together represent almost a third part (27.2%) of the specific energy consumption of the whole plant.

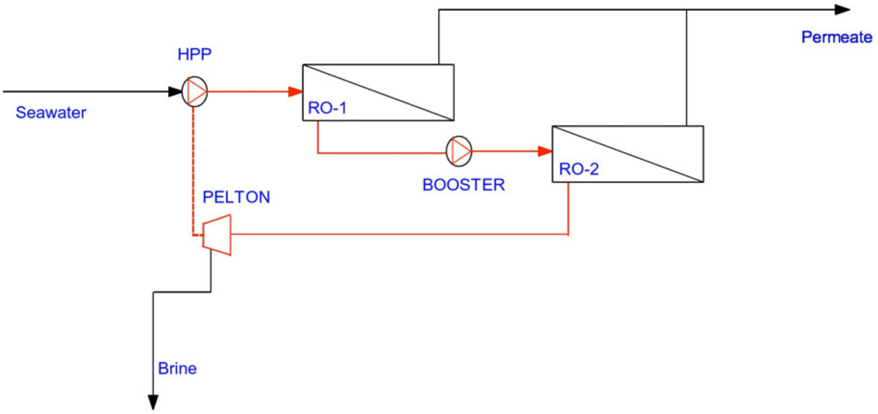

**Fig. 3.** Schematic of a line with a Pelton turbine.

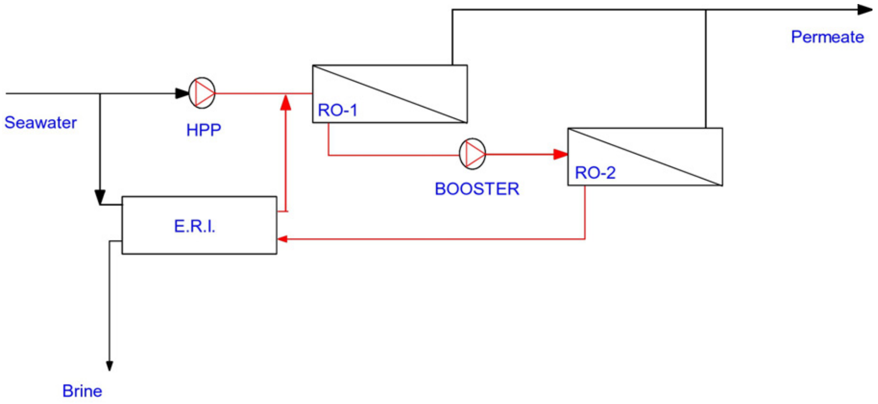

**Fig. 4.** Schematic of a line with an ERI system.

- Lines A–H present higher specific energy consumption values for seawater inlet pumping (0.66 kWh/m$^3$) than Lines I-K-L (0.53 kWh/m$^3$) because in Lines A-H this process is performed in two steps due to the atmospheric pressure intermediate tank.
- The higher the conversion factor, the higher the energetic efficiency of the plant, due to higher water production (see Lines B and C that have a similar configuration). But at the same time, the higher the conversion factor, the higher the inlet pressures at the membranes, and the higher the specific energy consumption. A compromise should be adopted between conversion factor, inlet pressure, and water production variables, in order to get an optimum value of the specific energy consumption. A deviation of this performance is shown in Line H when its specific energy consumption is compared to the specific energy consumption of Line E (both lines have similar devices and configurations). Next section brings to light that the RO modules of Line H have some operating malfunctions.
- Due to regulation necessities (flow rate, pressure, maintenance operations, …), sometimes the pumps do not work at design conditions. The disadvantage of this situation is the decrease in the performance of the device.

### *4.2. Second law assessment*

In this section, the results of the exergetic analysis are displayed. Table 1 shows the exergetic efficiency of all the representative components of the RO desalination plant. The exergetic efficiency gives information about how much exergy of the fuel can be found on the product of the system. It represents the percentage of the fuel exergy that has been lost or destroyed in the process. With this information, it is possible to evaluate the thermodynamic performance of one component related to the performance of similar components (the comparison between different components makes usually no sense) [26]. Thus, the thermodynamic inefficiencies are located and evaluated.

The highest performance components are highlighted in bold. The lowest performance components are highlighted also in italics. These components require urgent assistance because their performance is worse than expected.

Exergetic efficiency of HPP is usually within 75–80%. In this plant, the best operation corresponds to HPP of Line C, with an exergetic efficiency of 83%. The worst operation corresponds to Lines E and H, in the order of 73.2%. As similar flows are pumped in all ten lines, with similar pressure jumps, it is clear that HPP in Lines E and H present some performance deviation, probably related to the deviation from design operation characteristics. The rest of the pumps need no special considerations because they have exergetic efficiencies within the usual range.

The booster pump of Line G presents an outstanding exergetic efficiency value (96%). This pump represents an operational model. Booster pump of Line I has also a high exergetic efficiency value. However, the exergetic efficiency of booster pumps of Line E (44.8%) and Line H (38.8%) is too low, and they need, therefore, urgent maintenance actions.

Related to intake and transfer pumps, those of Lines A–I present very low exergetic efficiencies, between 20 and 27%. In Lines K–L, the

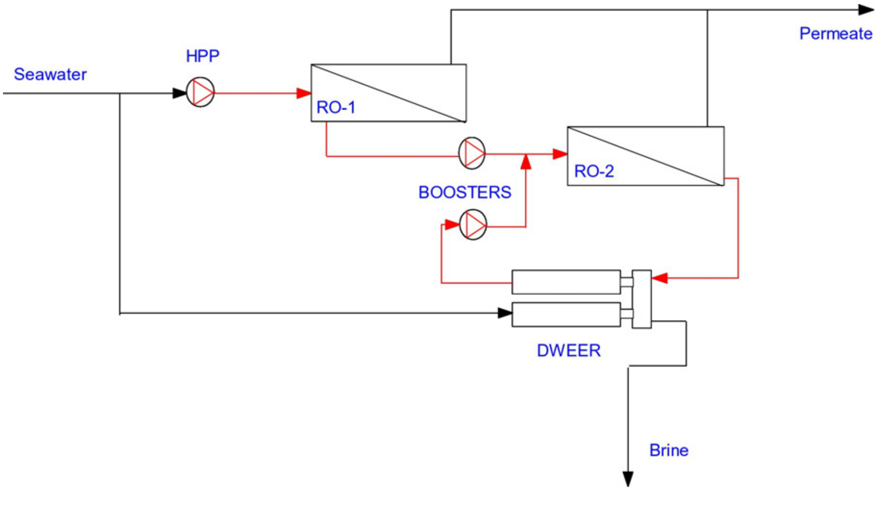

**Fig. 5.** Schematic of a line with a DWEER system.

**Table 2**
Thermodynamic parameters and results for the operation of the ten lines.

| *Line* | $\dot{V}$ $m^3/h$ | $p_1$ bar | $p_2$ bar | $\dot{V}_{per,1}$ $m^3/h$ | $\dot{V}_{per,2}$ $m^3/h$ | $\dot{V}_{per,tot}$ $m^3/h$ | $TDS_{pertot}$ ppm | $Cf_1$ % | $Cf_2$ % | $Cf_{tot}$ % | $c$ $kWh/m^3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| A (1) | 785 | 47.8 | 69.5 | 79 | 318 | 397 | 240 | 20.4 | 45.1 | 50.6 | 2,29 |
| B (2) | 642 | 61.6 | 59.9 | 254 | 62 | 316 | 288 | 41.1 | 16.4 | 49.2 | 3.75 |
| C (3) | 683 | 62.3 | 70.5 | 246 | 101 | 347 | 298 | 36.0 | 23.1 | 50.8 | 4.03 |
| E (4) | 759 | 67.9 | 71.7 | 335 | 114 | 449 | 448 | 44.1 | 26.9 | 59.2 | 3.49 |
| F–G (5–6) | 1299 | 61.0 | 67.0 | 450 | 200 | 650 | 354 | 34.6 | 23.6 | 50.0 | 3.15 |
| H (7) | 793 | 70.5 | 73.1 | 301 | 119 | 420 | 394 | 38.0 | 24.2 | 53.0 | 3.64 |
| I (8) | 661 | 54.2 | 79.1 | 187 | 135 | 322 | 465 | 28.3 | 28.5 | 48.7 | 4.12 |
| K–L (9–10) | 1227 | 63.0 | 70.5 | 461 | 157 | 618 | 269 | 37.6 | 20.5 | 50.4 | 4.57 |
| Total | 6849 | | | 2313 | 1206 | 3519 | 427 | | | | 3.55 |

corresponding value is in the order of 60%. This information reveals that intake process in Lines A–I presents some mechanical malfunctions.

Related to RO modules, it can be seen that the first stage operates worse than the second stage. This is related to the higher flow of permeate obtained in the first stage. Thus, irreversibilities due to chemical separation are higher in the first stage. Therefore, the exergetic efficiency in this first stage is lower than that of the second stage. In the first stage, the membrane modules with the better operation are those of Line B (60.92%) followed by the membrane modules of Lines I, K, and L. On the other hand, the worst operation corresponds to membrane modules of Line H (50.76%). Related to the second stage, the best operation corresponds to the Line E (81.86%), and the worst operation to Line I (63.38%). Anyway, this worst exergetic efficiency value in the second stage is better than the best exergetic efficiency value in the first stage of the membrane modules (Line B 60.92%). This information probably means that those membranes with lower exergetic efficiency need cleaning or replacement.

Pressure exchanger of Line A has a very high exergetic efficiency (98.56%). It cannot be compared with the other pressure exchangers because it is a different device (DWEER). Just its outstanding operation can be highlighted. Among the ERI devices, the best performance parameters correspond to those of Line H (97.25%), and the worst parameters to those of Line G (90.74%). According to this information, some of the ERI units of Line G should probably need to be repaired or replaced. Attention must be also paid to ERI modules of Lines E and F because their exergetic efficiency is not as good as expected.

The Pelton turbine with the highest exergetic efficiency corresponds to that of Line B (71.51%). Turbines of Lines K and L present very low exergetic efficiency (42.57% and 41.37%). Turbines of Lines K and L need urgently to be subject of some maintenance operations, because they are losing efficiency in the development of their energy recovery task.

Table 3 gives information about the exergy destruction in all the main components of the RO desalination plant. In order to perform a proper comparison among lines and devices, the specific exergy destruction related to freshwater production has been defined here as:

$$e_{D,k} = \frac{\dot{E}_{D,k}\ (kW)}{\dot{V}_{\ permeate}(m^3/s)} \tag{13}$$

This definition is more appropriate for the comparison performed in this work, because the different lines do not work with the same flowrate. With this variable, exergy destruction is defined for each component of the different lines at the same purpose basis: per cubic meter of permeate.

Table 4 shows that HPP and turbines are the components with greater exergetic destruction. This was expected because of the high mechanical irreversibilities that take place on them. Also reverse osmosis modules are important sources of irreversibilities, due to the chemical separation process. However, the pressure exchangers are the less exergy destroyer devices in almost all cases.

Among the pumps, the exergy destruction per cubic meter of permeate in HPP is clearly higher than in intake, transfer, or Booster pumps. HPP of Line A destroys less exergy per cubic meter of permeate than other lines, because the inlet pressure to its first RO stage is lower (47.8 bar); Lines F and G have also low values of exergy destruction because they share the HPP. Intake pumps of Lines A–H and I destroy a big amount of exergy, in comparison with that destroyed by intake pumps of Lines K–L. This is expected, because as we already mentioned-exergetic efficiency of intake pumps in Lines A–H and I was very low. In booster pumps exergy destruction per cubic meter of permeate is quite low, because their low pressure variation. In Line G this value is extremely low, because of its high exergetic efficiency.

As expected, the second RO stage destroys less exergy than the first one. The only exceptions are Line A, where the feed flowrate in the second RO stage is much higher than in the first stage, and Line I, where the exergetic efficiency of the RO modules in the second stage is quite low.

Related to the turbines, the higher exergetic destruction corresponds to Lines K–L. This is in accord with the low exergetic efficiency of these devices, shown in Table 3. On the other hand, Turbine of Line B has the

**Table 3**
Exergetic efficiency, ε, of the main components of the RO desalination plant.

| Line | Intake pumps | Transfer pumps | HPP | Booster pumps | RO-1 | RO-2 | PES | Pelton turbines |
|---|---|---|---|---|---|---|---|---|
| A | ***0,2060*** | ***0,2717*** | 0,7860 | 0,6787 | 0,5353 | 0,6761 | **0,9856** | |
| B | | | 0,7715 | 0,6058 | **0,6092** | 0,7323 | | **0,7151** |
| C | | | **0,8306** | 0,6704 | 0,5566 | 0,6914 | | 0,5965 |
| E | | | ***0,7320*** | ***0,4484*** | 0,5581 | **0,8186** | 0,9501 | |
| F | | | 0,7504 | 0,5745 | 0,5760 | 0,7512 | 0,9421 | |
| G | | | | **0,9604** | 0,5474 | 0,7224 | ***0,9074*** | |
| H | | | ***0,7324*** | ***0,3883*** | ***0,5076*** | 0,7044 | **0,9725** | |
| I | **0,2393** | | 0,7651 | **0,8805** | 0,5886 | ***0,6338*** | | 0,6890 |
| K | 0,6015 | | 0,7574 | 0,7447 | 0,5807 | 0,7124 | | ***0,4257*** |
| L | | | | 0,7331 | 0,5704 | 0,7036 | | ***0,4137*** |

**Table 4**
Specific exergy destruction, $e_D$ ($kJ/m^3_{permeate}$), of the main components of the RO desalination plant.

| Line | Intake pumps | Transfer pumps | HPP | Booster pumps | RO-1 | RO-2 | PES | Pelton turbines |
|---|---|---|---|---|---|---|---|---|
| A | 1137 | 520 | 1230 | 678 | 558 | 1664 | 87 | |
| B | | | 3515 | 125 | 2055 | 329 | | 1693 |
| C | | | 2373 | 687 | 2086 | 683 | | 2618 |
| E | | | 2352 | 778 | 2324 | 340 | 235 | |
| F | | | 957 | 610 | 2004 | 472 | 345 | |
| G | | | 992 | 50 | 1946 | 656 | 611 | |
| H | | | 2458 | 959 | 2599 | 642 | 169 | |
| I | 1255 | | 2946 | 477 | 1222 | 1449 | | 2030 |
| K | 388 | | 1875 | 386 | 2053 | 518 | | 3807 |
| L | 400 | | 1934 | 419 | 2050 | 593 | | 3883 |

lowest exergetic destruction and, as already mentioned, the higher exergetic efficiency.

The exergy destruction In the pressure exchangers is quite low, as expected. The higher the efficiency, the lower the exergy destruction per cubic meter of permeate. The pressure exchanger device of Line A (DWEER) destroys a really low amount of exergy, in comparison with the other devices.

The special distribution of this real plant, with ten RO desalination lines and different configurations, makes it possible to perform several interesting comparisons between different operation possibilities:

P1: Regarding the inter-stage pressurization: Line C (with BP) – Line B (without BP).

P2: Own or shared HPP in lines with ERI: E and H (own HPP) – F and G (shared HPP).

P3: Own or shared HPP in lines with ERI: E and H (own HPP) – F and G (shared HPP).

P4: Own or shared HPP in lines with Pelton turbines: I (own HPP) – K and L (shared HPP).

P5: Own or shared intake procedure (pumps and filters): I (own) – C (shared).

Results are shown in Figs. 6 and 7 based on the exergy destruction ratio, $y^*_{D,k}$, which compares the exergy destruction in the *k*-th component to the total exergy destruction rate in the evaluated line. $\dot{E}_{D,k}$ is an absolute measure of the inefficiencies in the *k*-th component, whereas $y^*_{D,k}$ is a relative measure of the same inefficiencies. Thus, with the exergy destruction ratio a more appropriate comparison between the lines can be carried out.

### *4.2.1. P1: regarding the inter-stage pressurization: Line C (with BP) – Line B (without BP)*

Reverse osmosis Lines B and C just differ in the booster inter-stage pump. In Line B, brine feeds the second reverse osmosis module directly, without booster pump.

Fig. 6 shows that in Line B, most of the exergetic destruction occurs in the HPP (46%). The remaining 64% is destroyed mainly in the first reverse osmosis stage (27%) and in the turbine (22%). In Line C, HPP, RO-1 and Pelton turbine participate likewise in the exergy destruction, with 28%, 25% and 31% respectively. Booster pump and RO-2 are responsible for just 8% of the exergetic destruction each of them.

Total exergy destruction in Line B and C amounts 657 kW and 815 kW, respectively. The exergetic efficiency (Eq. 9) represents 24,7% for Line B and 22,9% for Line C. Since the seawater feed flow rate is similar in two lines (642 $m^3$/h and 683 $m^3$/h respectively), the lower exergetic efficiency of Line C must be due to the higher irreversibilities of its components. In effect, Table 3 (Exergetic efficiency of the main components) shows that the turbine and the RO-1 of Line C are more inefficient than similar devices in Line B. And in Line B the high efficiency of RO-1 makes it unnecessary the inter-stage booster pump.

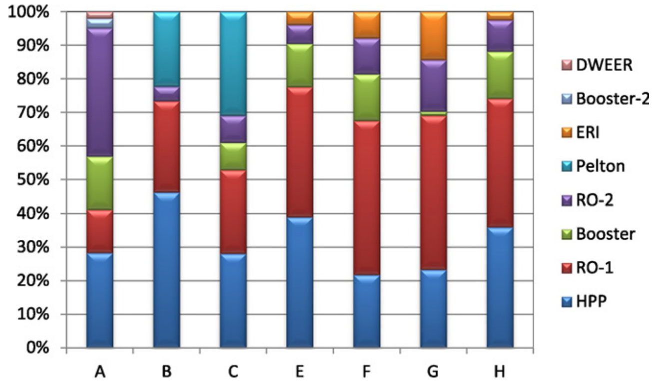

**Fig. 6.** Exergy destruction ratio in the components of Lines A–H.

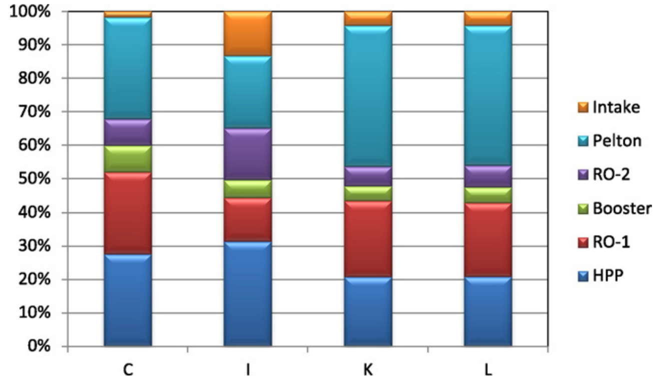

**Fig. 7.** Exergy destruction ratio in the components of Lines C (intake included), I, K and L.

### *4.2.2. P2: regarding the energy recovery procedure: Line C (Pelton turbine) – A (DWEER) – E (ERI)*

Lines C, A and E, share intake procedure, but they differ in the technology used in order to recover the energy of the brine: Line C has a Pelton turbine whereas in Line A and E a pressure exchanger has been installed (ERI in Line E and DWEER in Line A). Although the operation principle of both pressure exchangers is quite similar, Line A presents a special configuration. In Line E, the seawater exiting the pressure exchanger is fed into the RO-1 module (Fig. 4) but in Line A it is fed into the RO-2 with the help of a small booster pump (Fig. 5).

As already mentioned, exergy destruction in Line C is likewise split among HPP, RO-1 and Pelton turbine. In Line A (Fig. 6) the highest exergy destruction takes place in the RO-2, 38%. HPP-A has the same exergy destruction as HPP-C, 28%. RO-1 of Line A destroys 13% of the exergy, a little bit less than the booster-1 (16%). In the energy recovery system of Line A, the exergy destruction is very low: 2% in the pressure exchanger (DWEER) and 3% in the booster-2. In Line E, the exergy destruction in the HPP and the RO-1 amounts 40% in both of them. However, in RO-2 just 6% of the exergy destruction occur and only 4% in the pressure exchanger (ERI). These data bring to the conclusion of the high inefficient operation of HPP and RO-1 in Line E and of RO-2 in Line A. The high efficiency of pressure exchanger devices against Pelton turbines is also apparent.

Global exergetic efficiency of lines with pressure exchangers is also higher than that of lines with Pelton turbines: 33,6% for Line A, 27,2% for Line E and 22,9% for Line C. It is also clear that the special configuration of Line A highly contributes to improve the exergetic efficiency of the line.

### *4.2.3. P3: own or shared HPP in lines with ERI: E and H (own HPP) – F and G (shared HPP)*

Within the lines working with ERI pressure exchangers, Lines E and H have their own HPP, but Lines F and G share it. The effect of sharing the HPP in this kind of lines can be then checked out.

Fig. 6 shows that in Lines F and G, the exergy destruction of HPP represents just 22% and 23% whereas in Lines E and H, HPP destroys 39% and 36% respectively. Thus, to share the HPP is clearly more efficient from an exergetic point of view. In Lines F and G, however, the highest exergy destruction takes place in the RO-1 (44–45%). This means that the chemical irreversibilities are responsible for almost the half of the exergectic destruction in the line.

In Line G, the high efficiency of the booster pump stands out. It destroys just a 1% of the exergy against 13–14% in the other lines. On the contrary, on the ERI modules of Line G takes place 14% of the exergy destruction, against 3, 4 and 8% in the other lines. This means that the ERI modules of Line G should be repaired or replaced.

The total exergy destruction in Lines F and G (963 kW) is lower than exergy destruction in Lines E and H (1545 kW). As a result, the exergetic efficiency of Lines F and G (30,3%) is higher than the exergetic efficiency of Lines E and H (26,5%), which shows the high efficiency of sharing the HPP.

#### 4.2.4. P4: own or shared HPP in lines with Pelton turbines: I (own HPP) – K and L (shared HPP)

A similar comparison can be made in lines working with a Pelton turbine: I (with its own HPP), K and L (which share HPP). In this case, the comparison can be also interesting because the Line I has its own intake procedure and K and L share also the intake procedure.

Fig. 7 shows, as in the previous case, that the percentage of exergy destroyed in the pressurization process is lower when the pump is shared between two lines (21% in Lines K–L each) than when the pump serves just one line (31% in Line I). The same tendency occurs in the intake procedure: in Line I, 13% of exergy destruction takes place during intake, whereas in Line K and L only 4% of the destruction occurs.

Related to RO-1, the exergy destruction is higher in lines sharing HPP (22–23%) than in the line with its own HPP (13%). The opposite effect is shown in RO-2: 6% of the destruction in Lines K–L, but 16% in Line I. The highest exergy destruction in Lines K–L takes place in the Pelton Turbines (42%, each), which indicates some malfunction in the operation of these devices (see also Table 3).

Due to the inefficient operation of the Pelton turbines, the total exergy destruction in Lines K and L is very high (2107 kW) which leads to a very low exergetic efficiency in the line: 17.3%. In Line I the exergetic efficiency is also low (20.7%), but it is similar to that of other lines working with Pelton turbines.

#### 4.2.5. P5: own or shared intake procedure (pumps and filters): I (own) – C (shared)

Lines I and C differ just in the intake procedure: Line I has its own intake pump and filters, but Line C shares these devices with other lines. Both have Pelton turbines as the energy recovery procedure.

Fig. 7 shows that the exergy destruction during high pressurization is very similar in both lines (28–31%). Nevertheless, during intake the difference is clear: in Line I (with its own intake procedure), exergy destruction amounts around 13%, whereas in Line C (where the intake process is shared with other lines), exergy destruction stands for just 2%.

As already mentioned in case 1, exergy destruction in Line C is likewise split among HPP, RO-1 and Pelton turbine (28-24-30%); RO-2 and booster destroy just 8%. In Line I, the highest exergy destruction takes place in the HPP (31%), followed by the Pelton turbine (22%). In the rest of the components, the distribution is more balanced (16% RO-1; 13% RO-2), the booster destroys just 5%.

Exergetic efficiency of these two lines is very similar: 19.7%, in Line C (when the intake procedure is also considered), 20.7% in Line I.

## 5. Conclusions

This article deals with the assessment of exergetic efficiency as a performance evaluation tool in reverse osmosis desalination plants in operation. As a case study, a real plant with ten reverse osmosis desalination lines is considered. Different configurations depending on the energy recovery procedure (Pelton turbine or pressure exchanger devices), the reverse osmosis stages, the intake and filtration technologies, or the feed water pressurization procedure (high-pressure pumps, pressure exchangers, booster pumps) are possible.

The results of the energetic analysis show:

- The specific energy consumption in the whole plant has a value of 3.55 kW/m$^3$. An optimum value of the specific energy consumption can be achieved when a compromise between conversion factor, inlet pressure, and water production variables is adopted.
- As expected, frames using Pressure exchanger devices as energy recovery systems present lower values of specific energy consumption, c, than frames using Pelton turbines. The low specific exergy consumption reached by the line operated by a DWEER device with the special configuration showed in Fig. 5 highlights. Exergy destruction in pressure exchanger devices is very low, whereas Pelton turbines destroy a big amount of exergy, especially due to the deviation of their operation parameters from that of the design conditions. Regulation necessities affect also the energetic performance and exergetic efficiency of the pumps.

- Based on the values of exergetic efficiency, the most inefficient components are identified:
- HPP and Pelton turbines are the most inefficient components due to the high mechanical irreversibilities taking place on them. RO-1 is also an important irreversibilities source due to the chemical separation process. In general, RO-1 destroys more exergy than RO-2 because a bigger amount of salt is separated from it.
- In general, a booster inter-stage pump improves the process from an exergetic point of view. Nevertheless, in Line B, the high efficiency of the RO-1 makes the booster pump unnecessary.
- Pressure exchangers are clearly more efficient components than Pelton turbines. The special configuration of Line A, where seawater exiting the pressure exchanger is fed into RO-2 instead into RO-1, improves the exergetic efficiency of the line in 6.5%.
- Sharing HPP is more efficient because the exergy destruction can decrease over 18% in lines operating with ERI devices and almost 10% in lines with Pelton turbines. It is also more efficient to share the intake procedure: the decrease of the exergy destruction of the intake process decreases in almost 10%, leading to an improvement of the exergetic efficiency of the line within 1–4%.

Exergetic efficiency turns out to be a useful parameter to identify and locate the thermodynamic inefficiencies and malfunctions in the devices of the plant, provided that similar components are compared. Low exergetic efficiency values indicate operation defects that should be repaired. As a result of our study, the following recommendations can be proposed to the operators of this plant:

- The operation of Pelton turbines in Lines K and L need to be controlled.
- Intake pumps of Lines A–I, HPP of Lines E and H and booster pumps of Lines H and E should be regulated.
- The booster pump in Line G presents and outstanding exergetic performance. It can be used as a model to regulate the operation of the other booster pumps.
- Some of the RO-1 membrane modules of Line H and of the RO-2 of Line I should be cleaned or replaced.
- Pressure exchanger ERI modules of Line G should be subject of maintenance works.

This way, exergetic efficiency can be successfully used to control and to improve the operation of the plant.

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## 4.2. A critical review of definitions for exergetic efficiency in reverse osmosis desalination plants

*Article:* A critical review of definitions for exergetic efficiency in reverse osmosis desalination plants.

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### Abstract

Different approaches for formulating exergetic efficiency in desalination plants are suggested in literature. In this work these formulations, applied to the reverse osmosis technology, are compared and critically reviewed. As a case study, a reverse osmosis desalination plant in operation has been considered. A key factor is the proper definition of the exergy value of the product and the exergy value of the fuel. In reverse osmosis modules, where chemical separation is carried out, chemical exergy plays also an important role. Another influential issue is the thermodynamic model used in the calculation of the thermodynamic properties. Inappropriate thermodynamic models and ambiguous exergetic efficiency definitions bring confused and contradictory results: negative values of the chemical exergy, exergy production in pumps, or larger irreversibilities in the membranes than in the pumps. The enormous deviations found in the literature can only be due to different conceptual definitions. In order to clarify these contradictions, this work provides a precise definition for the exergetic efficiency in reverse osmosis desalination plants devices.

### Summary of the PhD student's contributions

The work has been entirely prepared by the PhD student. She is responsible for the conceptualization, methodology, data treatment, analysis of results, conclusions and preparation of both the draft and the final paper. In the design of the process, she has had the collaboration of an engineer of the plant (A. Lozano-Medina). The supervision of the whole work has been in charge of the director of the Thesis, J. Daniel Marcos.

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# A critical review of definitions for exergetic efficiency in reverse osmosis desalination plants

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ABSTRACT

Different approaches for formulating exergetic efficiency in desalination plants are suggested in literature. In this work these formulations, applied to the reverse osmosis technology, are compared and critically reviewed. As a case study, a reverse osmosis desalination plant in operation has been considered. A key factor is the proper definition of the exergy value of the product and the exergy value of the fuel. In reverse osmosis modules, where chemical separation is carried out, chemical exergy plays also an important role. Another influential issue is the thermodynamic model used in the calculation of the thermodynamic properties. Inappropriate thermodynamic models and ambiguous exergetic efficiency definitions bring confused and contradictory results: negative values of the chemical exergy, exergy production in pumps, or larger irreversibilities in the membranes than in the pumps. The enormous deviations found in the Literature can only be due to different conceptual definitions. In order to clarify these contradictions, this work provides a precise definition for the exergetic efficiency in reverse osmosis desalination plants devices.

## 1. Introduction and literature review

Desalination processes are nowadays considered as the most viable solution for providing fresh water to many areas around the globe. In many countries (i.e. the Gulf States, Mediterranean and Caribbean Islands) seawater desalination is the only possible solution [1]. Some countries like Qatar and Kuwait rely 100% on desalinated water [2]. In the Canary Islands, the irregular distribution of precipitated water, the rapid increase of population due most of all to tourism, and the development of industries and cities, have forced the implantation of desalination processes from the 1960's. First desalination installations on the Canary Islands were distillation processes and these were the dominant technologies until 1980's [3]. From then on, distillation was replaced with reverse osmosis, a more efficient technology from both the product and the economical points of view.

Energy research in desalination processes has contributed to lowering the water treatment energy footprint. In relation to reverse osmosis (RO) processes, the energy footprint would have dropped from approximately 20 kWh/m$^3$ in the 1970's to a value of less than 2 kWh/m$^3$ nowadays [4]. Several factors have contributed to these achievements: membranes development, pump and motor efficiency improvements, the use of variable speed drives and the implementation of energy recovery devices such as hydraulic turbines or pressure exchangers to harness wasted throttling valve energy.

Exergy analysis is a well-known methodology and has been widely accepted as a useful analytical tool for the characterization and optimization of energy systems. Its application to desalination processes date back to 1980's. Since then, many related articles have been published, as it is exposed in the next section. The exergetic efficiency characterizes the performance of a system or a system component from the thermodynamic viewpoint. Different approaches for formulating exergetic efficiency in desalination plants are suggested in literature. This work compares two classes of exergy efficiency definitions and applies them to reverse osmosis desalination plants. As a case study a reverse osmosis desalination

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plant in operation, located in Gran Canaria (Canary Islands) has been considered. The significance of an unambiguous definition for the exegetic efficiency is clearly set out in this analysis.

### *1.1. Literature review*

Hereby, a brief description of the most representative articles related to Second Law analysis applied to reverse osmosis desalination is chronologically displayed.

Second law analysis of desalination plants dates back to the 1960s: In 1963 Tribus and Evans [5] presented a wide report with the thermoeconomics of seawater conversion. In 1970 El Sayed and Aplenc [6] applied the thermoeconomic approach to the analysis and optimization of vapor-compression desalting systems.

Some years later, Goda et al. [7] evaluated the thermodynamic efficiency of water treatment systems through the rate of decrease in entropy of feed water and the rate of internal entropy production. Later on (1999), Criscuoli and Drioli [8] performed an energy and exergy analysis of an RO unit alone and coupled with a membrane distillation process. They evaluated the exergetic efficiency in terms of entropy losses. Spieglerand El-Sayed [9] (2001) set the foundation of the optimal design of most systems that use or produce heat and/or power including desalination. Both the energetics and the economics of the separation process are based on a quantitative formulation of the second law of thermodynamics in terms of the concept of exergy and its destruction. The determination of the driving force associated with exergy destruction occupies a central position in this comparison.

Fist exergy analysis of a reverse osmosis desalination plant in operation is performed by Cerci [10] in 2002. The brackish water plant had a production of 7250 $m^3$/d. The process had just one RO stage and the brine flowed through throttling valves directly into the ocean. The largest exergy destruction occurred in the membrane modules (74.07% of the total exergy input). The second law of efficiency of the plant defined as the net salinity exergy divided by the total exergy input provided by the pumps was calculated to be 4.3%. This value was increased to 4.9% by introducing a pressure exchanger on the brine stream. Kahraman et al. [11] presented also an exergy analysis of a brackish water RO desalination plant in operation. They calculated the exergy destruction within all the components and, afterwards, the exergetic efficiency by subtracting the ratio of the total exergy destruction to the total exergy input from the pumps. The largest exergy destruction occurred in the separation units and in the pumps. The plant was determined to have a Second Law efficiency of 8.0%. They proposed the use of high-efficiency pumps and motors equipped with variable frequency drives to reduce the cost of desalination. Romero-Ternero et al. [12] published in 2005 an exergy analysis of an RO desalination plant (21,000 $m^3$/d) located in Tenerife (Canary Islands). It had just one RO stage, but it operated already with Pelton turbines. The main results indicated that 80% of the exergy destruction is placed on core processes (high pressure pumping and valve regulation, reverse osmosis separation and energy recovery). The Pelton turbine and high-pressure pump accumulate 48% of this amount, despite their adequate performance (85%) with respect to typical operational data.

In 2006, Sorin et al. [13], considered the application of finite time thermodynamics to reverse osmosis (RO) processes. The results show the existence of a maximum value for the power of separation which corresponds to the maximum conversion rate of mechanical exergy into chemical exergy. In the paper of Drioli et al. [14] a microfiltration–nanofiltration–reverse osmosis membrane system was integrated with membrane distillation/crystallization units. Energy and exergy analysis permitted to individuate the points of higher entropy losses and low thermodynamic efficiency of the systems, and possible solutions based on the use of energy recovery devices were discussed in detail. In the article of Mehdizadeh [2], the thermodynamic property of exergy was combined with a mathematical model for multi-solute reverse osmosis systems to determine the optimum operating condition for an integrated nanofiltration –reverse osmosis seawater desalination plant.

Macedonio et al. [15] (2007) performed and energy and exergy analysis of different seawater desalination processes using membranes (RO and nanofiltration). They found that major irreversibilities were located in the membrane units and the throttling valves. Mabrouk et al. [16] presented an exergoeconomic analysis of several desalination plants in operation located in the Suez Gulf region, including an RO plant.

In the paper of Martínez et al. [17] (2009), the unit exergy cost (k) of the different technologies involved in the water treatment and supply chain were obtained. The results clearly demonstrate that the exergy needed to restore the ancient status of water bodies is considerably higher than the theoretical minimum established by Thermodynamics. Aljundi [18] analyzed thermodynamically the brackish water RO plant of Al-Hussein thermal power station using actual plant data. The highest exergy destruction occurred within the throttling valves followed by the exergy destruction in the two-stages RO units. The second law efficiency of the plant was very low, 4.1%. They proposed the use of a high-efficiency pump/motor set-up with a variable frequency drive and the replacement of the traditional throttling valves with energy recovery devices. Bouzayani et al. [19] modeled and calculated the performance of various systems combining reverse osmosis (RO) to produce drinkable water and a steam power plant. The effects of feed water flow rate and salinity, energy recovery system (hydraulic turbine or pressure exchanger) and operating pressures on the energy and exergy efficiencies and on the permeate quantity and quality were analyzed.

Gasmi et al. [20] (2010) performed the optimization of energy consumption in a brackish water reverse osmosis desalination unit with a capacity of 30,000$m^3$/day. The studied unit had four double staged lines, one of which was equipped with a booster pump. It was found that the presence of a BP in the fourth line reduces energy consumption by 21% approximately. The simulation was validated by an exergy analysis, which showed that the high pressure pump was responsible for roughly 44% of the total exergy loss. The use of a Booster pump has brought this contribution down by 8%. A techno-economic study was also carried out in order to assess the impact of using Pelton turbines and pressure exchangers on the performances of the unit. This study showed that the combination of a pressure exchanger and a Booster pump could lead to a reduction in energy consumption of around 40%. In the work of Nafey and Sharaf [21] an exergy and cost analysis of an organic Rankine cycle coupled with a RO desalination unit was carried out, although their results were more oriented to the optimization of the Rankine Cycle than to the desalination unit.

In 2011, Mistry et al. [22] postulated that when defining Second Law efficiency, the useful exergy output of the system must be properly defined. For desalination systems, this is the minimum least work of separation required to extract a unit of water from a feed stream of a given salinity. They applied their formulations to calculate the total entropy generation in several desalination systems including reverse osmosis. Within each technology, the relative importance of each source of entropy generation was discussed in order to determine which should be the target of entropy generation minimization. Sharqawy et al. [23] carried out a second law analysis of a reverse osmosis desalination plant using a new reliable seawater exergy formulation instead of a common model in literature that represents seawater as an ideal mixture of liquid water and solid sodium chloride. They demonstrated that the previous model had serious shortcomings, particularly with regard to the calculation of the seawater flow exergy, the minimum work of separation, and the second law efficiency. They founded that the studied reverse osmosis desalination plant had very low second law efficiency (<2%) even when using the available energy recovery systems. Therefore, an energy recovery system was proposed using the pressure retarded osmotic method. The proposed alternative design had a second law efficiency of 20%, and the input power was reduced by 38% relative to the original reverse osmosis system. Peñate and García-Rodríguez [24] studied the reduction of specific energy consumption in seawater reverse osmosis desalination plants in operation using energy recovery devices instead of Pelton turbines. Their study was technically and thermoeconomically justified.

In 2013, Al-Sulaiman et al. [25] presented and discussed an exergy analysis of a novel desalination system which combined humidification–dehumidification and reverse osmosis technologies. They defined a new parameter “total true specific exergy lost” as the summation of the specific exergy destroyed by all the system components and the specific exergy lost, and they found it more appropriate than the overall exergetic efficiency to assess the exergetic performance of the system.

In the work of Esfahani and Yoo [26] three power and fresh water cogeneration systems that combine a GT (gas turbine) power plant and an RO desalination system were compared based on the exergy viewpoint. Parameter optimization was achieved using a GA (genetic algorithm) to reach the maximum exergy efficiency, where the thermodynamic improvement potentials of the systems were identified. In Khoshgoftar-Manesh et al. [27] an optimization of coupling site utility to multiefect destillation-RO desalination was evaluated, using an accurate targeting model. The new procedure was developed based on the total site analysis and exergoeconomic optimization to find optimal coupling of site utility and multiefect destillation–RO desalination system. Koroneos et al. [28] published an exergy analysis of several desalination processes, including RO. They compared the different technologies using exergy efficiency. The exergy of dual-stage nanofiltration seawater desalination was analyzed by Liu et al. [29]. Three different processes were simulated by Dow's Reverse Osmosis System Analysis, and the exergies were compared. The results indicated that the main exergy destruction in the conventional process (single RO) occurred in the membrane and concentration stream valves. To reduce the exergy and energy consumption, concentration blending and an energy recovery device were applied.

El-Emam and Dincer [30], (2014) used Thermoeconomic analysis to obtain the performance of an RO plant as a function of salinity. The exergy analysis showed that the largest irreversibilities occurred in high pressure pump and RO module. For the base case; the system achieves an exergy efficiency of 5.82%.

In 2015, Fitzsimons et al. [4] reviewed the different exergy analysis approaches that have been proposed in the literature to calculate chemical exergy term in desalination processes. In addition, they proposed an accurate approach to calculate the chemical exergy of electrolyte solutions, based on the Pitzer equations. Their findings showed that the choice of exergy model can have a significant impact on the results and that considerable care must be taken to select the most suitable approach. Qureshi and Zubair [31,32] presented an exergetic analysis of a brackish water reverse osmosis desalination unit using different energy recovery methods. They also discussed the correct definition of exergetic efficiency for such systems, which can also be used to determine the specific energy consumption. The effect of feed salinity was also used for further illustrating the difference in the second-law efficiency definitions. Eveloy et al. [33,34] evaluated the technical and economic feasibility of integrating on-site gas turbine power generation and reverse osmosis equipment for the production of both electricity and fresh water in a coastal hydrocarbon production facility. The reverse osmosis unit operates at a specific energy consumption and exergy efficiency of 4.1 kWh/m$^3$and 29%, respectively.

And already in 2016, Khalid et al. [35] reported a comparative assessment of two systems for nuclear desalination using RO for desalination. Exergy analysis is used to assess the performance of the electric power generation and desalination processes, and overall system, for each of the systems, as well as the effects of varying significant design and operating parameters on the exergy efficiencies of the power generation process, desalination process and overall system. In the work of Mokhtari et al. [36] a multi-objective optimization was used in the design and energy, exergy, economic, and environmental analysis of direct two-stage reverse osmosis system.

## 2. Case study: a reverse osmosis desalination plant

The seawater desalination plant was described in detail in a previous work [37].

The plant is located in Gran Canaria (Canary Islands). It has a nominal production of 82,000 m$^3$/day using ten production lines. A schematic of the plant is shown in Fig. 1. Each line consists of two reverse osmosis stages with the concentrate solution of the first one feeding the second through a Booster pump. The energy recovery is performed either with Pelton turbines or by pressure exchanger energy recovery systems, ERI (Energy Recovery Inc.) or DWEER (Dual Work Exchange Energy Recovery).

Feed water is pumped from a pond, where a first physical pretreatment is achieved due to the natural driven filtration of the seawater through the porous walls of the pond. The feed water is characterized by an annual mean salinity of about 37,000 ppm. Feedwater temperature varies during the year between 19 °C and 26 °C. The pre-treatment and filtration procedure is similar in all ten lines. Filtration consists of sand filters, followed by precoat filters and finally by cartridge filters. Between precoat and cartridge filters, an antifouling/antiscaling agent (Hypersperse MDC220) is added, but not continuously. A common post-treatment for permeate of all ten lines is performed. The osmotised and remineralized water is collected in a regulator tank and pumped to

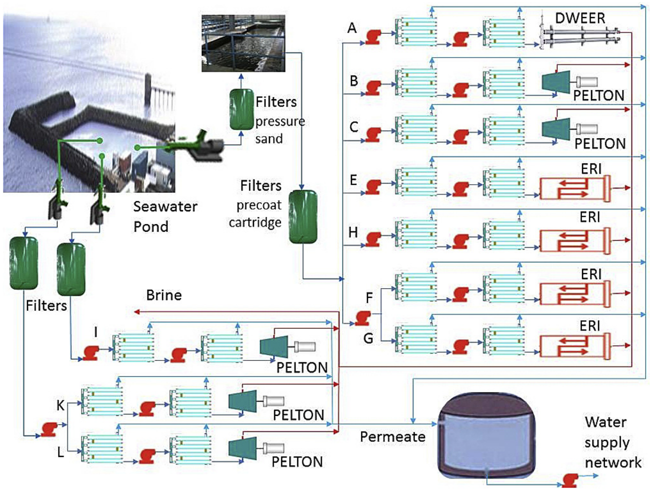

**Fig. 1.** Schematic of the reverse osmosis desalination plant.

**Table 1**
Thermodynamic parameters and results for the operation of the ten lines.

| Line | $\dot{V}$ m$^3$/h | p$_1$ bar | p$_2$ bar | $\dot{V}_{per,1}$ m$^3$/h | $\dot{V}_{per,2}$ m$^3$/h | $\dot{V}_{per,tot}$ m$^3$/h | TDS$_{\text{per tot}}$ ppm | TDS$_{\text{brine}}$ ppm | Cf$_1$ % | Cf$_2$ % | Cf$_{\text{tot}}$ % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| A (1) | 785 | 47.8 | 69.5 | 79 | 318 | 397 | 307 | 73,396 | 20.4 | 45.1 | 50.6 |
| B (2) | 642 | 61.6 | 59.9 | 254 | 62 | 316 | 414 | 72,463 | 41.1 | 16.4 | 49.2 |
| C (3) | 683 | 62.3 | 70.5 | 246 | 101 | 347 | 152 | 75,054 | 36.0 | 23.1 | 50.8 |
| E (4) | 759 | 67.9 | 71.7 | 335 | 114 | 449 | 269 | 90,316 | 44.1 | 26.9 | 59.2 |
| F-G (5–6) | 1299 | 61.0 | 67.0 | 450 | 200 | 650 | 210 | 73,823 | 34.6 | 23.6 | 50.0 |
| H (7) | 793 | 70.5 | 73.1 | 301 | 119 | 420 | 236 | 78,419 | 38.0 | 24.2 | 53.0 |
| I (8) | 661 | 54.2 | 79.1 | 187 | 135 | 322 | 249 | 80,310 | 28.3 | 28.5 | 48.7 |
| K-L (9–10) | 1227 | 63.0 | 70.5 | 461 | 157 | 618 | 191 | 74,490 | 37.6 | 20.5 | 50.4 |
| **TOTAL** | **6849** | | | **2313** | **1206** | **3519** | **427** | **76,536** | | | |

the municipal storage tanks. The brine rejected from the membranes is returned to the sea.

Table 1 presents some parameters and operational data of the ten lines: seawater inlet flow rate ($\dot{V}$), inlet pressure for reverse osmosis membranes (stage 1, $p_1$, and stage 2, $p_2$), flow rate of permeate (stage 1, $\dot{V}_{per,1}$, stage 2, $\dot{V}_{per,2}$, and total, $\dot{V}_{per,tot}$), purity of total permeate flow $TDS_{\text{per tot}}$ and of the brine, $TDS_{\text{brine}}$, and conversion factor of the membranes, (stage 1, $Cf_1$, stage 1, $Cf_2$, and total, $Cf_{\text{tot}}$).

## 3. Methodology

### 3.1. Exergy definitions

The exergetic efficiency evaluates the true performance of a process or energy system from the thermodynamic viewpoint. Its characterization is subjective to some extent, so that several definitions are presented in literature. They can be divided into two main groups [38,39]:

a) Considering the exergy balance as:

$$\sum \dot{E}_{in} = \sum \dot{E}_{out} + \dot{E}_D + \dot{E}_L \tag{1}$$

Where the subscripts *in*, *out* denote the inputs and outputs from the system, respectively, *D* the total destruction and *L* the loss.

Exergetic efficiency is then defined as the ratio of all exergy outflows to inflows [14,15,19–21,28,29]:

$$\varepsilon_a = \frac{\sum \dot{E}_{out}}{\sum \dot{E}_{in}} \tag{2}$$

To the total desalination system, this definition is applied by several authors [10,11,18,25,26] as the net salinity exergy divided by the total exergy input provided by the pumps:

$$\varepsilon_a = \frac{\dot{E}_{in} - \dot{E}_{out}}{\dot{W}_{\text{supplied to the plant}}} \tag{3}$$

The difference between the sum of the outlet and inlet stream exergies is associated with the least work of separation [22,23,30–32,35]. Two possibilities can be taken into account:

- The least work of separation: the reversible work needed, for a finite recovery ratio, to produce the required permeate [22]:

$$\varepsilon_{a-1} = \frac{\dot{E}_{in} - \dot{E}_{out}}{\dot{W}_{\text{supplied to the plant}}} = \frac{\dot{W}_{least}}{\dot{W}_{\text{supplied to the plant}}} \tag{4}$$

- The minimum least work, $\dot{W}_{least}^{min}$, minimum required work of separation in the limit of reversible operation and infinitesimal extraction (null recovery ratio) [22]:

$$\varepsilon_{a-2} = \frac{\dot{W}_{least}^{\text{min}}}{\dot{W}_{\text{supplied to the plant}}} \tag{5}$$

Mistry et al. [22] argued that the latter definition is preferred because the minimum least work of separation represents the actual exergetic value of the product water.

Qureshy et al. [32,33] further argued that the difference occurs in these two methodologies due to the way the process of discarding the brine stream is considered. In $\varepsilon_{a\text{-}1}$the exergy of the brine stream is used in the calculation as part of the exergy out term since it is taken as an exiting stream, while in$\varepsilon_{a\text{-}2}$ the exergy of the brine is not considered as an exergy out term but as an exergy lost in the system.

b) With the exergy balance formulated in terms of the *desired output* or *useful exergetic effect* and the *necessary input* or *driving exergy expense* named as *product* exergy and *fuel* exergy [40]:

$$\dot{E}_P = \dot{E}_F - E_D - \dot{E}_L \tag{6}$$

The exergetic efficiency becomes:

$$\varepsilon_b = \frac{\dot{E}_P}{\dot{E}_F} = 1 - \frac{\dot{E}_D + \dot{E}_L}{\sum \dot{E}_{in}} \tag{7}$$

In this case, the problem appears in the sometimes subjective definition of *fuel* and *product* exergy.

Some authors use this definition, but they do not specify what the fuel is and what the product exergy is [36]. In other articles [12,16,17,24] they consider that the product is just the total exergy of the permeate and the fuel is the sum of the total exergy of the seawater and the work supplied to the plant.

In other works, the authors do not give a definition of the exergetic efficiency, they just evaluate it in terms of other exergetic magnitudes: the rate of decrease in entropy of feed water and the rate of internal entropy production [7]; entropic losses [2,8]; the work lost in irreversible processes [9] or the exergy loss rate due to the irreversibilities [13].

In this work, we consider and validate the formulation of exergetic efficiency in terms of fuel and product exergy [40], as the most appropriate one for desalination systems. The product represents the (net) desired exergy result produced in the system and the fuel the net exergy resources which were spent to generate the product. Furthermore, following the recommendations of Lazzaretto and Tsatsaronis [41], the product is defined to be equal to the sum of all the exergy values to be considered at the outlet (including the exergy of energy streams generated in the component) plus all the exergy increases between inlet and outlet (i.e. the exergy additions

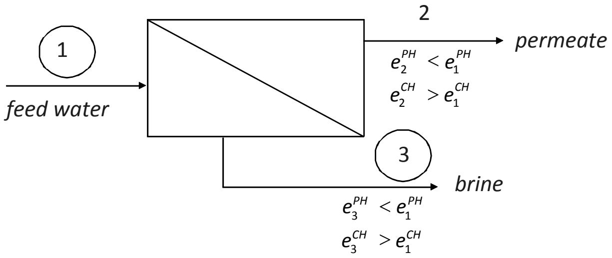

**Fig. 2.** Schematic of a general RO device.

to the respective material streams) that are in accord with the purpose of the component. And the fuel is defined to be equal to all the exergy values to be considered at the inlet (including the exergy of energy streams supplied to the component) plus all the exergy decreases between inlet and outlet (i.e. the exergy removals from the respective material streams) minus all the exergy increases (between inlet and outlet) that are not in accord with the purpose of the component.

Applied to the components involved in our RO plant this formulation leads to following definitions:

$$\varepsilon_{PUMPS} = \frac{\dot{E}_{out} - \dot{E}_{in}}{\dot{W}} \tag{8}$$

$$\varepsilon_{TURBINES} = \frac{\dot{W}}{\dot{E}_{in} - \dot{E}_{out}} \tag{9}$$

$$\varepsilon_{\text{Pressure Exchanger}} = \frac{\dot{E}_{seawater\ \ out} - \dot{E}_{seawater\ \ in}}{\dot{E}_{brine\ \ in} - \dot{E}_{brine\ \ out}} \tag{10}$$

In the reverse osmosis membranes the separation of the salt occurs: the chemical compositions of the inlet and outlet streams are different. Therefore, product and fuel exergy definitions must consider the chemical exergy difference of the inlet and outlet streams.

Fig. 2 shows a schematic of a general RO device.

Taking into account that the purpose of the RO membranes is the chemical separation of the salt, leading to an increase in the chemical exergy between inlet and outlet and to a decrease in the physical exergy within the same streams, the exergetic efficiency of the RO membranes can be unambiguously defined as:

$$\varepsilon_{RO} = \frac{\left(\dot{E}_2^{CH} + \dot{E}_3^{CH}\right) - \dot{E}_1^{PH}}{\dot{E}_1^{PH} - \left(\dot{E}_2^{PH} + \dot{E}_3^{PH}\right)} \tag{11}$$

This definition is in agreement with the formulation of Sorin et al. [13] who emphasized that “the thermodynamic analysis of the RO process throws a conversion of mechanical exergy into chemical exergy which generates two purified streams from a raw feed stream”.

In the total process, two situations can be taken into account:

- The only product of the plant is the permeate:

$$\varepsilon_{b,T} = \frac{\dot{m}_{H_2O\ permeate} e^{CH}_{H_2O\ permeate}}{\dot{W}_{Pumps} - \dot{W}_{Turbines} + \dot{m}_{H_2O\ \ permeate}\left(e^{PH}_{H_2O\ \text{seawater}} - e^{PH}_{H_2O\ \text{permeate}}\right)} \tag{12}$$

and the brine is a lost:

$$\dot{E}_{L,T} = \dot{m}_{brine}\left(e^{PH}_{brine} + e^{CH}_{brine} - e^{PH}_{H_2O\ \text{seawater}}\right) \tag{13}$$

- Both permeate and concentrate streams could be valorized in order to fully take advantage of their exergetic potential [2,13,17,22]:

$$\begin{aligned}\dot{E}_{P,T} = {} & \dot{m}_{H_2O\ permeate}\, e^{CH}_{H_2O\ permeate} \\ & + \dot{m}_{brine}\left(e^{PH}_{brine} + e^{CH}_{brine} - e^{PH}_{H_2O\ \ \text{seawater}}\right)\end{aligned} \tag{14}$$

Herein, the exergies of the flow streams were calculated according to the definitions given in Ref. [40].

The values of the chemical exergy of seawater, brine and permeate were calculated with the functions given by Sharqawy et al. [23]. The values of the specific physical exergy were calculated by:

$$e^{PH} = (h - h_0) - T_0(s - s_0) \tag{15}$$

where subscript 0 represents environmental conditions. Thermodynamic properties, $h$, $s$, of seawater, brine, and permeate were calculated from Sharqawy et al. functions [23]. The dead state was defined taking into account average environmental conditions: $T_0 = 21.5$ °C and $p_0 = 1$ bar in order to obtain a null value of exergy for the intake seawater, as Sharqawy et al. [23] recommend.

### 3.2. Thermodynamic model

An exergy analysis requires the proper calculation of the thermodynamic properties involved in it. In our desalination plant, the working fluids are seawater, with a salt concentration of 37,000 ppm, permeate, within 150–400 ppm and brine, within 72,000–90,000 ppm of salt concentration. Other chemicals are not considered because this plant does not use chemical products in the pre-treatment phase.

Seawater is an electrolytic compound that consists of water and sodium chloride. Most of the above cited articles do not take this characteristic into account. They just consider seawater as an ideal mixture and do not calculate the chemical exergy term [10–12,18,19,21,26,30]. As a result, erroneous values are obtained in the calculation of the exergy destruction or the exergetic efficiency. The work of Fitzsimons et al. [4] presents a review of the various exergy analysis approaches proposed in the literature. The main focus of their work is the chemical exergy term. The models assessed were: (1) the ideal mixture model [10,11,18,19,26,30] (2) the model used by Refs. [2,7,14,15,28] with the so called concentration exergy term; (3) exergy calculations based on seawater thermodynamic properties, the Leyendekker thermodynamics of seawater [12,24] or the updated seawater thermodynamic properties of Sharqawy et al. [23], used by Refs. [22,25,29,31,33,34] and (4) the electrolyte solution model [4,9,36]. The ideal mixture model was found to have serious limitations. The other approaches produced very similar results. Their findings showed the significance of calculating the chemical exergy term and that considerable care must be taken to select a suitable approach.

In this work the updated Sharqawy seawater functions [23] have been used.

## 4. Results and comparison with literature

In Literature some confusing and contradictory results are reported.

1. Related to the model used for the calculation of the thermodynamic properties:

The ideal mixture model leads to some mistakes in exergy calculations. For example [10,11,18,19,26], obtained negative values for the exergy of the brine. Cerci [10] explained that the exergies of the brine streams are negative due to salinities above the dead state level and that it means that the work input to the brine is required to bring it to the dead state. Romero-Ternero [12] used the Leyendekker thermodynamics of seawater, but they also obtained negative values for the exergy of the brine. They said that the negative exergy rate of blow down represents the potential use of rejected chemical exergy with respect to seawater. But Sharqawy et al. [23] explained that all of these authors have ignored the chemical exergy term in their model, and consequently they have sometimes obtained negative flow exergy at salinities higher than the environmental state salinity. The chemical exergy is the maximum work obtained when the concentration of each substance in the system changes to its concentration in the environment at the environment pressure and temperature. It has then no sense a negative value in the exergy flow of the brine. The flow exergy may have negative values if (and only if) the pressure of the system is lower than the dead state pressure [42].

2. Related to the definition of the exergetic efficiency:

The definition of the exergetic efficiency as the ratio of all exergy outflows to inflows ecc.(2) produces some misunderstandings.

- Drioli et al. [14] pointed out that a positive value of $\Delta E = E_{outflows}\text{-}E_{inflows}$ corresponds to a production of exergy, while a negative value is due to its irreversible destruction. According to this, they stated that pumps contribute consistently to exergy production, whereas all other stages lose exergy irreversibly. But a proper exergy analysis shows that all real components produce exergy destruction. Particularly, pumps destroy a big amount of exergy, as it is set out in our work.
- Several authors [10,15,18,23] stated that the largest irreversibilities occur in the membrane modules and in the valves. It seems that they did not take into account the irreversibilities in the pumps. Besides, a correct definition of exergy efficiency in the membranes, ecc (11), produces a great reduction of the exergy destruction calculated in the membranes. There is no article in the literature where physical and chemical exergy were taken into account separately in the definition of the exergetic efficiency of the membranes. In this article, we state that just the separation of the physical and chemical exergy in the definition of the fuel exergy and the product exergy of the membranes leads to a correct estimation of the exergy destruction in the membranes and of its exergetic efficiency.
  Related to the valves, Lazzaretto and Tsatsaronis [41], call them dissipative components, because exergy is destroyed without gaining something thermodynamically useful directly from the same component. In their opinion [41], when a dissipative component is involved, it is possible to define meaningful exergetic efficiency only if this component is considered together with all components it serves.
- Drioli et al. [14,15] found a similar value for the exergetic efficiency of the total plant when a Pelton turbine or a pressure exchanger was used. Since greater irreversibilities take usually place in the turbines this is out of logic. (In our work we have obtained exergetic efficiencies of 70–75% for the Pelton turbines and 92–98% for the pressure exchangers). The only reason for literature results is an inadequate definition of the exergetic efficiency.
- The exergetic efficiency of the total plant gives an unacceptable low value when it is defined as the ratio “the exergy of the permeate to the total exergy inlet”. It is due to the low value of the exergy of the product, the desalted water, compounded by the omission of the chemical exergy term in the calculations.
- Some authors [10,11,18] define the second law efficiency of the total plant using the ratio of all exergy outflows to inflows definition, eq. (2), but then they determine it by dividing the net salinity exergy by the total exergy input provided by the pumps. The problem of eq. (2) is that the exergy input and output are not equal to the consumed and produced exergies, as it is required in the calculation of the efficiency of the total plant.
- On the other hand, other authors [12,16,17,24] say that they use the “product-fuel” definition, eq. (7), but they consider that the product is just the total exergy of the permeate and the fuel is the sum of the total exergy of the seawater and the work supplied to the plant: the “inlet-outlet” formulation in the practice, which leads to very low exergetic efficiencies of the total plant.

These erroneous results lead to the consideration that in evaluating the performance of a component could be, in general, more appropriate to operate with exergy differences associated with each material stream between the inlet and the outlet of the component, as has been suggested by Lazzaretto and Tsatsaronis [41]. This becomes especially meaningful when the purpose of the component is to supply exergy to a stream (as it happens in pumps), to consume a part of the exergy of a stream (in the case of the turbines and in the pressure exchangers), or to provide at the outlet a different type of exergy than is available at the inlet (as it occurs in the membranes, where part of the mechanical exergy is converted into chemical exergy, as already mentioned).

If the exergetic efficiency is defined as the product exergy divided by the fuel exergy, eq. (7), attention must be paid to the proper formulation of fuel and product. As these definitions are sometimes subjective, they cannot be omitted [36] nor identified to inlet and outlet [12,16,17,24]. These definitions are based on the purpose of operating the component [41]: for example to supply exergy to a material stream in pumps or to convert mechanical exergy into chemical exergy in reverse osmosis membranes. Just in this way an unambiguous procedure for developing the exergetic efficiencies of a reverse osmosis desalination plant and its components can be introduced.

The comparison between our results and those reported in literature produce some interesting considerations. Main detailed results of the exergetic analysis of our seawater desalination plant are reported in a previous work [37]. Fig. 2 shows the comparison of our results with those provided in the literature in terms of the total exergetic efficiency of the reverse osmosis desalination process and the exergetic efficiency of the core components. In order to facilitate the comparison, regarding to our previous work [37], just the values obtained in line B, which consist of a high pressure pump, two reverse osmosis stages and a Pelton turbine, have been drawn.

Fig. 3 shows very dissimilar results. Regarding to total exergetic efficiency, values vary from <2% [23], 4.3% [10] to 48.91% [29], 50.9% [24], 55.5% [12] or even 92.44% [36]. In our work, the exergetic

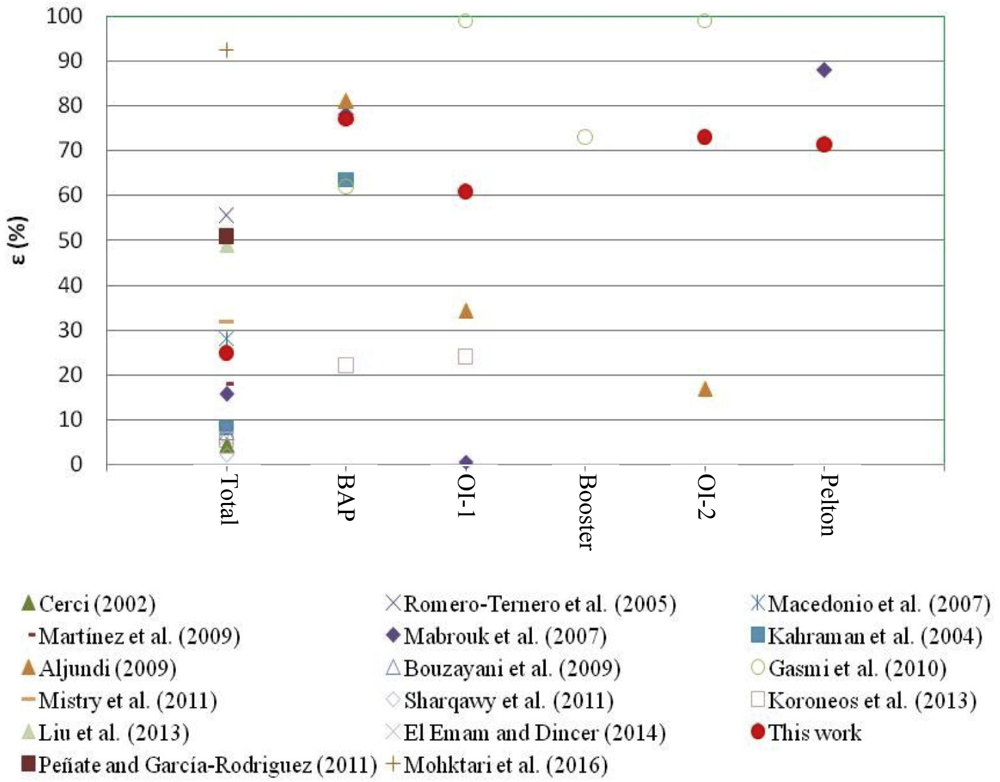

**Fig. 3.** Total exergetic efficiency of reverse osmosis desalination plants and exergetic efficiency of the core components. Data from Literature.

efficiency of reverse osmosis desalination line B corresponds to 24.6%, (34.0% when the brine is also considered as a product). Although the reverse osmosis processes presented by each article are not exactly the same, these enormous deviations can only be due to different conceptual definitions. In effect [10,23], defined the exergetic efficiency as the ratio of all exergy outflows to inflows [12,24]; gave incorrect definitions to fuel and product exergy [29]; and [36] did not specify how they performed the calculations, but values of [36] are clearly overestimated.

Related to the components, Koroneos et al. [28] reported very low values of the exergetic efficiency of the pumps. It can be due to the use of the ideal mixture model in the calculation of the thermodynamic properties. A too high value for the exergetic efficiency of the Pelton turbines is obtained by Ref. [16]. In the membranes, the exergetic efficiency values vary from the very low value of 0.5% [16], 24% [28], 34.2% [18] to the overestimated value of [20]. As has been already mentioned, none of the authors considered the separation of the physical and the chemical exergy on the definition of the exergetic efficiency of the membranes.

Table 2 shows the percentage of exergy destruction in the core components of the desalination process in Literature. Regarding our previous results [37], values from reverse osmosis desalination lines I and E have been reported: line I contains a Pelton Turbine and its own intake pump, and line E is provided with a pressure exchanger ERI.

In our work, we found that the largest exergetic destructions took place in the pumps and in the first reverse osmosis stage. Kahraman et al. [11] obtained the same results and they proposed the use of high efficiency pumps and motors equipped with variable frequency drives in order to reduce desalination costs. Exergy destruction in the membranes is very high in the works of [10], 74.1%; [16], 70.1%; [23], 78.8% and [30], 67.8%. With the formulation proposed in this work, the exergy destruction in the reverse osmosis membranes is within 13.0–38.5% for the first stage and 5.6–15.5% for the second stage. Just Gasmi et al. [20] performed the analysis of a double stage reverse osmosis process with an inter-stage Booster pump. The exergy destruction in their Booster pump corresponds to 14%. In our work this value is within 5.1 and 12.9%. All the authors agree with the recommendation of the use of energy recovery devices. The best results are obtained by the pressure exchanger devices (6.5% of exergy destruction in Ref. [22]; 3.9% in our work [37]).

**Table 2**
Exergy destruction in core components of the reverse osmosis desalination process. Data from Literature.

| Exergy destruction (%) | HPP | RO-1 | BP | RO-2 | Valve | Turbine | ERI |
|---|---|---|---|---|---|---|---|
| This work [37] (Line I) | 31.4 | 13.0 | 5.1 | 15.5 | | 21.6 | |
| This work [37] (Line E) | 39.0 | 38.5 | 12.9 | 5.6 | | | 3.9 |
| Cerci [10] | | 74.1 | | | 17.1 | | |
| Romero-Ternero et al. [12] | 7.2 | 34.5 | | | | 23.7 | |
| Mabrouk et al. [16] | 16.6 | 70.1 | | | | 4.9 | |
| Kahraman et al. [11] | 39.7 | 23.6 | | 12.6 | 10.6 | | |
| Aljundi [18] | 19.6 | 9.0 | | 12.0 | 56.8 | | |
| Bouzayani et al. [19] | 35.0 | 41.0 | | | | 24.0 | |
| Gasmi et al. [20] with BP | 44.0 | 16.1 | | 21.0 | | | |
| Gasmi et al. [20] without BP | 35.6 | 15.6 | 14.0 | 11.0 | | | |
| Mistry et al. [22]. | 20.0 | 54.8 | | | | | 6.5 |
| Sharqawy et al. [23] | | 78.8 | | | 19.4 | | |
| El Emam and Dincer [30] | 17.2 | 67.8 | | | | | |

## 5. Conclusions

This work performs a literature review and comparison of different approaches for formulating exergetic efficiency in reverse osmosis desalination plants.

Some confusing and contradictory results have been found in Literature due to inadequate thermodynamic models and to incorrect and ambiguous exergetic efficiency formulations: negative values of the chemical exergy, exergy production in pumps, larger irreversibilities in the membranes than in the pumps.

Regarding total exergetic efficiency, values vary from <2% [23] to 92.44% [36]. In our work, the exergetic efficiency of reverse osmosis desalination corresponds to 24.6%, (34.0% when the brine is also considered as a product). These enormous deviations can only be due to different conceptual definitions.

Exergy destruction in the membranes is very high in some works: 67.8% [30]-78.8% [23]. With the formulation proposed in this work, the exergy destruction in the reverse osmosis membranes is within 13.0–38.5% for the first stage and 5.6–15.5% for the second stage.

In this work we recommend:

- The use of the updated seawater thermodynamic properties of Sharqawy et al., [23], for the exergy calculations.
- The formulation of Lazzaretto and Tsatsaronis [41] for the fuel and product exergy in the definition of the exergetic efficiency of the total plant and the components.
- The separation of the physical and chemical exergy in the formulation of the exergy of the fuel and the exergy of the product in the reverse osmosis membranes and in the total plant. In this way, the conversion of mechanical exergy into chemical exergy, distinctive of reverse osmosis desalination processes [13], is appropriately considerate.

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## Nomenclature

| | |
|---|---|
| BP | Booster pump |
| *Cf* | Conversion factor |
| DWEER | *Dual Work Exchanger Energy Recovery* |
| ERI | Pressure exchanger *Energy Recovery Inc.* |
| RO | Reverse osmosis |
| TDS | Total dissolved solids |
| $e$ | Specific Exergy kJ/kg |
| $\dot{E}$ | Exergy rate kW |
| $\dot{m}$ | Mass flow rate kg/s |
| $P$ | Pressure bar |
| $\dot{W}$ | Power kW |
| $\dot{V}$ | Flow rate $m^3/h$ |

*Greek symbols*

| | |
|---|---|
| $\varepsilon$ | Exergetic efficiency |

*Subscripts and superscripts*

| | |
|---|---|
| CH | Chemical |
| *D* | Destroyed |
| *in* | inlet |
| *F* | Fuel |
| *L* | Loss |
| *P* | Product |
| PH | Physical |
| *out* | outlet |
| *T* | Total |

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## 4.3. Key issues on the exergetic analysis of $H_2O$/LiBr absorption cooling systems.

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### Abstract

This paper deals with the key aspects of the exergy analysis of $H_2O$/LiBr absorption refrigeration cycles where, instead of agreement, disparity of opinion exists among researchers. As a result, comparisons with the literature are often difficult or meaningless. Based on an in-depth literature review, the key issues highlighted were: a) the identification of the dead state, b) the calculation of the exergy of the currents, and c) the definition of the exergy efficiency of the devices and of the overall system. This study clarifies controversial and divergent assumptions and proposes a coherent approach. In addition, a comparison with the literature is performed. As a case study, a single effect absorption cycle, refrigerated with water, has been considered. Related to the dead state, consideration of different subsystems results in practical interest. The results highlight the importance of the correct calculation of the chemical exergy for the exergy analysis of the absorption refrigeration system. It is also described here how to define the rational exergetic efficiency, or fuel-product exergy, according to physical and chemical exergies of the streams. The comparison with the literature shows discrepancy specially in the exergy analysis of the desorber and the absorber, where the chemical exergy plays an important role.

### Summary of the PhD student's contributions

The work has been entirely prepared by the PhD student. She is responsible for the conceptualization, methodology, data treatment, analysis of results, conclusions and preparation of both the draft and the final paper. The supervision of the whole work has been in charge of the director of the Thesis, J. Daniel Marcos.

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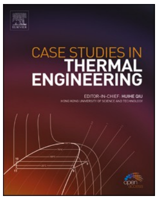

# Key issues on the exergetic analysis of $H_2O$/LiBr absorption cooling systems

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ABSTRACT

This paper deals with the key aspects of the exergy analysis of $H_2O$/LiBr absorption refrigeration cycles where, instead of agreement, disparity of opinion exists among researchers. As a result, comparisons with the literature are often difficult or meaningless. Based on an in-depth literature review, the key issues highlighted were: a) the identification of the dead state, b) the calculation of the exergy of the currents, and c) the definition of the exergy efficiency of the devices and of the overall system. This study clarifies controversial and divergent assumptions and proposes a coherent approach. In addition, a comparison with the literature is performed. As a case study, a single effect absorption cycle, refrigerated with water, has been considered here. Related to the dead state, consideration of different subsystems results in practical interest. The results highlight the importance of the correct calculation of the chemical exergy for the exergy analysis of the absorption refrigeration system. It is also described here how to define the rational exergetic efficiency, or fuel-product exergy, according to physical and chemical exergies of the streams. The comparison with the literature shows discrepancy specially in the exergy analysis of the desorber and the absorber, where the chemical exergy plays an important role.

## 1. Introduction

Exergy analyses are very useful tools in the design, optimization and assessment of energy processes [1] However, far from existing an agreement among researchers, there are several key points of the analysis where disparity of opinions is found [2]. As a result, comparisons with the literature are often difficult or not very meaningful. Plant analyses involving absorption systems are not an exception.

### 1.1. State of the art

The scientific articles that somehow study or mention the exergy analysis of an absorption system are numerous. It is not the purpose of this paper to list them all. We will only refer to the really significant ones for our work, which are presented hereafter. We have focused on the works that include the methodology of exergy analysis of single $H_2O$/LiBr absorption cooling systems, providing

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some novel point of view or aspect.

One of the first works related to the topic, a joint work carried out by the University of Minnesota and the Technische Universität München [3] presented the availability analysis of a lithium bromide absorption heat pump. They applied the second law analysis to detect internal losses and to obtain a clear trend for design optimization. On the work of Arh and Gaspersic [4], different advanced absorption cycles working between four temperature levels and two or three pressure levels were compared on the basis of the coefficient of performance COP and exergy efficiency. Results for the working mixture $H_2O$/LiBr were there presented. Jernqvist et al. [5] pointed out that the COP is not always adequate to describe the effectiveness of a sorption heat pump. They proposed the thermodynamic efficiency, the exergetic efficiency and the exergetic index, instead. They also stressed that exergy analysis should be used as a compliment to the First Law analysis. Oliveira and Le Goff [6] identified the sources of entropy production within an absorption-desorption cycle trough energy, entropy and exergy balances. They also represented the exergy balances on two types of diagrams: exergy-composition and exergy-enthalpy, for the identification of exergy losses in the separation and mixing operations. Aprhornratana and Eames [7] presented the results of the exergy analysis of a single effect absorption refrigerator cycle in a graphical format. In addition, they introduced a method for the calculation of entropy of water-lithium bromide solutions. Talbi and Agnew [8] applied a design and optimization procedure where the exergy losses and the overall exergetic efficiency were taken as optimization parameters. In addition, an availability analysis was carried out for each component of the system. Sencan et al. [9] calculated all exergy losses in a lithium bromide/water absorption system and they carried out the exergy analysis for different operating conditions. The exergetic efficiency for cooling and heating applications was also determined and shown graphically. Kilic and Kaynakli [10] used the first and second law of thermodynamics to analyze the performance of the cycle while varying some working parameters. A mathematical model based on the exergy method to evaluate the exergy loss of each component and total exergy loss of all the system components was introduced. Kaushik and Arora [11] developed a computational model for the parametric investigation of the cycle using new property equations of water-lithium bromide solution. Among the performance parameters computed were the exergy destruction and exergetic efficiency. Gebreslassie et al. [12] conducted an exergy analysis for single, double, triple and half effect cycles only considering the unavoidable exergy destruction. Thus, the obtained performances represented the maximum achievable performance under the given operation conditions. Palacios-Bereche et al. [13] presented a methodology to calculate the exergy of $H_2O$/LiBr solution, they applied it to the evaluation of absorption refrigeration systems and compared some cases in the literature. Avanessian and Ameri [14] studied and compared different water-cooled systems under different operating and climatic conditions. They proved the effect of considering the chemical exergy of the $H_2O$/LiBr solution on the exergetic analysis. Joybari and Haghighat [15] investigated absorption refrigeration systems with different heat exchanger designs having the same COP value. The effect on the outlet specific exergy and exergy destruction rate of each component was checked. Mussati et al. [16] applied a non linear mathematical model for the optimization of the cycle using the exergy loss rate, heat transfer area and cost as single objective functions. Pandya et al. [17] optimized the system from both the energy and the exergy point of view and focused on the generator temperature. The exergy destruction rate was selected as objective parameter and they evaluated the influence of the condenser and evaporator temperature on the optimum desorber temperature. Maryami and Dehghan [18] performed an exergy based comparative study between $H_2O$/LiBr absorption refrigeration systems from half effect to triple effect. An optimum generator temperature, where the total exergy change was a minimum and the exergy efficiency a maximum, was found for all the configurations. A small capacity system was analyzed by Modi et al. [19] using a mathematical model. The rational efficiency and the exergy losses for all system components were obtained. Mohtaram et al. [20] compared the components of the cycle in terms of thermodynamic efficiency and rate of exergy destruction. Singh and Verma [21] used computational intelligence to perform the energy and exergy analysis of the system. The specific enthalpy and entropy were predicted through an artificial neural network and their results compared with published works. And, recently, Sala-Lizárraga and Picallo-Pérez [22] described the simple cycle of an absorption refrigerator, with the exergy analysis of each one of its components. The irreversibilities and the exergy efficiency were calculated.

Interest in integrating $H_2O$/LiBr absorption refrigeration cycles into more complex or polygeneration systems has grown exponentially in recent years. For example, Ghaebi et al. [23] carried out an exergoeconomic optimization of a trigeneration system for heating, cooling and power production, where cooling was produced by an absorption chiller. Godarzi et al. [24] designed a PCM storage system for a solar absorption chiller based on exergoeconomic analysis ans genetic algorithm. Gutiérrez-Urueta et al. [25] analyzed a single effect system where two evaporators and a sub-cooler, in addition, were introduced. Cimsit et al. [26] considered a R-134a compression – $H_2O$/LiBr absorption cascade refrigeration cycle and performed an exergy-based thermoeconomic optimization. Rashidi and Yoo [27] performed both an exergetic and an exergoeconomic analysis of power-cooling cogeneration systems based on the kalina and absorption refrigeration cycles. Akrami et al. [28] used the same exergy approaches to assess a cogeneration hydrogen and cooling production plant equipped with concentrated PVT, an electrolyzer and an absorption chiller. Salhi et al. [29] studied a compression-absorption cascade refrigeration system powered by geothermal energy. Also a geothermal reservoir was used by Leveni et al. [30] to provide energy into a cascade organic Rankine Cycle and a water/lithium bromide absorption chiller. The integrated unit was analyzed trough an exergy analysis. Salehi et al. [31] carried out an exergoeconomic comparison of solar assisted absorption heat pumps, solar heaters and gas boilers for space heating. Behzadi et al. [32] optimized the production of electricity, cooling and hydrogen based on a solar system. A thermoelectric generator unit was used instead the condenser of the double effect $H_2O$/LiBr absorption cooling system. The conventional and proposed systems were compared from energy, exergy and exergoeconomic points of view. Wu et al. [33] performed a thermoeconomic analysis of a composite district heating substation composed of an absorption heat pump. Agarwal et al. [34] presented an energy and exergy analysis of a vapor compression-triple effect absorption cascade refrigeration system. Recently, Sharifi et al. [35] maximized the exergetic and energetic efficiencies of a solar assisted absorption chiller. And Jain et al. [36] performed an advanced exergy analysis of a novel and integrated $NH_3$/H2O and $H_2O$/LiBr vapor absorption refrigeration system.

### 1.2. Controversial and diverging hypotheses

A careful inspection of the exergy analyses carried out in all these cited articles reveals a disparity of methodologies. This discrepancy is most pronounced on several points. One of them is related with the conditions of the dead state. Most of the articles take the ambient pressure [3,25] or similar values (1 bar [11,28,36], 1 atm [15,18,19,27], 100 kPa [6,12,35], 101,3 kPa [13,14,26,30,33, 34]) as the dead state pressure. But, other authors do not mention this parameter [8–10,20,21,23,31,32] and in the work of Salhi et al. [29] the value of 0.01 bar is considered without justification. The reference temperature also adopts different values around 20 °C [7, 25], 25 °C [6,11,13,26–28,30,32–34,36], 30 °C [24,29], or the ambient temperature [3,35]. But Jernqvist et al. [5] consider that $T_0$ "*may be chosen at a level where heat energy is considered worthless for an actual application*" and they take the temperature of the medium on the heating side of the evaporator. The selection of a suitable reference state is important, as it is involved in the exergy calculation. Therefore, changing the values of the reference state will result in different exergy values. Authors state that it is usually the exergy differences that are of interest and not the absolute values, so this limitation is not considered too serious [5]. In our paper we will show that it can be important, both conceptually and in terms of results.

Another point of divergence is the inclusion or not of the chemical exergy of the streams in the analysis. Misra et al. [37] calculates the chemical exergy of the refrigerant (water) but do not considers the chemical exergy of the solution, because there is no chemical reaction in the process. Other authors are of a similar opinion [15,24]. Agarwal et al. [34] think that kinetic, potential and chemical exergy are negligible for a flowing stream in control volume, though they are not. Gomri et al. [38] argue that "*because there is no departure of chemical substances from the cycle to the environment, the chemical exergy is zero*". Other authors do not calculate it because they do not need it for the analysis [4,8–12,20–22,30,36]. Some authors simply do not even mention it [5,7,9,17–19,25,32,33]. In contrast, some articles carry out a detailed and in-depth calculation of the chemical exergy of all substances and streams, but using different approaches [3,6,26,39]. The methodology used by Palacios-Bereche et al. [13] has been cited later on [14,31,40,41]. Avanessian and Ameri [14] calculate the error of neglecting chemical exergy and they obtain a value of 30% in the desorber and 50% in the absorber.

The definition of the exergetic efficiency is usually another controversial point regarding exergy analysis [2]. The different definitions of this parameter applied to absorption refrigeration systems have been detailed by Palacios-Bereche et al. [13]. Basically, two main definitions can be found. The first one relates exergy outflows to inflows. The second one is the so called rational efficiency, and relates exergetic gain (fuel exergy) to exergetic expenditure (product exergy). Actually, most of the literature articles cited here use this fuel-product exergetic efficiency definition. Some of them are just interested in the exergetic efficiency of the total system [10–12, 14–16,18,20,21,25,29,30,34]. Other authors perform the exergy analysis of all the devices of the system, but they just provide the exergy destruction [7,8,17,22,29,36] or the exergy losses [9,33]. The exergetic efficiency of the different components of the system is analyzed by Refs. [3,13,19,24,26–28,31,32,35,39], but the comparison of their results usually becomes difficult or complex due to the lack of uniformity in the methodology, as already pointed out.

### 1.3. Novelty and interest of the work

From the literature review, three key points have been identified in the exergy analysis of the absorption cycle:

a) the definition of the dead state,
b) the calculation of the exergy of the material streams, and
c) the definition of the exergy efficiency of the devices and of the overall system.

This paper takes a detailed look at all these key aspects from the point of view of the methodology and the concepts. As a case study, the single effect $H_2O$/LiBr absorption refrigeration system [42] is used. The literature review shows a large discrepancy in the conceptual formulation of the exergy analysis of the absorption refrigeration cycle by various authors. This raises a problem when carrying out validations and formulating comparisons. In this paper, controversial and diverging hypothesys are cleared up and a comprehensive, coherent and consistent approach is proposed. In the practice, this proposal will ultimately lead to optimizing the design and operation of the system with much greater precision.

In addition, the comparison with the literature presenting a complete and original method of the exergetic calculation of the absorption machine, is performed.

### 1.4. Structure of the article

The article is structured as follows: First, the key points in the exergy analysis of the absorption cycle are identified and defined. Each of these points is presented with the solution adopted in this work. Next, the exergy analysis of an absorption cycle is carried out following the proposed methodology. In the following section, other literature approaches are detailed and the analysis of the same cycle is conducted with each one of them. The results are compared with those of this study. Finally, the conclusions of the work are provided.

## 2. Methods: key issues in the exergy analysis of the absorption cycle

From the literature review presented in the introduction, three key aspects were identified in the exergy analysis of the absorption cycle: a) the identification of the dead state, b) the calculation of the exergy of the streams, and c) the definition of the exergy efficiency of the devices and of the overall system. Each of these aspects and the solution adopted in this work are presented below.

### 2.1. Dead state

In exergy analysis it is necessary to choose a reference environment. Usually the environmental conditions surrounding the system are chosen. However, for some systems, the external environmental conditions may not be the best choice as a dead state. This happens, for example, when the system has no or only partial interaction with the environment [43]. In exergy analyses, it may be practical to divide a system into subsystems. This enables the analysis of the constraints affecting every subsystem and the choice of the appropriate dead state for each one individually, which may not be the same for all of them. The first step in establishing the appropriate dead states for each subsystem would be to state the parts of the universe that have a significant effect on the performance. Then, the practical and technological constraints on the interactions between the subsystems would be specified [44].

In this case study, the absorption cycle, the overall system can be considered as consisting of the following subsystems:(a) the absorption machine itself, confining the cooling fluid, $H_2O$, and the solution with the absorbing fluid $H_2O$/LiBr; (b) the heat source and the fluid circulating through it and exchanging heat with the absorption machine; (c) the evaporator and the fluid to be chilled; (d) the absorber and the condenser with the fluids that refrigerate the absorption machine.

Regarding the absorption machine itself, it is obvious that the working fluids confined in the machine do not exchange mass with the external fluids. The mass and total volume of these interior fluids are fixed, they are bounded. They can balance neither their pressure nor their composition with the environment surrounding the machine, they can only balance their temperature. Their equilibrium is therefore constrained.

Since a mechanical equilibrium with the environment cannot be reached, it makes not much sense to take the pressure of the external environment as the dead state pressure. And, since the chemical equilibrium with the environment cannot be reached, neither does it appear reasonable to consider as the chemical potential of these substances in the dead state that which corresponds to them in the external environment. For this case, Gagioli [44] proposes as dead state the state reached when the system is turned off, once the temperature reaches equilibrium with the environment.

For the heat source, it will be analyzed whether the fluid is confined in the system, where the above would apply. If the fluid is in contact with the environment at some point in the process, the ambient conditions can be taken as reference. The same reasoning applies to the external fluids flowing through the evaporator, absorber and condenser.

### 2.2. Estimation of the exergy of the working fluids

In exergy analysis, the exergy of the working fluid at different points of the process has to be calculated. The exergy of a fluid, in the absence of electrical, magnetic, nuclear or surface tension effects, consists of four components: kinetic, potential, physical and chemical. And, when the kinetic and potential effects are negligible, it is enough to obtain the physical and chemical components of the exergy. Moreover, when the scope of the exergy analysis is limited to obtaining the destroyed exergy, the application of the Gouy-Stodola equation is sufficient and it is not necessary to calculate the chemical exergy of the working fluid. Similarly, if in a process there is no change in the composition of the fluid, no chemical reaction, and no separation of its components, the calculation of chemical exergy is not required since its value does not change.

In the case of the absorption machine, the exergy balances of some components, where the composition of the working fluid changes, require not only the values of the physical exergy, but also those of the chemical exergy. Although there are numerous exergy analyses of $H_2O$/LiBr absorption machines in the literature, very few studies consider the calculation of the chemical exergy (see Introduction section). This has a significant influence on the value of some parameters, such as, for example, the exergy efficiency, as will be discussed below.

The physical component of the exergy of a stream of matter per unit mass, $ex^{PH}$, is given by Ref. [45]:

$$ex^{PH} = (h - h_0) - T_0(s - s_0), \tag{1}$$

where $h$ and $s$ are the specific enthalpy and entropy values of the fluid at the operating pressure and temperature, respectively. The subscript “0″ indicates that the value of the properties is obtained at the dead state pressure and temperature conditions ($p_0$ and $T_0$).

Chemical exergy is “*the maximum work that can be achieved when a substance is driven from its equilibrium state at the environment pressure and temperature (dead restricted state) to the equilibrium state of equal chemical potentials (dead unrestricted state) by means of processes that involve heat, work and mass transfers with the environment*” [13]. For a mixture or solution, it is obtained, at the pressure and temperature conditions of the dead state ($p_0$ y $T_0$), by means of [46]:

$$ex^{CH} = \sum_i \chi_i \left(\mu_{i,0} - \mu^*_{i,0}\right), \tag{2}$$

where $\mu_{i,0}$ (kJ/kg) is the chemical potential of “$i$”, at $p_0$ y $T_0$, when the composition is that of the state under consideration, $\boldsymbol{\mu}^*_{i,0}$ (kJ/kg) is the chemical potential of “$i$” when, at $p_0$ and $T_0$, the system reaches chemical equilibrium with the environment, $\chi_i$ is the mass fraction of component “$i$”.

As it follows from equations (1) and (2), for the calculation of exergy, it is essential to accurately obtain the thermodynamic properties of the fluid: enthalpy, entropy and chemical potential. There are several works in the literature providing these properties accurately over a wide range of temperatures and compositions (Yuan and Herold [47], Kim and Infante-Ferreira [48], Pátek and Klomfar [49], Palacios-Bereche et al. [13]). In this work we have used the correlations proposed by Yuan and Herold [47], implemented in the Engineering Equation Solver v. 10.836, EES.

### 2.3. Exergetic efficiency

Exergy efficiency is a parameter that can be tricky to calculate due to the lack of uniformity in the literature. Two are the most widespread definitions:

a) Input-output efficiency, $\eta_{ex}$: where the exergy of the outflows is divided by the exergy of the inflows [50–52]:

$$\eta_{ex} = \frac{\sum Exergy\ \ out}{\sum Exergy\ \ in}. \tag{3}$$

Lior and Zhang [51] suggest the use of this expression for processes where most of the outputs can be considered as products. Moran [50] indicates its use also for dissipative elements, such as throttling valves.

b) Fuel-product Efficiency, ε: accounts for the relationship between the exergy of the desired product, $\dot{\boldsymbol{E}}_{\boldsymbol{P}}$, and the exergy resources consumed to generate it, $\dot{\boldsymbol{E}}_{\boldsymbol{F}}$, [45,53,54]:

$$\varepsilon = \frac{\dot{E}x_P}{\dot{E}x_F}. \tag{4}$$

This expression is more consistent with the conventional definition of energy efficiency, which relates energy produced to energy consumed, and will be used in this paper. It presents the difficulty of defining fuel and product, which depend on the operating purpose. To avoid ambiguities, Lazzareto and Tsatsaronis [55] define in detail, for a given device, which exergy terms are to be considered as part of the fuel or as part of the product:

“The product is defined to be equal to the sum of

- *all the exergy values to be considered at the outlet (including the exergy of energy streams generated in the component) plus*
- *all the exergy increases between inlet and outlet (i.e. the exergy additions to the respective material streams) that are in accord with the purpose of the component.*

Similarly, the fuel is defined to be equal to.

- *all the exergy values to be considered at the inlet (including the exergy of energy streams supplied to the component) plus*
- *all the exergy decreases between inlet and outlet (i.e. the exergy removals from the respective material streams) minus*
- *all the exergy increases (between inlet and outlet) that are not in accord with the purpose of the component.”*

Exergy increases and decreases refer mainly to increments or reductions in the exergy of a mass flow, associated with a change either of the physical exergy or of the chemical exergy.

#### 2.3.1. Dissipative components

It could be argued that for some elements, such as expansion valves, it is not possible to obtain a “fuel-product” exergy efficiency value, since they are merely dissipative elements, without a product. But the fact is that it is not possible to define an energy efficiency for them either, precisely because their mission is to dissipate energy, not to produce it. Therefore, it may not make much sense to speak, in general, of exergy efficiency in these devices. One approach to addressing the inclusion of these elements in the exergy analysis and in the calculation of an exergy efficiency is proposed by Tsatsaronis [54]. This author indicates that, since expansion valves serve other devices, when formulating exergy efficiency, the valve and the device they serve should be considered together. This approach will be used in this paper regarding the two expansion valves in the absorption cycle, those that decrease the inlet pressure to the evaporator and the absorber, respectively.

## 3. Results

### 3.1. Case study

As a case study, the $H_2O$/LiBr single effect absorption cycle analyzed by Herold et al. [42] has been adopted. The scheme of this cycle, with the operating conditions, is presented in Fig. 1.

Main assumptions in the calculation of this absorption cycle are:

- Solution heat exchanger efficiency: 0.64.
- Vapor quality of points 1, 4, 8 set to 0.
- State 7: zero salt content.
- State 10: vapor quality set to 1.0.
- Pump: isoentropic.
- No chemical reactions occur between water and lithium bromide.
- The solution circulation ratio (liquid flow rate through the solution pump to vapor flow rate leaving the desorber: $f = 10.94$.
- Valves: adiabatic expansion. Kinetic energy effects are not included.
- Heat transfer coefficient-area product (*UA*):
  Absorber: 1.8 kW/K
  Condenser: 1,2 kW/K
  Desorber: 1.0 kW/K
  Evaporator: 2.25 kW/K

With the operating conditions of Fig. 1, the energy transfers in the cycle are calculated:

- Pump power: $\dot{\boldsymbol{W}} = 0.205\ \boldsymbol{W}$
- Heat transfer rate in the absorber: $\dot{\boldsymbol{Q}}_{\boldsymbol{a}} = 14.09\ \boldsymbol{kW}$
- Heat transfer rate in the desorber: $\dot{\boldsymbol{Q}}_{\boldsymbol{d}} = 14.73\ \boldsymbol{kW}$
- Heat transfer rate in the evaporator: $\dot{\boldsymbol{Q}}_{\boldsymbol{e}} = 10.67\ \boldsymbol{kW}$
- Heat transfer rate in the condenser: $\dot{\boldsymbol{Q}}_{\boldsymbol{c}} = 11.31\ \boldsymbol{kW}$
- Heat transfer rate in the solution heat exchanger: $\dot{\boldsymbol{Q}}_{\boldsymbol{hx}} = 3.11\ \boldsymbol{kW}$
- Coefficient of performance: COP = 0.724

### 3.2. *Exergy analysis of the case study*

The exergy analysis of the case study has been carried out taking into account the key aspects identified in this work (section 2). Their application to the present case is detailed as follows:

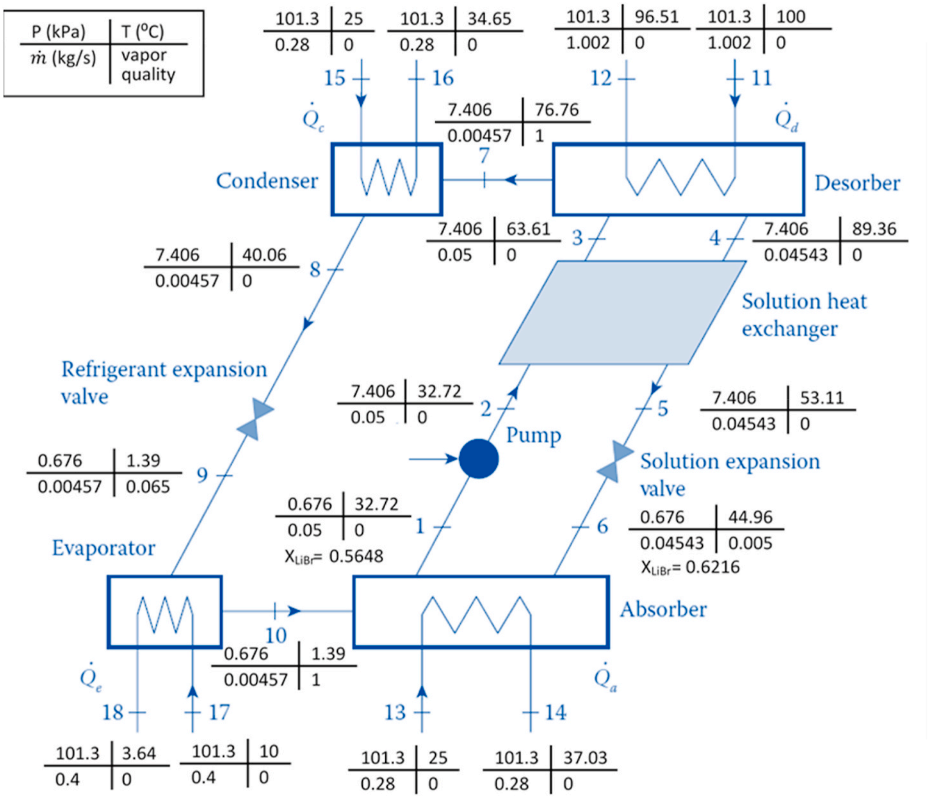

**Fig. 1.** Schematic and operation conditions for the simple absorption $H_2O$/LiBr refrigeration cycle [42].

a) Dead State.

As mentioned in the previous section (section 2.1.), an absorption machine can be divided into several subsystems. First, the absorption cycle itself, a closed system where the working fluid is the $H_2O$/LiBr mixture. If this subsystem interacts with the environment until equilibrium, only a thermal equilibrium will be achieved, since the mechanical and chemical equilibrium is restricted by the limits of the system (closed and rigid). Following Paulus and Gaggioli [43], we take as dead state, for this subsystem, the state obtained when the machine is turned off, and the ambient temperature is attained ($T_{0,1} = 25\ ^\circ\mathrm{C}$). A company specialized on absorption chillers (Absorsistem) indicate that this state pressure can be taken as the pressure of state 1 ($p_{0,1} = 0.676$ kPa). This has been substantiated by Viswanathan et al., 2021 [56], in their dynamic analysis of a small-scale ammonia-water absorption chiller. Then, the composition of the dead state can be calculated when the chemical equilibrium is reached, it means that the chemical potential of water in the $H_2O$/LiBr solution matches the Gibbs free energy of the water vapor [47]; here, $\chi_{0,\mathrm{LiBr}} = 0.5186$.

The heat source and the fluid outside the generator form another subsystem. In this paper, no specific heat source is taken and the external fluid is water. The dead state is the ambient pressure and temperature, $T_{0,2} = 25\ ^\circ\mathrm{C}$ and $p_{0,2} = 101.3$ kPa. There is no need to define the composition of the dead state since the external fluid does not change its composition as it passes through the generator, nor, therefore, does its chemical energy.

Regarding the external fluids circulating through the evaporator, absorber and condenser, in this work the ambient conditions are taken as dead state conditions. In the evaporator water is cooled; and through the absorber and condenser circulates cooling water, which enters at ambient pressure and temperature. Again, the composition of the dead state does not need to be defined.

b) Calculation of the exergy values.

The thermodynamic properties have been obtained with the correlations proposed by Yuan and Herold [47], used in the EES calculation program, as stated in the previous section. For the refrigerant, $H_2O$ (states 7–10), and the $H_2O$/LiBr solution (states 1–6), not only the physical exergy but also the chemical exergy has been calculated, since the fluid undergoes a change in composition as it passes through the absorber and the generator. Equations (1) and (2) introduced in the previous section 2.2 have been used for the calculations of the physical and the chemical exergy, respectively. For the external flows (states 11–18), as already indicated, the calculation of the chemical exergy is not required, since their composition does not change. The values of these thermodynamic properties, for all the streams of the system, are given in Table 1.

c) Exergetic efficiency.

In this work, the concept of rational exergy efficiency is used [45,53,54], as pointed out in section 2.3. This implies that, previously, the "*Fuel*" and the "*Product*", from the exergy point of view, must be identified for each device. Next, we analyze, from Lazzareto and Tsatsaronis's [55] perspective, (section 2.3), every device of the cycle.

### 3.2.1. Desorber

The function of the desorber is to provide the energy required to separate the refrigerant from the liquid working solution by a boiling process. The energy source in this case is water entering in liquid state at 100 °C. The $H_2O$/LiBr solution (stream 3) enters diluted in the desorber ($\chi_1 = 0.5648$), releases the refrigerant (stream 7) and returns concentrated (stream 4, $\chi_2 = 0.6216$). Considering the values of physical and chemical exergies of the desorber input and output streams (Table 1), the following is observed:

**Table 1**
Specific values of de enthalpy, *h*, entropy, *s*, physical exergy, $ex^{PH}$, chemical exergy, $ex^{CH}$, and total exergy, $ex^{TOT}$, for all the material streams.

| Stream | *h (kJ/kg)* | *s (kJ/k·kg)* | $ex^{PH}$ *(kJ/kg)* | $ex^{CH}$ *(kJ/kg)* | $ex^{TOT}$ *(kJ/kg)* |
|---|---|---|---|---|---|
| 1 | 87.74 | 0.2010 | 0.195 | 2.849 | 3.044 |
| 2 | 87.74 | 0.2010 | 0.195 | 2.849 | 3.044 |
| 3 | 149.85 | 0.3943 | 4.640 | 2.849 | 7.489 |
| 4 | 223.32 | 0.4966 | 11.449 | 14.855 | 26.304 |
| 5 | 154.97 | 0.2980 | 2.317 | 14.855 | 17.172 |
| 6 | 154.97 | 0.2987 | 2.110 | 14.855 | 16.965 |
| 7 | 2643.62 | 8.4659 | 336.612 | 0.000 | 336.612 |
| 8 | 167.76 | 0.5731 | 213.999 | 0.000 | 213.999 |
| 9 | 167.76 | 0.6111 | 202.674 | 0.000 | 202.674 |
| 10 | 2503.46 | 9.1187 | 1.851 | 0.000 | 1.851 |
| 11 | 419.17 | 1.3072 | 33.982 |  | 33.982 |
| 12 | 404.46 | 1.2676 | 31.081 |  | 31.081 |
| 13 | 104.92 | 0.3672 | 0.000 |  | 0.000 |
| 14 | 155.20 | 0.5325 | 0.988 |  | 0.988 |
| 15 | 104.92 | 0.3672 | 0.000 |  | 0.000 |
| 16 | 145.26 | 0.5003 | 0.639 |  | 0.639 |
| 17 | 42.12 | 0.1511 | 1.636 |  | 1.636 |
| 18 | 15.40 | 0.0556 | 3.372 |  | 3.372 |

- The main exergy of fuel oil consists of the exergy decrease from stream (11) to (12), namely the heat source.
- The physical exergies of the output streams (4 and 7) are both higher than that of the input stream (stream 3), therefore, this exergy increase will be part of the product exergy.
- The chemical exergy of stream (4) is also higher than that of stream (3), so this exergy increase in the solution, $\dot{\boldsymbol{m}}_4(\boldsymbol{ex}_4^{\boldsymbol{CH}} - \boldsymbol{ex}_3^{\boldsymbol{CH}})$, will be also part of the exergy of the product.
- However, the chemical exergy of stream (7) (refrigerant) is lower than that of stream (3). We have here an exergy decrease, $\dot{\boldsymbol{m}}_7(\boldsymbol{ex}_3^{\boldsymbol{CH}} - \boldsymbol{ex}_7^{\boldsymbol{CH}})$, that should be part of the fuel.

$$\dot{E}x_{F,DES} = \left(\dot{E}_{11} - \dot{E}_{12}\right) + \dot{m}_7\left(ex_3^{CH} - ex_7^{CH}\right). \tag{5}$$

$$\dot{E}x_{P,DES} = \dot{E}_7^{PH} + \dot{E}_4^{PH} - \dot{E}_3^{PH} + \dot{m}_4\left(ex_4^{CH} - ex_3^{CH}\right). \tag{6}$$

### 3.2.2. *Absorber*

In the absorber the refrigerant (stream 10) is absorbed by the concentrated $H_2O$/LiBr solution (stream 6) in an exothermic process. As a consequence, energy is released to an external fluid (water) which enters at 25 °C. Considering the values of physical and chemical exergies (Table 1), the following is observed:

- The fuel consists of the decrease of physical and chemical exergy of the solution from stream (6) to stream (1).
- The product is the exergy increase of the cooling water from stream (13) to stream (14). And, there is also an exergy increase of the physical and chemical exergy of the refrigerant when it is absorbed by the solution, from stream (10) to stream (1).

$$\dot{E}x_{F,ABS} = \dot{m}_6\left(ex_6^{TOT} - ex_1^{TOT}\right). \tag{7}$$

$$\dot{E}x_{P,ABS} = \left(\dot{E}_{14} - \dot{E}_{13}\right) + \dot{m}_{10}\left(ex_1^{TOT} - ex_{10}^{TOT}\right). \tag{8}$$

If the expansion valve is considered as an element that serves the absorber and its effect on the absorber's exergy efficiency is included, the fuel of the assembly absorber + valve should be calculated as:

$$\dot{E}x_{F,ABS+VAL} = \dot{m}_6\left(ex_5^{TOT} - ex_1^{TOT}\right). \tag{9}$$

Obviously, the product of the absorber would not change.

### 3.2.3. *Condenser*

In the condenser the refrigerant (stream 7) transfers heat to the cooling water (stream 15), which enters at 25 °C, and, as a consequence, can be defined:

$$\dot{E}x_{F,CON} = \dot{E}_7 - \dot{E}_8. \tag{10}$$

$$\dot{E}x_{P,CON} = \dot{E}_{16} - \dot{E}_{15}. \tag{11}$$

### 3.2.4. *Evaporator*

The function of the evaporator is to remove heat from an external fluid (stream 17), which enters at 3.6 °C:

$$\dot{E}x_{F,EVAP} = \dot{E}_9 - \dot{E}_{10}. \tag{12}$$

$$\dot{E}x_{P,EVAP} = \dot{E}_{18} - \dot{E}_{17}. \tag{13}$$

If, as in the case of the absorber, the valve that serves the evaporator is included, the fuel of the set would be:

$$\dot{E}x_{F,EVAP+VAL} = \dot{E}_8 - \dot{E}_{10}. \tag{14}$$

### 3.2.5. *Heat exchanger*

$$\dot{E}x_{F,HX} = \dot{E}_4 - \dot{E}_5. \tag{15}$$

$$\dot{E}x_{P,HX} = \dot{E}_3 - \dot{E}_2. \tag{16}$$

The pump has been considered isentropic, so its exergetic efficiency will be 100%.

The efficiency of the overall system depends on whether it works as a refrigeration machine or as a heat pump. Even a process in which both products are of interest could be considered. In this work we will deal only with the case where cooling is the desired product.

$$\dot{E}x_{F,TOT} = \dot{E}_{11} - \dot{E}_{12}. \tag{17}$$

$$\dot{E}x_{P,TOT} = \dot{E}_{18} - \dot{E}_{17}. \quad (18)$$

## 4. Discussion

### 4.1. Literature approaches

As we mentioned in the Introduction, an exhaustive search of published articles mentioning the exergy analysis of the absorption cycle with $H_2O$/LiBr was carried out. Among them, we have extracted those articles presenting a complete and original methodology of the exergetic calculation of the absorption machine, which could be compared with that of this work. For this reason, articles that do not mention or provide the calculation of the chemical exergy of the streams have not been included in the comparison. As indicated in section 2.2, the calculation of the chemical exergy in the absorption cycles is important because the solution changes its composition as it passes through some devices. Neither have been taken into account those articles whose only objective was the determination of the exergy destruction, since its value can be obtained by simply applying the Gouy-Stodola equation. Thus, only the articles published by Koehler et al. [3], Oliveira and Le Goff [6], and Palacios Bereche at al [13]. have been included in this comparison.

The methodology used by each of these authors [3,6,13] regarding the key aspects identified in this work is briefly described below in Table 2.

Although it was cited in the introduction as an alternative methodology for calculating the chemical exergy of streams, we have not included in our comparison the methodology proposed by Cimsit et al. [26]. The reason is that these authors calculate the chemical exergy just through the equation:

**Table 2**
Methodology used by several authors Koehler et al. [3], Oliveira and Le Goff [6], Palacios-Bereche et al. [13], for the exergy analysis of absorption machines with $H_2O$/LiBr solution.

| Dead State | |
|---|---|
| Koehler et al. [3] | $T_0 = T_{environment}$, $p_0 = p_{environment}$.<br>For composition: they postulate that, due to the irreversible nature of any mixing process, the lowest potential for a mixture to do useful work is when it is in the saturation state at $T_0$ y $p_0$. Then, $\chi_0 = \chi_{sat,\ LiBr}$ at $T_0$, $p_0$. |
| Oliveira and Le Goff [6] | $T_0 = 25\ ^\circ C$, $p_0 = 100$ kPa.<br>For the composition: being a binary solution that undergoes composition change processes, they consider as reference conditions the conditions of chemical equilibrium at $p_0$ y $T_0$. For the solution: $\chi_{0,LiBr} = 20$ wt%. For the refrigerant: $\chi_{0,w} = 0$. |
| Palacios-Bereche et al. [13] | $T_0 = 25\ ^\circ C$, $p_0 = 100$ kPa.<br>Composition: Reference species, common components present in the environment, as proposed by Szargut [57]. |
| Calculation of exergy values | |
| Koehler et al. [3] | $\psi(T,p,\chi) = \psi_\chi(T,p) + \psi_0(\chi)$. (19)<br>The term $\psi_\chi(T,p)$ represents the physical exergy and $\psi_0(\chi)$ is the chemical exergy defined by:<br>$\psi_0(\chi) = \frac{\chi_{sat} - \chi}{1 - \chi_{sat}}[h(T_0,p_0,\chi_{add}) - h(T_0,p_0,\chi_{sat}) - T_0[s(T_0,p_0,\chi_{add}) - s(T_0,p_0,\chi_{sat})]] - [h(T_0,p_0,\chi_{sat}) - T_0 s(T_0,p_0,\chi_{sat})]$ (20) |
| Oliveira and Le Goff [6] | The chemical exergy is obtained by calculating the work of separation of the mixture at $p_0$ and $T_0$ from the state of composition considered, $\chi_M$, to the reference state $\chi_0$:<br>$ex_M = (h_M - h_{M0}) - T_0(s_M - s_{M0})$, (21) where<br>$h_{M0} = \frac{x_M}{x_0} h(p_0, T_0, x_M) + \left(1 - \frac{x_M}{x_0}\right) h(p_0, T_0, 0)$, (22)$s_{M0} = \frac{x_M}{x_0} s(p_0, T_0, x_M) + \left(1 - \frac{x_M}{x_0}\right) s(p_0, T_0, 0)$. (23) |
| Palacios-Bereche et al. [13] | They use the expression [58]:<br>$ex^{CH} = \left(\frac{1}{\overline{M}_{sol}}\right)\left[\sum_{i=1}^{n} y_i \overline{\varepsilon}_i^0 + \overline{R} T_0 \sum_{i=1}^{n} y_i \ln a_i\right]$. (24)<br>Applied to the $H_2O$/LiBr solution:<br>$ex^{CH} = \left(\frac{1}{\overline{M}_{sol}}\right)\left[y_{H_2O}\overline{\varepsilon}_{H_2O}^0 + y_{LiBr}\overline{\varepsilon}_{LiBr}^0 + \overline{R} T_0 (y_{H_2O} \ln a_{H_2O} + y_{LiBr} \ln a_{LiBr})\right]$, (25) where the standard chemical exergy, $\overline{\varepsilon}_i^0$, is calculated with Szargut's approach [57]. |
| Exergetic efficiency | |
| Koehler et al. [3] | The rational efficiency definition is used:<br>$\varepsilon = \frac{\Psi_{profit}}{\Psi_{fuel}}$. (26) |
| Oliveira and Le Goff [6] | They advocate the application of the fuel-product exergetic efficiency:<br>$\varepsilon = \frac{\text{Product}}{\text{Fuel}}$. (4) |
| Palacios-Bereche et al. [13] | The rational efficiency concept is utilized:<br>$\varepsilon = \frac{\text{Product}}{\text{Fuel}}$. (4)<br>For dissipative components, as the expansion valve, they use the Exergetic effectiveness, defined as:<br>$\eta_{ex} = \frac{\text{Exergy Outlets}}{\text{Exergy inlets}}$. (3) |

$$e^{CH} = RT_0 \ln y_i, \tag{27}$$

which, to the best of our knowledge, cannot be applied to a real solution [1].

### *4.2. Comparison with literature regarding the calculation of exergy and the dead state*

Table 3 shows the physical and chemical exergy values for the case study streams using the methodology proposed in this work and the other methodologies published by Refs. [3,6], and [13].

Regarding the physical exergy, although its values are low, the following comments can be made. The values obtained by the different authors are the same in all streams, because they use the same dead state, $T_{0,\text{lit}} = 25$ °C and $p_{0,\text{lit}} = 101.3$ kPa. The physical exergy of the $H_2O$/LiBr solution is the same regardless of the considered dead state. This is because the correlations used to calculate the specific enthalpy and entropy of the $H_2O$/LiBr solution neglect the dependence of these properties on pressure, and, for this subsystem, the dead state of this work and the one used by the other authors have the same temperature. However, despite its low amounts, the physical exergy of the refrigerant, $H_2O$ (streams 7 to 10), presents significant differences from the dead state taken in this work, $p_{0,1} = 0.676$ kPa, and from that of other authors, $p_{0,\text{lit}} = 101.3$ kPa. Our approach avoids the negative physical exergy values, which occur with literature methodologies when the working pressure is lower than that of the dead state (streams 9–10). The physical exergy of the external streams, obtained with the different methodologies, do not differ significantly.

The chemical exergy has been calculated only for the fluids confined in the machine (streams 1 to 10), since, when passing through some devices (absorber and desorber) their composition varies. As mentioned above, it is not necessary to calculate the chemical exergy of the external fluids, since their composition does not vary in the process.

It is evident that the chemical exergy values of the solution, $H_2O$/LiBr (streams 1 to 6), and of the refrigerant, $H_2O$ (streams 7 to 10), show significant differences depending on the assumed dead state:

- Koehler et al. [3] consider that the minimum potential of a solution to perform useful work occurs when it is in a saturated state. The chemical exergy is calculated by supposing that the mixture at $T_0$ and $p_0$ evolves from a certain state of composition $\chi$ to the dead state, of composition $\chi_{\text{sat}}$, admitting a certain amount of solute. Thus, the minimum value of chemical exergy corresponds to the saturated solution and the highest value to pure water. The chemical exergy of pure water is calculated considering also as reference state the saturated state of the $H_2O$/LiBr solution.
- Oliveira and Le Goff [6] calculate the chemical exergy as the work required to separate the components of the mixture from the composition of the state under consideration to the composition of the chemical equilibrium state at $p_0$ and $T_0$. In the process, they follow a path that also considers $\chi_{0,w} = 0$ as a reference, thus canceling the chemical exergy of pure water.
- Palacios Bereche et al. [13] take into account both the standard chemical exergy of the components and the dissolution exergy to calculate the chemical exergy of the $H_2O$/LiBr mixture. The standard chemical exergy of the elements of the solution, $H_2O$, Li and Br is obtained by taking frequent components of the environment as reference species. Perhaps the only thing that could be pointed out is that, according to Szargut [57], in closed systems there is a certain freedom in choosing the state of reference. Since there is no material interaction with the environment, it does not seem meaningful to take as a dead state a state of the external environment that, due to physical restrictions, can never be reached.

**Table 3**
Physical and chemical exergy values for the single effect $H_2O$/LiBr absorption machine obtained with the methodologies proposed in this work and in the literature.

| Stream | $Ex^{PH}$ (kW) | | $Ex^{CH}$ (kW) | | | |
|---|---|---|---|---|---|---|
| | This work | [3,6,13] | This work | [3] | [6] | [13] |
| 1 | 0.01 | 0.01 | 0.14 | 1.30 | 6.08 | 25.71 |
| 2 | 0.01 | 0.01 | 0.14 | 1.30 | 6.08 | 25.71 |
| 3 | 0.23 | 0.23 | 0.14 | 1.30 | 6.08 | 25.71 |
| 4 | 0.52 | 0.52 | 0.67 | 0.00 | 8.14 | 27.02 |
| 5 | 0.11 | 0.11 | 0.67 | 0.00 | 8.14 | 27.02 |
| 6 | 0.10 | 0.10 | 0.67 | 0.00 | 8.14 | 27.02 |
| 7 | 1.54 | 0.57 | 0.00 | 2.90 | 0.00 | 0.23 |
| 8 | 0.98 | 0.01 | 0.00 | 2.90 | 0.00 | 0.23 |
| 9 | 0.93 | −0.05 | 0.00 | 2.90 | 0.00 | 0.23 |
| 10 | 0.01 | −0.96 | 0.00 | 2.90 | 0.00 | 0.23 |
| 11 | 34.04 | 34.04 | | | | |
| 12 | 31.14 | 31.14 | | | | |
| 13 | 0.00 | 0.00 | | | | |
| 14 | 0.28 | 0.28 | | | | |
| 15 | 0.00 | 0.00 | | | | |
| 16 | 0.18 | 0.18 | | | | |
| 17 | 0.65 | 0.65 | | | | |
| 18 | 1.35 | 1.35 | | | | |

### *4.3. Comparison with the literature in terms of the calculation of exergy efficiency*

As can be seen in Table 2, the authors we are considering have a common view of what should be defined as exergy efficiency, namely the fuel-product efficiency, ε, that considers the ratio between the exergy of the desired product, $\dot{Ex}_P$, and the exergy resources spent on its generation, $\dot{Ex}_F$. However, since the calculation of exergy differs between them, the values of the exergy efficiency of the devices and even, in some cases, their definition will also differ. The following tables and figures show a comparison between the results obtained with the methodology proposed by these authors and those obtained with the methodology used in this work.

First, it is necessary to review whether the definitions of fuel and product for the different devices proposed in equations (8)–(21) are applicable according to the results of physical and chemical energies obtained with the methodologies in the literature and presented in Table 3.

To understand the reasoning, let us detail, for example, the case of the desorber. Fig. 2 shows the schematic diagram of the desorber with indication of the input and output flows. The values of the physical and chemical exergies for each of the material streams entering and leaving the device, obtained with the different methodologies in the literature [3,6,13], have also been included in the figure. We take into account that the function of the desorber is to extract the refrigerant, $H_2O$, from the $H_2O$/LiBr solution, using energy from a thermal source.

Considering the values of physical and chemical exergies of the desorber input and output streams, obtained with the methodology presented by Koehler et al. [3], the following is observed:

- The main exergy of fuel oil consists of the exergy decrease from stream (11) to (12), namely the heat source.
- The dilute $H_2O$/LiBr solution (stream 3) is split into a concentrated $H_2O$/LiBr solution (stream 4) and a stream of $H_2O$ as a refrigerant (stream 7). The physical exergies of the output streams (4 and 7) are both higher than that of the input stream (stream 3), therefore, this exergy increase will be part of the product exergy.
- The chemical exergy of stream (7) is also higher than that of stream (3), so this exergy increase, $\dot{m}_7(ex_7^{CH} - ex_3^{CH})$, will be also part of the exergy of the product.
- However, the chemical exergy of stream (4) is lower than that of stream (3). We have here an exergy decrease, $\dot{m}_4(ex_3^{CH} - ex_4^{CH})$, that should be part of the fuel.
- Thus, we have:

$$\dot{E}x_{F,DES,[3]} = \left(\dot{E}x_{11} - \dot{E}x_{12}\right) + \dot{m}_4\left(ex_3^{CH} - ex_4^{CH}\right). \quad (28)$$

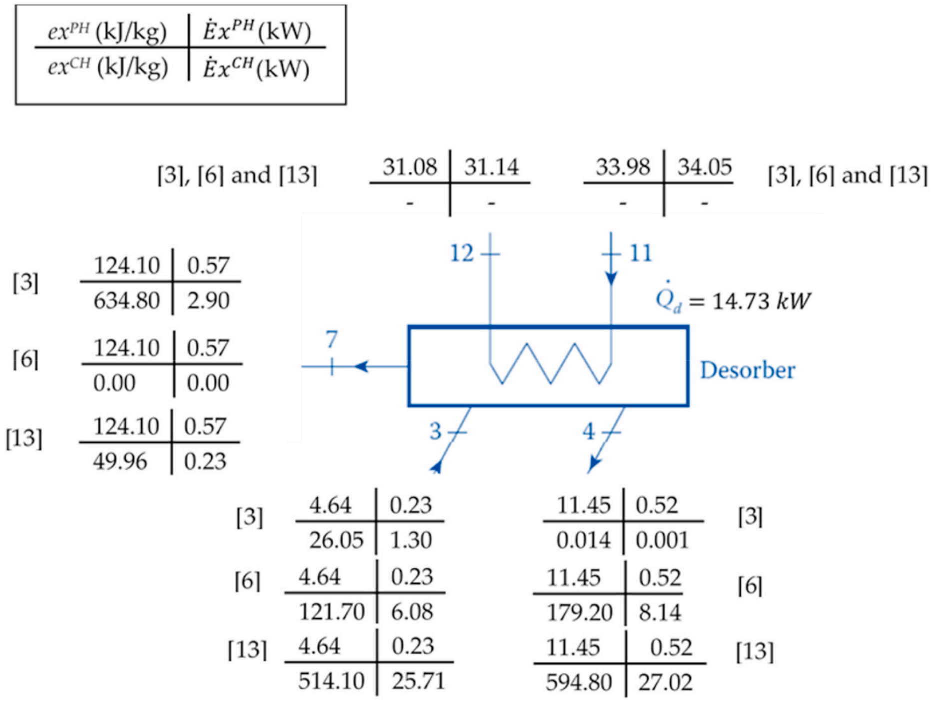

**Fig. 2.** Schematic of the desorber and values of the physical and chemical energies of the input and output streams, in mass units and per unit of time.

$$\dot{E}x_{P,DES,[3]} = \left(\dot{E}x_7^{PH} + \dot{E}x_4^{PH} - \dot{E}x_3^{PH}\right) + \dot{m}_7\left(ex_7^{CH} - ex_3^{CH}\right). \tag{29}$$

Regarding the values obtained with the methodology of Oliveira and Le Goff [6], the following is observed:

- The main fuel remains, logically, the exergy decreases from streams (11) to (12).
- The physical exergy of streams (7) and (4) is still higher than that of stream (3), so this exergy increase is part of the product.
- The chemical exergy of stream (7) is lower than that of stream (3), so now, this exergy decrease, $\dot{\boldsymbol{m}}_7(\boldsymbol{ex}_3^{CH} - \boldsymbol{ex}_7^{CH})$, is part of the fuel exergy.
- However, the chemical exergy of stream (4) is higher than that of stream (3), resulting in an exergy increase, $\dot{\boldsymbol{m}}_4(\boldsymbol{ex}_4^{CH} - \boldsymbol{ex}_3^{CH})$, which will be part of the product.

And the following is obtained:

$$\dot{E}x_{F,DES,[6]} = \left(\dot{E}x_{11} - \dot{E}x_{12}\right) + \dot{m}_7\left(ex_3^{CH} - ex_7^{CH}\right), \tag{30}$$

$$\dot{E}x_{P,DES,[6]} = \left(\dot{E}x_7^{PH} + \dot{E}x_4^{PH} - \dot{E}x_3^{PH}\right) + \dot{m}_4\left(ex_4^{CH} - ex_3^{CH}\right). \tag{31}$$

The results with the methodology of Palacios-Bereche et al. [13] lead to the following reasoning:

- The exergy decrease of the heat source fluid, $\dot{\boldsymbol{E}}_{11} - \dot{\boldsymbol{E}}_{12}$, is the main fuel of the device.
- The physical exergy of the output streams, (7) and (4), is higher than that of the dilute $H_2O$/LiBr solution, therefore this difference accounts for the product.
- The chemical exergy of stream (4) is higher than that of stream (3), so that the exergy increase, $\dot{\boldsymbol{m}}_4(\boldsymbol{ex}_4^{CH} - \boldsymbol{ex}_3^{CH})$, is also a product.
- The chemical exergy of stream (7) is lower than that of stream (3), so that the exergy decrease, $\dot{\boldsymbol{m}}_7(\boldsymbol{ex}_3^{CH} - \boldsymbol{ex}_7^{CH})$, is a fuel.

This results in:

$$\dot{E}x_{F,DES,[13]} = \left(\dot{E}x_{11} - \dot{E}x_{12}\right) + \dot{m}_7\left(ex_3^{CH} - ex_7^{CH}\right), \tag{32}$$

$$\dot{E}x_{P,DES,[13]} = \left(\dot{E}x_7^{PH} + \dot{E}x_4^{PH} - \dot{E}x_3^{PH}\right) + \dot{m}_4\left(ex_4^{CH} - ex_3^{CH}\right). \tag{33}$$

A similar analysis can be done for the absorber (see Fig. 3), where the concentrated $H_2O$/LiBr solution (6) absorbs the refrigerant, $H_2O$ (10), and exits diluted, stream (1).

Thus, following the methodology of Koehler et al. [3], it is observed that the product is the exergy increase from stream (13) to stream (14). And, the fuel consists of:

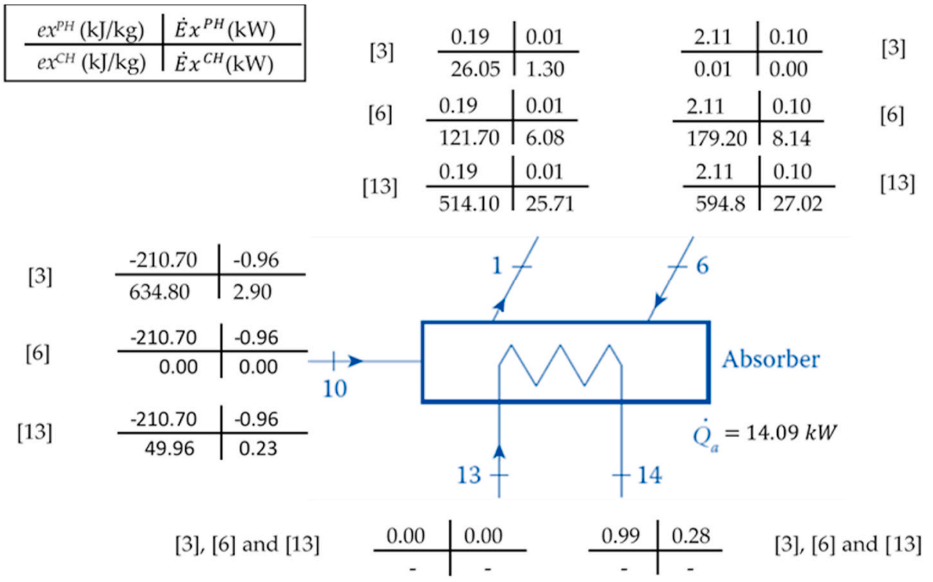

**Fig. 3.** Schematic of the absorber and values of the physical and chemical energies of the input and output streams, in mass units and per unit of time.

- The decrease of physical exergy from stream (6) to stream (1).
- The decrease of chemical exergy from stream (10) to stream (1).
- Minus the increase in physical exergy from stream (10) to stream (1) and the increase in chemical exergy from stream (6) to stream (1), which cannot be considered as products.

This results in:

$$\dot{E}x_{F,ABS,[3]} = \dot{m}_6\left(ex_6^{PH} - ex_1^{PH}\right) + \dot{m}_{10}\left(ex_{10}^{CH} - ex_1^{CH}\right) - \dot{m}_6\left(ex_1^{CH} - ex_6^{CH}\right) - \dot{m}_{10}\left(ex_1^{PH} - ex_{10}^{PH}\right) = \dot{E}x_{10} + \dot{E}x_6 - \dot{E}x_1, \tag{34}$$

$$\dot{E}x_{P,ABS,[3]} = \dot{E}x_{14} - \dot{E}x_{13}. \tag{35}$$

Using values obtained with the methodologies of Oliveira and Le Goff [6], and Palacios Bereche et al. [13], the procedure would be:

- The product is again the exergy increase from stream (13) to stream (14).
- From stream (6) to stream (1) there is a reduction in both physical and chemical exergy, so these exergy decreases are part of the fuel.
- From stream (10) to stream (1) there is a non-productive increase in both physical and chemical exergy, so this difference must be subtracted from the fuel.

And, thus:

$$\dot{E}x_{F,ABS,[6,13]} = \dot{m}_6\left(ex_6^{TOT} - ex_1^{TOT}\right) - \dot{m}_{10}\left(ex_1^{TOT} - ex_{10}^{TOT}\right) = \dot{E}x_{10} + \dot{E}x_6 - \dot{E}x_1, \tag{36}$$

$$\dot{E}x_{P,ABS,[6,13]} = \dot{E}x_{14} - \dot{E}x_{13}. \tag{37}$$

A certain discrepancy is observed with the expressions obtained in this work, where the fuel exergy is only due to the exergy decrease of the solution, Equation (7), and the product exergy also includes the increase of exergy of the refrigerant when it is absorbed by the solution, Equation (8).

In the other devices, evaporator, condenser and heat exchanger, these discrepancies in the definitions of fuel and product are not observed, since the variation of chemical exergy does not play an important role. Then, equations (9)–(16) should be used. Similarly, for the system as a whole, equations (17) and (18) apply.

Fig. 4 shows the values of the exergy of the fuel and the exergy of the product obtained by the different methodologies for the desorber and the absorber. The uncertainties of these calculations, following a simple Gauss law [59], are presented in Table 4.

In the desorber, significant mismatches are observed in the fuel exergy or product exergy calculations from the different methodologies. This is due to the fact that, in this case, chemical exergy has an important role and, as we have seen, it has a very different value according to the different methodologies. As a consequence, the expressions defining the value of fuel and product are different from each other, as we have seen above.

With the methodology proposed by Ref. [6], an important inconsistency is obtained, namely that the desorber product exergy results slightly higher than the fuel. This high value of the desorber product can only be due to an unbalanced calculation of the chemical exergy of the solution, as a consequence of the dead state composition, or of the formulation applied.

In the absorber, the differences between the fuel and product values obtained with the different methodologies are lower. Only some discrepancy is observed in the fuel obtained with [6].

In the other devices, and in the total system, the fuel and product values do not differ between the different methodologies. This is reasonable, since:

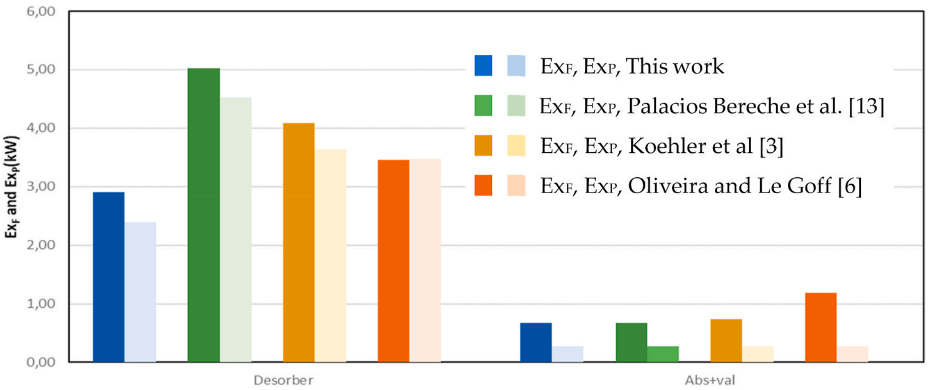

**Fig. 4.** Exergy of the fuel and exergy of the product for the desorber and the absorber, using the methodology of this work and that proposed by other authors.

**Table 4**
Uncertainties in the calculation of the exergy values.

| Parameter | This work | Koehler et al. [3] | Oliveira and Le Goff [6] | Palacios Bereche et al. [13] |
|---|---|---|---|---|
| $T$ (ºC) | ±.0.05 | ±0.05 | ±0.05 | ±0.05 |
| $p$ (kPa) | ±0.1 | ±0.1 | ±0.1 | ±0.1 |
| $h$ (kJ/kg) | ±0.01 | ±0.01 | ±0.01 | ±0.01 |
| $s$ (kJ/kg·K) | ±0.0002 | ±0.0002 | ±0.0002 | ±0.0002 |
| $\dot{m}$ (kg/s) | ±0.005 | ±0.005 | ±0.005 | ±0.005 |
| X | ±0.001 | ±0.001 | ±0.001 | ±0.001 |
| $\mu$ (kJ/kg) | ±0.002 | ±0.002 | ±0.002 | ±0.002 |
| $\dot{E}x^{PH}$ (kW) | ±0.07 | ±0.07 | ±0.07 | ±0.07 |
| $\dot{E}x^{CH}$ (kW) | ±0.02 | ±0.09 | ±0.08 | ±0.05 |
| $\dot{E}x_F$ (kW) | ±0.2 | ±0.3 | ±0.3 | ±0.2 |
| $\dot{E}x_P$ (kW) | ±0.2 | ±0.3 | ±0.3 | ±0.2 |

- In the evaporator and condenser, the definitions of fuel and product involve only differences in physical exergies. $\dot{\boldsymbol{Ex}}_{\boldsymbol{F,EVAP}} = 0.97\ \boldsymbol{kW}$, $\dot{\boldsymbol{Ex}}_{\boldsymbol{P,EVAP}} = 0.69\ \boldsymbol{kW}$; $\dot{\boldsymbol{Ex}}_{\boldsymbol{F,COND}} = 0.56\ \boldsymbol{kW}$, $\dot{\boldsymbol{Ex}}_{\boldsymbol{P,COND}} = 0.18\ \boldsymbol{kW}$.
- In the heat exchanger, the composition of the solution does not change while flowing through the device. $\dot{\boldsymbol{Ex}}_{\boldsymbol{F,HX}} = 0.41\ \boldsymbol{kW}$, $\dot{\boldsymbol{Ex}}_{\boldsymbol{P,HX}} = 0.22\ \boldsymbol{kW}$.
- In the total system, the total fuel is the exergetic decrease within the fluid used by the heat source, equation (17), and the total product becomes the exergetic increase on the fluid to be cooled, equation (18). In both definitions, only the physical exergy of the external streams is used, and this is the same in all cases because the dead state is practically the same. $\dot{\boldsymbol{Ex}}_{\boldsymbol{F,TOT}} = 2.91\ \boldsymbol{kW}$, $\dot{\boldsymbol{Ex}}_{\boldsymbol{P,TOT}} = 0.69\ \boldsymbol{kW}$.

Table 5 shows the exergy destroyed in the different devices, $\dot{\boldsymbol{Ex}}_{\boldsymbol{F}} - \dot{\boldsymbol{Ex}}_{\boldsymbol{P}}$, calculated in this work, with the methodology of other authors and with the Gouy-Stodola equation. In the case of the evaporator and the absorber, two values are included: those obtained considering only the device and those obtained by including the throttling valve. Obviously, in all cases, when the valve is included in the analysis of the evaporator and the absorber, the exergy destruction increases, due to the exergy destroyed in the valve.

The first aspect that stands out is the negative value obtained by Ref. [6] for the desorber, as a consequence of the inconsistency noted above. Similarly, in the absorber, they obtain an extremely high exergy destruction. The value of exergy destruction in the desorber with the methodology of Koehler et al. [3] is slightly low, and the value of the exergy destruction in the absorber is somewhat high. In the other devices, and in the overall system, no significant differences were observed.

With the methodology of this work, that of [3,13], the exergy destruction is quite distributed and in no device is negligible. The device that destroys the highest amount of exergy is the desorber, with 29%. It is followed by the absorber and the condenser, where the exergy destroyed is almost a quarter of the total, 23 and 22% respectively. The condenser destroys 15% of the total and the heat exchanger 11%.

Following Oliveira and Le Goff's methodology [6], the desorber does not destroy exergy. And the device that destroys the highest amount of exergy is the absorber, almost twice as much as the condenser. In the evaporator and heat exchanger the percentage destroyed is the same as with the other approaches.

Regarding the exergetic efficiency of the different devices of the absorption cycle, the only appreciable differences between the values obtained with the different methodologies are in the desorber and in the absorber. The comparison is shown in Fig. 5.

In the desorber, the work of Oliveira and Le Goff [6] indicates an efficiency of 100%. With the works of Koehler et al. [3] and Palacios Bereche et al. [13], values around 89% are obtained, and with our work a value, perhaps more realistic, of 81% is obtained.

In the system consisting of the absorber and the valve, our work indicates an exergy efficiency of 44%, while the other methodologies give a lower value: 41% [13], 38% [3], and [6] a nearly half value, 23%.

For the rest of the devices, no significant differences are observed between the values obtained with the different methodologies.

**Table 5**
Exergy destruction (kW) in the simple absorption cycle devices using the methodology of this work, that proposed by other authors and the Gouy-Stodola equation.

| | This work | Koehler et al. [3], | Oliveira and Le Goff [6], | Palacios-Bereche et al. [13], | Gouy-Stodola |
|---|---|---|---|---|---|
| Desorber | 0.55 | 0.45 | −0.01 | 0.50 | 0.56 |
| Evaporator | 0.22 | 0.22 | 0.22 | 0.22 | 0.21 |
| Evap + vale | 0.27 | 0.27 | 0.27 | 0.27 | 0.26 |
| Absorber | 0.35 | 0.45 | 0.91 | 0.39 | 0.33 |
| Abs + vale | 0.36 | 0.46 | 0.91 | 0.40 | 0.34 |
| Condenser | 0.38 | 0.38 | 0.38 | 0.38 | 0.36 |
| Heat exchanger | 0.19 | 0.19 | 0.19 | 0.19 | 0.19 |
| TOTAL | 1.76 | 1.75 | 1.75 | 1.75 | 1.71 |

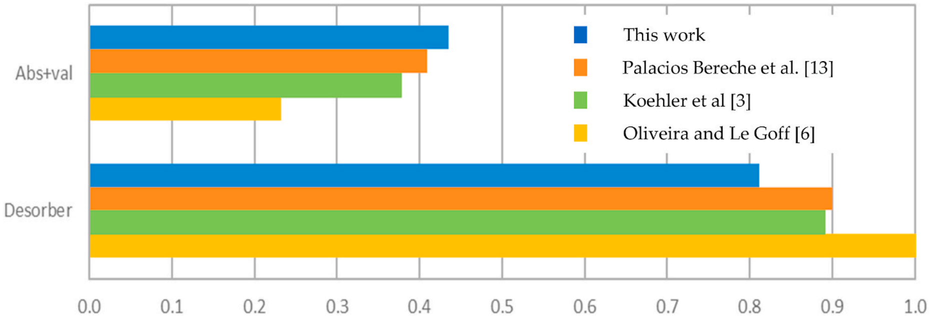

**Fig. 5.** Exergetic efficiency of the desorber and the absorber, using the methodology of this work and that of other authors.

Thus, for the evaporator + valve assembly, the energy efficiency reaches 72%; the heat exchanger offers 53% and the condenser 32%.

In the overall system, no differences are observed between the different methodologies, as expected from the fuel and product calculations. The overall energy efficiency is 24%.

## 5. Conclusions

In this paper, several key issues related to the exergy assessment of $H_2O$/LiBr absorption cooling systems are identified and addressed. These core aspects are: a) the definition of the dead state b) the methodology and assumptions in the calculation of the physical and chemical exergy of the streams, and c) the definition of the exergy efficiency of the devices and of the overall system. As a case study, a single effect absorption cycle was studied.

The methodology proposed has been compared with other main approaches published in the literature [3,6,13].

Following conclusions have been drawn:

1. Consideration of different subsystems in the definition of the dead state of the absorption cycle results in practical interest. In particular, the working fluids confined in the machine can reach neither mechanical nor chemical equilibrium with the environment. Therefore, it does not appear reasonable to choose the environmental pressure and the chemical potential of the environmental as dead state conditions.
2. For the calculation of exergy, it is essential to accurately obtain the thermodynamic properties of the fluid: enthalpy, entropy and chemical potential. Chemical exergy does play an important role in the analysis of the absorption machine due to the chemical separation processes that occur.
3. For these systems, the fuel-product exergetic efficiency is more consistent with the conventional definition of energetic efficiency than the inlet-outlet approach. The identification of fuel and product is not straightforward, and ambiguities should be avoided.
4. The comparison with the literature shows:
   - The approach presented here avoids the negative physical exergy values, which occur with literature methodologies when the working pressure is lower than that of the dead state. Negative values of exergies in this situation, although commonly accepted, are meaningless from the point of view of the concept.
   - The definitions of fuel and product for the different devices should consider the results of physical and chemical exergies of the related fluids. Thus, we have obtained that the chemical exergy value of the fluids flowing through the desorber and the absorber is critical for obtaining the exergetic efficiency of these components.
   - Significant mismatches are observed in the calculation of the fuel and product exergy for the desorber and the absorber from the different methodologies. As a result, the values of the exergetic efficiencies of these components differ.
   - Also, the exergy destructions in the desorber and the absorber present some discrepancies depending on the methodology used to calculate it.

All these discrepancies show that the methodology used in the exergy analysis is not indifferent. The aspects identified in this work as key issues really have an important influence on the calculation of the properties and the thermodynamic analysis of the process.

In subsequent works, this methodology will be applied to all types of absorption cycles, covering the full range of number of stages, absorber solutions and cooling system. A thorough critical review of the literature will also be carried out.

## Declaration of competing interest

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.

## Nomenclature

| | |
|---|---|
| COP | Coefficient of performance |
| HX | Heat exchanger |
| $a$ | activity |
| $ex$ | Specific exergy, kJ/kg |
| $\dot{E}x$ | Exergy flow rate, kW |
| $f$ | solution circulation ratio |
| $h$ | Specific enthalpy, kJ/kg |
| $\dot{m}$ | Mass flow rate, kg/s |
| $\overline{M}$ | Molar mass |
| $p$ | Pressure, kPa |
| $\overline{R}$ | Universal gas constant, kJ/(K·kmol) |
| $s$ | Specific entropy, kJ/kg·K |
| T | Temperature, °C |
| $UA$ | Overall heat transfer coefficient-area product, kW/K |
| $\dot{W}$ | Electric power, kW |
| $y$ | Molar fraction |

*Greek letters*

| | |
|---|---|
| $\varepsilon$ | Rational exergetic efficiency |
| $\overline{\varepsilon}$ | Standard chemical exergy, kJ/kmol |
| $\eta$ | Efficiency |
| $\mu$ | Chemical potential, kJ/kg |
| $\chi$ | Mass fraction |
| $\Psi$ | Exergy |

*Subscripts and superscripts*

| | |
|---|---|
| 0 | Dead state |
| *a, ABS* | Absorber |
| *add* | added (from actual state to saturation) |
| *CH* | Chemical |
| *c, CON* | Condenser |
| *D* | Destruction |
| *d, DES* | Desorber |
| *e, EVAP* | Evaporator |
| *ex* | exergetic |
| *F* | Fuel |
| *HX* | Heat exchanger |
| *i* | i-th substance |
| k | k-th component |
| *M* | Mixture |
| *P* | Product |
| *PH* | Physical |
| *sat* | Saturation |
| *sol* | Solution |
| *TOT* | Total |
| *VAL* | Expansion valve |

## Author contributions

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# 5. CONCLUSIONS

The conclusions of this work, which meet the objectives set, are summarized as follows:

**Objective 1:**

*Comparing, in terms of their exergy efficiency, similar devices, but with different operating configurations. In this way, the exergy efficiency will allow to identify and locate the most inefficient components (the most inefficient pump among the pumps, or the most inefficient reverse osmosis unit among the reverse osmosis units, for example). As a final objective, this parameter can be used to control and improve plant performance.*

1. The assessment has been performed on a real desalination plant with ten reverse osmosis desalination lines. Different configurations depending on the energy recovery procedure (Pelton turbine or pressure exchanger devices), the reverse osmosis stages, the intake and filtration technologies, or the feed water pressurization procedure (high-pressure pumps, pressure exchangers, booster pumps) are possible. Based on the values of exergetic efficiency, the most inefficient components are identified:

    - HPP and Pelton turbines are the most inefficient components due to the high mechanical irreversibilities taking place on them. RO-1 is also an important irreversibilities source due to the chemical separation process. In general, RO-1 destroys more exergy than RO-2 because a bigger amount of salt is separated from it.

    - In general, a booster inter-stage pump improves the process from an exergetic point of view. Nevertheless, in Line B, the high efficiency of the RO-1 makes the booster pump unnecessary.

    - Pressure exchangers are clearly more efficient components than Pelton turbines. The special configuration of Line A, where seawater exiting the pressure exchanger is fed into RO-2 instead into RO-1, improves the exergetic efficiency of the line in 6.5%.

    - Sharing HPP is more efficient because the exergy destruction can decrease over 18% in lines operating with ERI devices and almost 10% in lines with Pelton turbines. It is also more efficient to share the intake procedure: the decrease of the exergy destruction of the intake process decreases in almost 10%, leading to an improvement of the exergetic efficiency of the line within 1–4%.

2. Exergetic efficiency turns out to be a useful parameter to identify and locate the thermodynamic inefficiencies and malfunctions in the devices of the plant, provided that

similar components are compared. Low exergetic efficiency values indicate operation defects that should be repaired. As a result of our study, the following recommendations can be proposed to the operators of this plant:

- The operation of Pelton turbines in Lines K and L need to be controlled.
- Intake pumps of Lines A–I, HPP of Lines E and H and booster pumps of Lines H and E should be regulated.
- The booster pump in Line G presents and outstanding exergetic performance. It can be used as a model to regulate the operation of the other booster pumps.
- Some of the RO-1 membrane modules of Line H and of the RO-2 of Line I should be cleaned or replaced.
- Pressure exchanger ERI modules of Line G should be subject of maintenance works.

**Objective 2:**

*Providing a precise and unambiguous definition of exergy efficiency in reverse osmosis desalination plant devices. Proposing the use of correct models for the calculation of the thermodynamic properties. And, making critical comparisons of the results obtained with our definitions with what is found in the literature.*

3. Some confusing and contradictory results have been found in Literature due to inadequate thermodynamic models and to incorrect and ambiguous exergetic efficiency formulations: negative values of the chemical exergy, exergy production in pumps, larger irreversibilities in the membranes than in the pumps.

4. Regarding total exergetic efficiency, values vary from <2% to 92.44% . In our work, the exergetic efficiency of reverse osmosis desalination corresponds to 24.6%, (34.0% when the brine is also considered as a product). These enormous deviations can only be due to different conceptual definitions.

5. Exergy destruction in the membranes is very high in some works: 67.8% -78.8%. With the formulation proposed in this work, the exergy destruction in the reverse osmosis membranes is within 13.0-38.5% for the first stage and 5.6-15.5% for the second stage.

6. In this work we recommend:

- The use of updated seawater thermodynamic properties (Sharqawy et al., 2011), for the exergy calculations.
- The application of SPECO formulation (Lazzaretto & Tsatsaronis, 2006) for the fuel and product exergy in the definition of the exergetic efficiency of the total plant and the components.
- The separation of the physical and chemical exergy in the formulation of the exergy of the fuel and the exergy of the product in the reverse osmosis membranes and in the total plant. In this way, the conversion of mechanical exergy into chemical exergy, distinctive of reverse osmosis desalination processes, is appropriately considered.

**Objective 3:**

*Clearing up controversial and diverging hypothesis related to the exergy analysis of a single effect* $H_2O/LiBr$ *absorption refrigeration system. Formulating a comprehensive, coherent and consistent approach. Presenting a complete and original method of the exergetic calculation of the absorption machine. Comparing the results with those of the literature.*

7. Consideration of different subsystems in the definition of the dead state of the absorption cycle results in practical interest. In particular, the working fluids confined in the machine can reach neither mechanical nor chemical equilibrium with the environment. Therefore, it does not appear reasonable to choose the environmental pressure and the chemical potential of the environmental as dead state conditions.

8. For the calculation of exergy, it is essential to accurately obtain the thermodynamic properties of the fluid: enthalpy, entropy and chemical potential. Chemical exergy does play an important role in the analysis of the absorption machine due to the chemical separation processes that occur.

9. For these systems, the fuel-product exergetic efficiency is more consistent with the conventional definition of energetic efficiency than the inlet-outlet approach. The identification of fuel and product is not straightforward, and ambiguities should be avoided.

10. The comparison with the literature shows:

- The approach presented here avoids the negative physical exergy values, which occur with literature methodologies when the working pressure is lower than that of the dead state. Negative values of exergies in this situation, although commonly accepted, are meaningless from the point of view of the concept.

- The definitions of fuel and product for the different devices should consider the results of physical and chemical exergies of the related fluids. Thus, we have obtained that the chemical exergy value of the fluids flowing through the desorber and the absorber is critical for obtaining the exergetic efficiency of these components.

- Significant mismatches are observed in the calculation of the fuel and product exergy for the desorber and the absorber from the different methodologies. As a result, the values of the exergetic efficiencies of these components differ.

- Also, the exergy destructions in the desorber and the absorber present some discrepancies depending on the methodology used to calculate it.

11. All these discrepancies show that the methodology used in the exergy analysis is not indifferent. The aspects identified in this work as key issues really have an important influence on the calculation of the properties and the thermodynamic analysis of the process.

**Objective 4:**

*To critically analyze the definitions, present in the literature. Looking at the sources: what do the pioneers of exergy analysis have to say about the subject? Adoption of solutions consistent with the basic concepts.*

12. It has been demonstrated that exergy is the maximum useful work output, but also the maximum useful heat output. That is, heat could also be used to define exergy. Therefore, a more coherent definition of energy might be: the maximum useful energy that can be obtained from the interaction between a system and the environment, until equilibrium is reached.

13. The dead state conditions of a system are not necessarily conditions of a reference environment: practical circumstances should be, for each system, considered. For example: in absorption refrigeration machines, the interior fluid, no matter how much it evolves until it reaches equilibrium with the environment, will never be able to achieve mechanical equilibrium. In this dissertation, the dead state pressure is proposed as the pressure that

would be reached when the machine stops and reaches the ambient temperature. Similarly, that fluid, being confined, will never reach chemical equilibrium with the environment. In this work, the composition of the dead state of the solution is proposed as that corresponding to the chemical equilibrium between the solution and the coolant at the ambient temperature.

14. The physical exergy can never be negative; the opposite statement contradicts the fact that the exergy is the *available energy*. It has been shown here that the negative values of the physical exergy, that, mathematically, could appear, actually indicate that the exergy follows a direction opposite to the flow of matter.

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