A comprehensive review of water distillation technologies for green hydrogen production

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Abstract:

The use of low-carbon hydrogen is called to be one of the key vectors for the decarbonization of the energy sector and industry. In that regard, green hydrogen, which is produced through the electrolysis of water using renewable sources of electricity, is the process that offers the most advantages. In order to operate efficiently, water electrolysis technologies require a water source of near-ultrapure quality. To achieve this, a preceding water treatment stage is necessary, and reverse osmosis technology is currently the most widely used. This pressure-driven technology has reached maturity, but it still has certain technological limitations and energy consumption to be considered. This paper presents a comprehensive literature review of water distillation technologies currently available for obtaining the water quality required by green hydrogen electrolyzers. The comparison between mature and innovative water distillation processes showed that membrane distillation is one of the most promising technologies and that it has proved its effectiveness in the desalination sectors, but it has yet to be exploited to produce green hydrogen. This technology uses hydrophobic membranes and can be powered by a low-temperature heat source (between 40 °C and 90 °C), which provides opportunities to use alternative sources of heat, such as solar, geothermal, and even low-quality waste heat. This presents a great opportunity for energy integration with water electrolysis processes, as they generate a low-temperature waste heat flow (around 80 °C) during operation, which is compatible in quality and quantity with membrane distillation process requirements.

Keywords:

Water Distillation; Green Hydrogen; Membrane distillation; Energy Integration.

1. Introduction

It is well-known that the fight against climate change and environmental degradation has intensified in recent years. In that regard, the energy sector has proposed solutions for its decarbonization, with hydrogen (H_2) playing an important role as a possible alternative to the use of fossil fuels [1]. Among the main advantages of the use of H_2 is that it is abundant, non-toxic [2], and has one of the highest energy densities among the well-known fuels [3] (reaching a low heat capacity of 120 MJ/kg [4]). Additionally, H_2 only emits water as a by-product during combustion [2], is much easier to store and transport than electricity [3] and is flexible enough to be used in sectors such as power generation and buildings [5], as well as being a potential solution for the decarbonization of sectors difficult to electrify, such as transport [3].

Although the use of H_2 has increased to a global consumption of almost 90 Mt of H_2 in 2020 [6], there is still no accurate projection of its demand in the years to come. Several authors [3,5,7–10] have taken different base scenarios to make their projections, stating that it will be required from 50 Mt/y of H_2 [10] to 2.3 Gt/y by 2050 [9]. Despite the lack of homogeneity in the projections, a considerable amount of H_2 would be required, and therefore it would be necessary to find a reliable source from which to obtain it.

It should be noted that H_2 is an energy vector, not an energy source, so its veritable contribution to carbon neutrality will depend on how it is produced [1] since it can derive from fossil fuels as from electricity [11]. Therefore, a color-coding system is often used to describe the level of "cleanliness" depending on the type of source and technology used for obtaining the H_2 [4]. The most commonly used colors for H_2 are grey (obtained by steam methane reforming, SMR), blue (obtained by SMR with carbon capture and storage), turquoise (obtained by methane pyrolysis), and green (obtained by water electrolysis) [12].

Almost all types of H_2 mentioned above are considered pollutants to some degree [13] since they are obtained using fossil energies as their primary source. Only the green one is considered a clean source of H_2 [4,14] since the electricity required comes from low-carbon sources such as renewable energy sources (RES) [13]. However, it should be noted that H_2 is currently mainly produced by SMR systems of natural gas (48% of the

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total) or using other fossil sources (48%) [2]. This means that only 4% of the total H_2 produced corresponds to green H_2 [15].

Therefore, boosting the production of H_2 through water electrolysis using RES presents great potential to decarbonize the energy sector [3] and could be crucial in addressing the climate crisis [16–18]. In addition, coupling the production of green H_2 with electricity generated from RES (which are considered unstable in terms of generation) is one of the best methods for storing the excess energy from RES, known as power-to-gas storage [2]. Other benefits of green H_2, and its direct relationship with RES, include its compactness, the possibility of being independent of the existing electrical infrastructure, and its attractiveness towards emerging markets [19].

However, it should be noted that the production of green H_2 is still under development, therefore it is currently more expensive than the production methods based on fossil fuels [2]. Nevertheless, it is expected that the use of green H_2 electrolyzers with extended operating hours will enable them to reach competitive costs [20]. Furthermore, due to the many advantages listed above, as well as the fact that the price of RES electricity continues to decrease [16], it is estimated that its production will expand to reach at least 22% of the total H_2 produced in 2050 [2].

The production of green H_2 is defined by two main components: the use of RES and the use of water electrolyzers [19]. The latter are electrochemical devices that separate water molecules (H_2O) into H_2 and oxygen by passing an electric current through them [20]. In order to operate efficiently, water electrolysis technologies require to be fed by a water source of near-ultrapure quality [16]. Consequently, they require a previous water treatment (distillation) stage to protect the electrochemical process. This paper presents a comprehensive literature review of the water distillation technologies currently available for obtaining the water quality required by electrolyzers to produce green H_2, as well as other developing processes that show considerable potential for entering this market.

2. Electrolyzers

Currently, there are several electrolyzer technologies already developed, all of which share the same fundaments: water separation in the electrodes, allowing the transport of ions (H^+ and OH^-) through liquid electrolytes or solid membranes [20]. The two main commercial varieties are alkaline water electrolyzers (AWE) and proton exchange membrane electrolyzers (PEME) [16].

AWE technology has been developed since the 1920s [21], making it the most mature and well-established technology on the market [2]. This technology uses aqueous solutions of KOH or NaOH as electrolytes and typically operates at temperatures between 60 °C and 90 °C [22] and pressures below 30 bar. Its costs are significantly lower than those of other technologies because it does not require the use of expensive catalysts [23] and utilizes simple stainless-steel electrodes [22]. This technology presents a response to sudden changes in power supply in the order of seconds [23], although very abrupt changes can cause soda-like eruptions in the electrolyte [22]. On the other hand, its H_2 purity level is slightly lower than those of other technologies (in the order of 99.95% [19]), due to the use of a relatively permeable separator that can sometimes allow bubbles to pass through [2]. Its feed water quality requirements are slightly more flexible than those of other technologies; however, if impurities are present, they can clog the device and contaminate the electrolyte [22]. Additionally, very low-quality water feed can lead to faster equipment deterioration. Impurities such as Fe, Cr, Cu, Si, AL, and B have the greatest impact on the performance of the system [20].

On the other hand, PEME technology began its history in the early 1950s [16] and is now close to its full technological development [19]. This system features a compact modularity thanks to the membrane-electrode assembly (MEA) concept, which allows easy downsizing [2]. Unlike AWE technology, this system only requires the supply of pure water (no electrolyte is necessary), thus its service life is longer, due to the absence of KOH-induced corrosion [16]. The electrolyte is formed by a solid polymer that allows high conduction of H^+ protons [22]. Its operating temperature is lower than AWE, being able to operate in a range between 50 °C and 80 °C and at pressures below 70 bar [20]. One of its key points is its flexible operation with a fast response time (in the order of milliseconds) [23], which allows it a suitable solution for coupling with RES electricity.

Additionally, the H_2 obtained through PEME presents a high purity, typically around 99.99% [19,24]. This technology, however, has the disadvantage of being more costly than AWE due to the high-cost catalysts [2] and other noble materials, such as Pt or Ir [25], used in the electrolyzer. Furthermore, the precision required for the bipolar dishes due to the MEA system contributes to the increased cost of production [22]. In terms of purity requirements in the water supply, PEME is one of the most demanding technologies as it is quite sensitive to the presence of impurities [22] and this is one of the main reasons for its failure [26]. The components most vulnerable to impurities are the solid membrane, the catalyst, and the porous transport layers [20]. Among the most harmful elements for the system is the presence of Mg_2 and Ca_2, as they generate precipitates on the cathode side [27], which can lead to irreversible damage.

Today, the industry is shifting towards the use of PEME systems due to their compact design, fast response to dynamic changes, and high purity in the generation of H_2 [23,24]. However, AWE systems still have a significant market presence due to their lower cost.

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3. Water requirements

3.1. Quality requirements

As can be seen, water electrolysis technologies require a minimum degree of water purity to function properly and avoid damaging their components [26]. However, detailed studies on the required water quality for each type of electrolysis technology are not available [28].

Nevertheless, the industrial standard adopted for this purpose is the ASTM standard specification for Reagent Water [29]. In this sense, it is recommended to use pure water with a minimum quality of type II of the ASTM standard, being preferred type I (ultrapure) for PEME systems [16], as they are more sensitive to impurities. Table 1 summarizes the ASTM water quality types. It can be seen that the purity requirement for electrolyzer feedwater is quite high, considering that commercially sold distilled water typically has a conductivity lower than 10 µS/cm [30].

Table 1. ASTM water quality standard [29].

Parameter	Type I	Type II	Type III	Type IV
Conductivity, min µS/cm (25 °C)	0.056	1	0.25	5
Resistivity, min MΩ-cm (25 °C)	18	1	4	0.2
TOC, max µg/l	50	50	200	No limit
Sodium, max µg/l	1	5	10	50
Silica, max µg/l	3	3	500	No limit
Chloride, max µg/l	1	5	10	50
pH value (25 °C)	-	-	-	5-8

3.2. Quantity requirements

Stoichiometric theory indicates that 9 kg of input water are required for each kg of H_2 produced [20]. In reality, considering the inefficiencies in the electrochemical reaction, this water demand is typically higher, being commonly used an average value of 15 kg of water per kg of H_2 [3,8]. Given the maximum projected H_2 demand of 2.3 Gt/y by 2050 [9], and assuming that all the production relies on generating green H_2, the total direct water consumption for this projected demand would be around 34.5 Gt/y of H_2O [8].

However, it should be noted that this water demand only considers the direct consumption by the electrolysis process; the indirect consumption of the system, which comes from upstream and includes the water consumption for power generation and secondary equipment (mainly water treatment process and cooling water requirements) [3], can be up to 20 times higher than the direct consumption [11]. A maximum value of 126 kg of water per kg of H_2 is currently used for global system estimations [11].

It must be considered that the production of green H_2 will interlock the energy-water-nexus in unpredictable ways given its direct relation [3]. This relationship, together with the significant water demand, has raised doubts about the viability of a green hydrogen-based economy in certain authors [8,31], considering that there are already water shortages (of fresh water), and this demand may pose greater water stress in certain already affected areas [3].

4. Water resource

The world's total water resources are about 1.4 billion km^3 [32], from which 97.5% is sea and ocean saltwater and only 2.5% is fresh water [33]. However, of this total, only 0.27% is accessible for direct use [34], approximately 94500 Gm^3, with the rest being ice and groundwater. Therefore, the projected water requirement for direct electrolyzation feed is relatively small in comparison [3]. Despite this, the idea is not to sum any additional burden to freshwater use, considering that certain areas of the planet already have limited or no access to fresh water supply [8].

It must be taken into account that population growth and increased water demand per capita are among the main factors contributing to the problem of water scarcity. Additionally, it should be noted that the effects of climate change act in synergy with these two factors to increase water stress [35].

The water stress index (WSI) measures the amount of water used relative to the amount of water available [35]. However, it should be noted that the WSI only considers the physical availability of the resource. To gain a more comprehensive understanding of water security, the inclusion of economic and social indices is suggested. In this regard, Gain et al. [36] presented a global water security index (GWSI) that considers criteria such as availability, accessibility, security and quality, and resource management. The results of their analysis indicated that some regions, particularly in the South, are beginning to experience a water safety problem.

Moreover, projected scenarios of water scarcity have been generated, estimating that by 2025, the number of people facing this problem will reach 2.8 billion, and by 2050 it could reach 4 billion [35]. Similarly, the World Water Program estimates that by 2030, only 60% of the world's required water will be available, and according to the OECD, this will drop to 55% by 2050 [32]. These factors have prompted a debate on the need to seek

new sources of fresh water [32]. Given that, in the context of global water distribution, saltwater is the most abundant resource [33], and in light of the other aquatic stressors mentioned above, the possibility of using seawater as a source for obtaining fresh water has been encouraged [37].

Furthermore, in the context of H_2 production, marine environments could be a source of renewable energy for green H_2 [38]. Moreover, recent decades have seen some researchers [1,16,22,26] consider the possibility of generating H_2 through direct electrolysis of seawater. In this sense, efforts have been made to develop electrolyzers, membranes, and catalysts that can operate with seawater without prior purification [26]. However, most studies have come to the same conclusion: a seawater desalination process and subsequent feeding of a classic electrolyzer is much cheaper than a potential direct seawater electrolysis process [1,16,22,26]. This is mainly because the costs of water desalination, which is estimated to be around 0.1 $/kg H_2 in the case of using a reverse osmosis (RO) process [1], are minimal compared to the other costs associated with a classic water electrolysis process, such as the cost of energy consumed [16]. Additionally, the expensive materials needed for direct seawater electrolysis and its technical uncertainties [16], made this technology economically non-attractive [16,26,28].

Therefore, as seawater desalination processes have already reached a level of maturity and are now considered reliable water sources [39], it is recommendable to focus efforts on the technical and economic improvement of these processes [16].

5. Seawater desalination processes

The first desalination technologies date back to World War II and have since been gaining traction around the globe in response to the increasing demand for water [40,41]. As of now, the global desalination capacity is 115 Mm^3/d [42], with 65% of that total capacity located in the Middle East, particularly in the Persian Gulf [32]. The global distribution of different water sources used to supply desalination systems demonstrates that 60% of production uses seawater due to its abundance, while brackish water is the second most used resource, with nearly 21% of the share [43].

There are currently 16876 desalination plants [44] utilizing various technologies to carry out the process. Figure 1 illustrates the global desalination plant distribution. It is evident that RO technology is the most prevalent on the market today, as it consumes less energy than thermal systems and has seen tremendous progress in membrane technology [45] since the 1960s [46]. It is worth noting, however, that in some regions such as the Middle East (which accounts for 47.5% of the overall market [47]), thermal technologies, including multi-stage flash distillation (MSF), are the most widespread [46] and are used in thermal cogeneration.

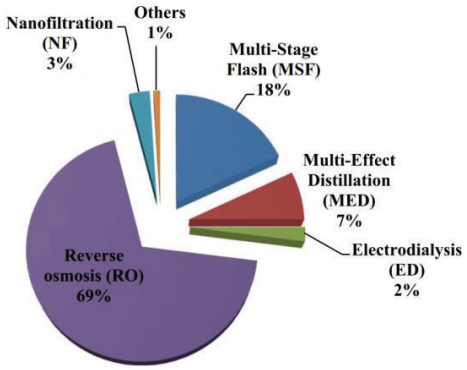

Figure. 1. Worldwide water desalination processes distribution [32].

In general, technologies are currently classified into two major groups: thermal desalination processes and membrane desalination processes [48].

5.1. Thermal desalination processes

In synthesis, thermal desalination processes are phase change techniques [49] that involve heating the feed liquid, under certain temperature and pressure conditions, to create a water vapor that will separate it from the salts and other non-volatile components in the feed stream. This vapor is then condensed to produce a stream of distilled water [50]. The most used thermal desalination processes today include MSF and multi-effect distillation (MED).

As noted above, MSF is based on the principle of boiling seawater (or other feed fluid) at a temperature below its normal boiling point, due to the “flashing effect” [40]. An external heat source, usually steam [41], is required to heat the feed fluid between 90°C and 115 °C [33]. The feed fluid passes through several stages, where the temperature and pressure of each stage decrease compared to the preceding stage [32]. As it passes through

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the stages, some of the heated fluid will evaporate due to the stages being at a pressure lower than their vapor pressure. The vapor formed is then condensed on the outer surface of heat exchange tubes where low-temperature salinized water passes [40], and therefore, a distilled condensate could be collected. MSF facilities can consist of 4 to 40 stages [51].

Among thermal desalination technologies, MSF is the most widely used method due to its lower maintenance costs and longer service life [52]. MSF systems, however, face important technological challenges, such as the precipitation of Ca and Mg salts on the tubes of the heat exchanger [53], corrosion [40], and high thermal energy consumption [40,49]. Despite these issues, MSF systems provide good-quality desalinated water [54]. Although the conductivity values of the desalinated product are scarce at the literature level, Deghani et al. [55] demonstrated through experimentation the production of distillate with less than 30 µs/cm from a feed flow with 73 mS/cm.

For its part, MED technology is older than MSF [40] and operates on a similar principle (using a series of vessels at pressures lower than ambient). The main difference between them is that MED generates steam by spraying the feed water in the form of a thin film [40] onto heat exchanger tubes (evaporator), where steam from the previous stage passes [32]. Generally, MED has between 4 to 14 effects [40] and has the advantage of working at temperatures and pressures lower than those of MSF, requiring the heating of salinized water to only 66 °C [51], thus consuming less energy [40]. MED is suitable for small to medium size plants but is subject to corrosion [40] and high maintenance costs due to the utilization of spraying water systems [52]. Their desalinated water quality is comparable to that of MSF, given their similar processes [52].

In general, the operating principle of thermal distillation technologies is simple, but their operating and maintenance costs are high due to the high pressures and temperatures needed to operate them. Moreover, they have low desalination efficiency [56] and require large amounts of energy for the evaporation of water which needs sensitive and latent heat [47], making it difficult to implement them on a large scale [57].

5.2. Membrane desalination processes

Membrane technologies utilize various types of permeable membranes to separate and isolate salts and impurities on one side of the membrane, thereby achieving salt-water separation [56]. The most common membrane processes are RO, nano-filtration (NF), and electrodialysis (ED). The membrane characteristics required for effective separation, such as pore size and mechanical strength, will depend on the type of process.

The RO process is the most widely used membrane technology, and it involves forcing seawater through a semi-permeable membrane (water permeable, but not salt permeable) using a pumping system that requires an electrical supply. The hydraulic pressure applied must be higher than the osmotic pressure, which is related to the concentration of salts in the feed stream [57]. Therefore, the salt concentration directly affects the electrical energy consumption of the system and thus its operating cost (which is one of its main operating costs) [40]. Typically, these systems operate at pressures between 54 bar and 83 bar for seawater desalination [40].

Despite the development of energy-efficient RO systems, as well as energy recovery devices, which have resulted in decreasing the capital and operating costs of the system [16], the increased electrical energy demand to process high salinity solutions remains one of their primary challenges [50]. Additionally, the presence of fouling, defined as the process in which an undesirable material (foulant) adheres to the surface or pores of the membrane [58], is another issue that must be addressed as it can lead to blockage of the membrane and, eventually, complete plugging of the system [40]. Therefore, in order to maintain a constant permeate flow, an increase in the operating pressure will be required, resulting in higher operating costs [59] and reduced process efficiency. This will ultimately impact the overall performance of the process.

For this reason, RO systems typically require a pre-treatment stage, both physically and chemically [16], to ensure their proper operation and to reduce the risks posed to the membrane [57]. However, this also carries environmental risks due to the use of chemicals to control fouling, which could have an adverse impact on the sea [60,61]. For example, the use of coagulants such as ferric salts can cause the coloring of the outlet stream (called red brine) and thus increase the turbidity and reduce the light penetration in the water [62]. In terms of water quality, the distillate produced will depend on the initial quality of the feed stream, the membrane properties, and the operating pressure of the system [52]. However, it has been demonstrated that the quality of desalinated water tends to be lower than that obtained from thermal systems [63], and therefore in many cases a second desalination stage or supplementary process is required.

NF is a pressure-driven process with certain similarities to RO (in fact, its operation is between that of RO and ultrafiltration [64]) but it is capable of operating at lower pressures, higher flow rates, and with lower investment costs [65]. NF has a membrane pore structure that is larger than that of RO, allowing more salts to pass through it [66]. Generally, it has a high rejection rate for divalent ions (around 98%) [64], however, there are certain issues when it comes to the total removal of NaCl in desalination processes [59]. Despite this, some studies [67] have achieved quality results comparable to those of RO when used with salinized water. Ultimately, the choice between NF and other water treatments will depend on the quality requirements, the

quality of the input water, and the capacity required [67]. As is the case with RO, NF also presents problems with fouling control and difficulty in controlling the pore size of the membrane [68].

Another membrane process is the ED, which is an electro-membrane process in which ions are transported from one solution (the feed) to another via a membrane, due to the application of an electrical potential difference [66]. It should be noted that the cost of the process is proportional to the number of salts transported to the membrane, so it is recommended to use it for fluids with a low concentration of solids (between 8 g/L and 10 g/L) [49]. Furthermore, other membrane-based processes, such as microfiltration and ultrafiltration, are not recommended for desalination processes. Nevertheless, these technologies have found a market as a pre-treatment process for RO systems [49].

5.3. Problems of current desalination technologies

As has been seen, the increasing demand for fresh water coupled with its scarcity has led to the use of desalination technologies as one of the main solutions. Although these technologies have already reached a certain level of maturity, they still have challenges to overcome, particularly those related to the discharge of brine [49], high investment costs [56], and high energy consumption [45]. Concerning the latter, it has been noted that desalination processes can consume from 8 to 20 times more energy (thermal or electrical, depending on the process) than conventional surface water treatments [69]. For example, the current consumption of electric energy by desalination processes is 56 TWh, however, it is estimated that by 2040, this consumption would become the second-largest energy-intensive process in the entire water sector with 345 TWh, only surpassed by the water supply energy demand [70]. In addition, high energy consumption is often accompanied by increased greenhouse gas emissions [46]. This is especially true because many desalination systems are still powered by fossil fuels [71]. It is estimated that, overall, 23 kg of CO_2/m^3 of desalinated water are currently being released [63].

Moreover, the technologies mentioned above are designed to be economically viable in large-scale operations (in most cases, the scale is the most influential factor when it comes to capex). For example, in the case of RO, a typical current plant produces 0.1 Mm^3/d of water [72], while commercial electrolyzers do not exceed a power of 10 MW, which is equivalent to the use of approximately 125 m^3/d of water [26]. This illustrates the significant difference in scale between the two processes.

Therefore, it is necessary to find alternative desalination processes with reduced greenhouse gas emissions, lower energy requirements and that can be powered by renewable sources or waste heat [37], in order to sustainably meet the world's growing demand for fresh water and feed water for electrolyzers. In this regard, forward osmosis (FO), reverse electrodialysis (EDR) and membrane distillation (MD) are the principal emerging technologies on the market (the 1% of others, as seen in Figure 1).

FO consumes less energy than RO, since it does not require external hydraulic pressure and has a lower fouling tendency [50]. However, it still poses certain technological challenges in extracting water from the draw solution to regenerate the cyclic process [47]. For its part, EDR works similarly to ED (see section 5.2) but with the added capability of reversing the polarity of its electrodes during specific time intervals, enabling it to minimize fouling and remove deposited materials [47]. However, like ED, its energy consumption depends on the feed concentration, making it more suitable for solutions with low salinity. Finally, MD doesn't require a high electrical consumption and has the potential to be more energy efficient than other processes when valorising waste heat or renewable heat sources, which make it one of the most promising technologies to date for desalination.

5.4. Membrane distillation technology

MD is a non-isothermal membrane process that is based on the generation of a steam phase in a hot solution stream, close to the surface of a membrane [34]. The vapor will be able to pass through the membrane (the hot side of the system) and then condenses onto the cold side of the system, where cold distilled water circulates. This process is made possible by the use of hydrophobic membranes, which allow only the passage of steam, and volatile compounds, while retaining the liquid part in the hot stream (which contains dissolved salts and other non-volatile compounds) [73]. In this way, a permeate (distilled water) can be obtained on the cold side of the system. Figure 2 shows a diagram of a counter-current MD system.

The driving force of MD is the difference in partial vapor pressure between the hot and cold side of the system. This difference is responsible for converting some of the molecules in the supply liquid into vapor [48], thus initiating the mass transfer process described above. MD systems are considered thermal-driven since the partial pressure difference is related to the temperature gradient on the membrane sides [74]. In order for MD to be effective, a temperature difference of at least 20 °C must exist between the two sides of the system [75].

The membrane material and its characteristics are among the most important parameters for the successful operation of MD systems. As the physical barrier between the hot and cold side of the system, its properties will influence the heat and mass transfer. Generally, MD membranes have a pore size between 0.2 μm and 1 μm [76], with a porosity between 65% and 85% [77], a tortuosity regularly assumed to be 2 [78], and a thickness between 0.04 mm and 0.25 mm [79]. Polymers such as PTFE, PP, and PVDF are commonly used for the

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fabrication of MD membranes [61], due to their ability to be modulated in terms of intrinsic properties and low surface tension [77].

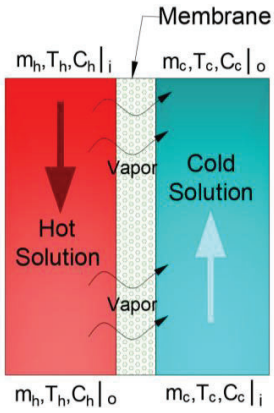

Figure. 2. Diagram of a counter-current MD system.

In addition to the previously mentioned points, MD technology has other advantages. For instance, it is almost insensitive to the initial concentration of the feed stream, which causes problems in other distillation systems [61], and has a high rejection factor, with leads to a theoretically complete separation [80]. Additionally, MD systems are robust, compact, and modular [73], thus reducing investment costs [34].

On the other hand, the main drawbacks of MD technology are its low permeate flow and high energy consumption [50] (cf. 5.4.1). The low permeate flow can be attributed to the air trapped in the membrane, which introduces resistance to the mass transfer [80], with a greater effect than on pressure-driven processes. The high energy consumption is due to MD being a phase change process, which requires a large amount of thermal energy [74], but at a low temperature.

Studies [39,81–84] have shown that distillates produced through MD technology can have electrical conductivities ranging from 2 and 5 µS/cm, with high salt rejection (higher than 99.7%). Furthermore, a second MD distillation stage can improve the purity of the distillate, reaching values near 0.7 µS/cm [81]. It has been found that the quality of the distillate is not affected by the initial operating conditions (temperatures, flows, concentrations) [39,82], due to the membrane, which does not allow for the passage of liquid. However, it is important to note that the operating conditions will influence the time required to achieve low-conductivity distillates since MD technology tends to start its operation producing distillates with high conductivity, which will decrease over time (generally taking a bit less than an hour) [82].

5.4.1. Comparison with other technologies

Table 2 shows a comparison of parameters between the main water desalination technologies used to date and MD technology.

Table 2. Comparison of water desalination technologies.

Parameter	RO	MSF	MED	MD
Electric consumption (kWh/m^3) [63]	3.7 - 8	2.5 - 5	2 - 2.5	0.6 - 1.8
Thermal energy consumption (kWh/m^3) [49]	-	190-390	230-390	100 - 800
Water quality (ppm TDS) [63]	200 - 500	10	10	10
Unit product cost (USD/m^3) [49]	0.52-0.56	0.52-1.75	0.52-1.01	No information
Maximal feed salinity (g/L) [43]	70	180	180	350
Water composition changes tolerance [57]	Very low	Medium - High	High	High
Fouling [57]	High	-	-	Low - Medium
CO_2 emissions (kgCO_2/m^3) [51]	1.75 - 2.79	5.56 -25	4.38 - 17.6	No information

Table 2 reveals that MD technology has several advantages over conventional technologies, and a comparison with the dominant technology in the market, the RO, reveals even more advantages. For example, MD is not limited by a maximum osmotic pressure [85], and the hydrostatic pressure required is much lower than that of RO systems [80], which allows for the use of less resistant materials. Additionally, the membrane required for MD is simpler and has a larger pore size, which reduces the risk of fouling [48], resulting in improved cost recovery [74].

In addition, focused on obtaining adequate water quality to feed water electrolyzers, it can be seen that RO yields the lowest quality among the compared technologies, due to its reliance on the quality of the input water.

Typically, at the industrial level, at least two RO stages are needed to achieve acceptable quality. On the other hand, thermal technologies, MED and MSF, yield better-quality water, albeit with somewhat higher conductivity than with MD [55,82].

Even though the amount of thermal energy needed for MD is much higher than for other systems, there is a critical point to consider: the thermal energy required differs in quality from the thermal systems. Conventional thermal systems require energy sources with temperatures above 90 °C for MSF and at least 70 °C for MED, while MD systems require flexible low-temperature heat, in the 40 °C to 90 °C range [86], making it more economically attractive [63]. Furthermore, the quality of the required heat provides opportunities to use alternative sources of heat, such as solar, wind, geothermal, or even waste heat, making the MD technology more environmentally attractive.

5.4.2. Potential use of waste heat

In this regard, the use of waste heat is versatile due to its various forms (liquid, gaseous or diffuse) and temperatures, which are specific to the industrial process from which they originate [71] and gives it different valorizations. However, its ease of use depends on aspects such as continuity, temperature range, heat transfer modes, and location between source and place of use [87]. Despite these barriers, there is immense potential for this resource to be exploited in various ways [87].

Estimating the existing total waste heat is complicated by the fact that it is difficult to quantify with certainty due to the constant changes in the overall energy mix [88] and changes and variations in the processes that generate this heat. Few studies have sought to quantify the potential of the waste heat field, yet, some estimations indicate that the total waste heat released at a global level would be between 68.2 PWh [87] and 72.7 PWh [88]. It is also estimated that the waste heat could reach 89.4 PWh by 2030 [88].

However, it should be noted that these projected values only reflect the amount of waste heat, not the amount of energy that can be converted into work, known as exergy [87]. Thus, an exergy analysis, taking into account the quality factors, known as the Carnot factor [88], related to the source temperature, is necessary to quantify the true potential of the waste heat that can be used [87]. To this end, it is necessary to recognize different temperature scales at which waste heat occurs. For example, according to the quantification of Forman et al. [87], 20.6% of the waste heat is above 300 °C (high quality), 16% is between 100 °C and 300 °C (medium quality) and the rest is below 100 °C (low quality). By applying the corresponding Carnot factors for each temperature range, and for each sector from which the waste heat originates, the authors obtained a theoretical waste heat potential of 13400 TWh, which is only about 20% of the total waste heat that can be recovered and used.

As can be seen, there is an abundance of waste heat resources that can be recovered and exploited. Moreover, when using this heat source, it is considered that its utilization will not add CO_2 emissions to the balance, as there is no additional fuel needed [71]. However, it is worth noting that it is not entirely free energy (although some studies consider an investment of 0 to simplify the calculations) since its use entails costs related to collection, transportation, processing, and operation, which in some cases may make the use of conventional energy sources more feasible [89]. For this reason, a technical-economic analysis should be carried out in each case of study to ensure the usefulness of the exploitation of this resource.

5.4.3. Potential coupling with hydrogen electrolyzers

The coupling of MD systems and green H_2 generation systems also presents multiple opportunities for exploiting waste heat. The electrochemical reaction of the electrolyzers generates residual heat, due to their inefficiencies [90], which is usually dissipated by a cooling water circuit. The operating temperature of the electrolyzers is typically between 50 °C and 90 °C (depending on the type of electrolyzer) [91,92], which has already been shown to be useful to powered district heating networks when the urban area is close to the electrolization plant [90,93].

Therefore, the heat dissipated by the electrolyzer has a quality that can be used by an MD system, which can be energetically powered by the cooling water of the system. Additionally, the regular configurations of electrolyzers AWE and PEME have certain heat exchangers (for refrigeration) [20] with potentially usable dissipated heat. Some examples are the KOH cooling system in the electrolyzer stack (in AWE systems) or the inter-stage cooling system in the hydrogen compression process.

Some studies have detailed figures on the heat dissipated during the operation of water electrolyzers. Tiktak [90] reported 171 MW of heat dissipated at a temperature of 77 °C while operating at a nominal production rate of 5.25 kg/s of H_2. Similarly, Burrin et al. [91] estimated 0.31 kW of heat at 75 °C during the generation of 18.7 kg/h of H_2. When taking into consideration the equivalence of kg of water required per kg of H_2 (as discussed in Section 3.2), it can be estimated that the electrolysis systems release 604 and 1120 kW/m^3 of required water, respectively. The potential to use this heat in MD systems can be clearly appreciated when compared with the energy demand values presented in Table 2. Despite the potential presented, the MD-green H_2 coupling has not been studied yet, so it is essential to promote these projects to dispel the uncertainties of these systems.

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6. Conclusions

The present study conducted a comprehensive literature review of water distillation technologies oriented towards producing hydrogen using water electrolyzers that are powered by renewable electric energy (green H_2). These devices require water of a quality bordering on ultrapure to operate without the risks associated with their electrochemical reaction. Therefore, considering the projections of water requirements for a future green H_2 market, the most viable form of water treatment appears to be seawater desalination.

In this regard, today two large groups of technologies dominate the market: thermal technologies (25%) and membrane technologies, where the main and dominant is RO (69%). However, these technologies still present technical and economic challenges, including high investment costs, high energy consumption (either electrical or thermal), and carbon emissions (linked to the use of fossil fuels).

For this reason, several new technologies are being proposed as potential solutions to these challenges. Among them, membrane distillation technology presents the greatest potential, due to the quality of water it produces, its flexibility with different feed fluids, and its low-quality heat requirement, which opens the possibility of working with renewable heat sources and waste heat. The latter opens the door for the coupling of MD systems with green H_2 generation systems, as there is potential waste heat, in quantity and quality, during the electrochemical reaction on the electrolyzers that could be used to power the MD process. Nevertheless, this technology is still under development, and the study of being coupled with green H_2 generation systems has yet to be conducted, so there remain uncertainties to address.

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