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Membrane engineering for environmental protection and sustainable industrial growth: Options for water and gas treatment

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Abstract

The increasing demand for materials, energy and products drives chemical engineers to propose new solutions everyday able to promote development while supporting sustainable industrial growth. Membrane engineering can offer significant assets to this development. Here, they are identified the most interesting aspects of membrane engineering in strategic industrial sectors such as water treatment, energy production and depletion and reuse of raw materials. The opportunity to integrate membrane units with innovative systems to exploit the potential advantages derived from their synergic uses is also emphasized. The analysis of the potentialities of these new technologies is supported by the introduction of process intensification metrics which provide an alternative and innovative point of view regarding the unit performance, highlighting important aspects characterizing the technology and not identified by the conventional analysis of the unit performance.

Keywords: Green process engineering, Membrane, Metrics

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1. Introduction

Process intensification is a key strategy that the chemical and petrochemical industry is adopting to increase energy efficiency and profitability [1, 2]. In the last few years the potentialities recognized to membrane operations in this field have contributed to confirm membrane engineering as a powerful tool to fulfil process intensification strategy in the best way. Today, membrane technology has well-established uses in many industrial processes including water desalination, wastewater treatments, agro-food, gas separation, and in chemical and petrol chemical industry. Membrane operations are already dominant technologies in molecular separations but they are becoming of interest also as membrane reactors and membrane contactors. Practically all of the typical unit operations of process engineering could be redesigned as membrane unit operations (Membrane Distillation, Membrane Crystallizer, Membrane Reactors, Membrane Condensers and Membrane Gas Separation).

The significant positive results achieved in various membrane systems are, however, still far from realizing the potentialities of this technology. There are still problems related to pre-treatment of streams, membrane life time, aging, fouling, and sealing, slowing down the growth of large-scale industrial use. A good understanding of the materials properties and transport mechanisms, as well as the creation of innovative functional materials with improved properties, are key challenges for a further development of this technology, which requires further intensive research activities both at academic and industrial level. In addition, the design and optimization of the membrane process will lead to significant innovation toward large-scale diffusion of membrane technologies in various sectors and the role of membrane engineering is crucial in this respect.

In recent years, Process Intensification has been hailed as a new design philosophy in which membranes are well adapted to the re-designing of industrial uses [3, 4]. However, to use this new philosophy to design unit operations in practice, it is now time to “quantify” some of the related

aspects. One of the roles of membrane engineering is thus the introduction of process intensification metrics for comparing membrane performance with those of traditional operations. Metrics consist in useful indices able to give an easy immediate idea of the eventual gain offered by membrane systems. Moreover, they also allow a better understanding of the application limits of membrane systems for obtaining a set quality target of a process. These metrics do not replace the existing indicators, referring to other aspects of the production plants. Therefore, the final evaluation of processes "sustainability" can be always carried out by considering the new metrics together with the environmental, economic, and society indicators. The new metrics would be, in fact, "something more to think about" in performing the overall analysis of processes.

In this work some of the most significant unit operations involved in the areas of water treatment, energy production, raw materials exploitation and reuse which can be considered as well consolidated technologies, at least at lab scale, will be discussed. Desalination, waste water treatment, crystallization, condensers, reactors and gas separation all by means of membranes will be considered and case studies utilized to show how the metrics can be used to supply additional and complementary information to that provided by conventional analysis useful for the proper evaluation of the potentialities of these operations.

2. Membrane engineering strategies for solving "current limitations of main industrial unit operations in different sectors"

2.1. Water Treatment and Recovery

Together with energy consumption and raw materials deployment, water scarcity is one of the major issues affecting every continent around the world. According to the latest report of the World Health Organization and UNICEF "Progress on Drinking Water and Sanitation – 2014 update" [5], in 2012, 748 million people still lacked access to improved sources of drinking water and more than

one third of the global population – some 2.5 billion people — did not use an improved sanitation facility [5].

Hydrologists typically assess scarcity by looking at the population-water relationship. An area is experiencing water stress when annual water supplies drop below 1,700 m^3 per person. When annual water supplies drop below 1,000 m^3 per person, the population faces water scarcity, and below 500 cubic meters "absolute scarcity". Three years of research from Aarhus University in Denmark, Vermont Law School and CNA Corporation in the US, published in 2014, show that by 2020 about 30-40% of the world will have water scarcity and by the year 2040 there will not be enough drinking water in the world to quench the thirst of the world population. Moreover, taking into account that in many countries, electricity is the biggest source of water consumption because the power plants need cooling cycles in order to function, it will be impossible to continue to produce electricity in this way and meet the water demand by 2040. Agriculture is another sector consuming a huge amount of water, involving about 70% of worldwide water use, increasing to over 90% in developing countries. In a range of industries – from beverages to chemicals and energy, from construction to metals – water is a key part of the manufacturing process. Water supply issues are increasing in importance, because the freshwater supply is limited and the forecasts are alarming. Hereby some membrane based technologies for water recovery from seawater, wastewater and humidified waste gaseous streams are discussed.

2.1.1. Membrane-based desalination systems

Water scarcity has always encouraged the development of water saving/treatment technologies, through requiring both the optimization of water conveying and distribution systems, and the reuse and production of potable water from *alternative and non-conventional water sources* (such as seas, oceans, municipal and industrial wastewaters). The most ancient water conveying systems date back

to 7th century BC when the Assyrians built an 80 km long limestone aqueduct to carry water to their capital city. Aqueducts to convey watercourses across gaps were a distinctive feature of the Roman Empire, which built aqueducts everywhere from Germany to Africa, and especially in the city of Rome, where they supplied water to public baths and for drinking, setting a standard of engineering that was not surpassed for more than a thousand years.

The possibility of extracting potable water from seawater was a dream of all the populations living near seas and without access to fresh water. Aristotle (384-322 BC) in his *History of Animals* recounts of filtration through an earthenware jar. San Basilio (239-379) in "Omelie sui primi sei giorni della creazione" affirmed that sailors of his time obtained fresh water through the boiling of seawater and collecting the water vapor produced with some sponges to be wrung out to give water. This was the working principle of the distiller, developed until 1961 at the start-up of the first desalination plant at Freeport (Texas). At that time, boiling or evaporating water was used to separate water from salt. Desalination by Reverse Osmosis (RO) entered the market only in the late 1960s when the membrane manufacturing process became efficient enough in producing desalted water that it was competitive with thermal processes. However, though more efficient than vaporization or distillation and requiring far less physical space for the same operation, the first plants demanded a high energy input. In the late 1970s early Sea Water Reverse Osmosis (SWRO) plants consumed as much as 16 kWh/m^3 [5]. Over time, this amount decreased dramatically due, in particular, to the installation of energy recovery systems (like the Pelton turbine, Pressure Exchanger System, etc.), the use of more efficient pumps and the development of higher-permeability membranes[6]. Current state-of-the art SWRO plants consume between 3 and 4 kWh/m^3. Recent demonstration studies performed in the United States by the Affordable Desalination Collaboration demonstrated that energy requirements for the RO desalination process alone could be lowered to 2 kWh/m^3 through the use of highly-efficient energy recovery devices and low energy RO membranes. A recent requirement is to aim for a consumption of 1.5 kWh/m^3 by 2030, not far

from the theoretical inferior limit that Elimelech [7] postulates at 1.06 kWh/m^3 for seawater at 35,000 ppm salt and at a typical recovery of 50%. Differently, the energy consumption of thermal desalination plants has remained much higher, since the most frequently applied technology in the Middle East today is fossil fuel, owing to its low cost in this region. As a matter of fact, at present RO is the leading desalination technology accounting for around 60% of all desalination plants [7] mainly due to its higher recovery factor, lower investment and total water cost compared to other conventional source development, and to the continuing technological advances enabling RO desalination to treat high salinities raw water (Table 1 and Table 2). Membrane fouling is one of the major problems of RO and it cannot be omitted. It can never fully be prevented but it can be reduced and controlled through an adequate pre-treatment of the feed solution. Pressure-driven membrane operations (such as microfiltration –MF- and ultrafiltration -UF) are the new trend in designing pre-treatment systems because they can handle a large variation in raw water quality and still produce water for the RO unit that is of better quality than water produced by conventional technology. Membrane pretreatment systems are also more compact and have lower operating costs than conventional processes.

According to [7, 8], further improvements to RO pre-treatment can be achieved through the utilization of nanofiltration (NF) for the removal of most multivalent ions, hardness, turbidity and microorganisms. This reduces the osmotic pressure of the RO feed so that a coupled NF + RO seawater desalination system can be operated at recovery factors 10–12% higher than that of an SWRO plant based on conventional pre-treatment.

Table 1. Comparison of operational data of thermal and membrane based desalination technologies. Adapted from [12] with permission of Elsevier.

Thermal desalination processes (MSF, MED, VC)	Membrane desalination processes (RO)
Typical salt content of raw water[F] = 30,000 – 100,000 ppm	Typical salt content of raw water[F] = 1,000 – 45,000 ppm
Desalted water with low total dissolved solids concentrations (10-20 ppm)	Desalted water with total dissolved solids concentrations between 100 and 550 ppm

Thermal energy consumption = 12 kWh/m^3 (data for MSF)[F]	Thermal energy consumption = 0
Energy consumption (MSF)[A, L] = 17 ÷ 18 kWh/m^3	Energy consumption [B, C, D, L] =2.2 ÷ 6.7 kWh/m^3
Recovery factor ≈ 40%	Recovery factor [E, F] ≈ 40 ÷ 60[A] %
High capital costs High operating costs	Low capital costs Low operating costs
Desalted water cost ≈ 0.9÷1.4 \$/m^3 (MSF) [E, F] ÷ 0.7-1.0 (MED, TVC)[I]	Desalted water cost ≈ 0.50 ÷ 0.70\$/m^3 (in the most part of SWRO plants [C, G]) and 0.36\$/m^3 (from brackish water sources [F, H])

A: The International Desalination&Water Reuse, Nov./Dec. 2008 – Volume 18/No 3.
B: W. J. Koros, AIChE Journal, Volume 50, Issue 10, October 2004, Pages:2326-2334
C: http://www.water-technology.net/projects/israel/specs.html (2008)
D: Water Desalination Report, Volume 14, Number 12 (2008)
E: Ettouney et al., December 2002, pp. 32-39, www.cepmagazine.org
F: C. Fritzmann, Desalination 216 (2007) 1–76;
G: B. Van der Bruggen et al., Desalination, 143 (2002) 207-218
H: El Paso Desalination Plant, Texas, http://www.epwu.org/167080115.html (2008)
I: Semiat R., Water International, 25 (2000) 54-65.
L: More information on energy consumption of the different desalination techniques may be found in

Table 2. Main advantages and drawbacks of the most widespread thermal and non-thermal desalination systems.

Desalination processes	**Advantages**	**Drawbacks**
Multi-stage-flash distillation (MSF)	Ease of the process; No risk of reduced heat transfer by scaling since heat exchange with the saline water does not occur through heat transfer surfaces; MSF is also insensitive to the initial feed concentrations and to the presence of suspended particles; Desalted water contains about 50 ppm of total dissolved salts.	The most important disadvantages of MSF are that the top brine temperature is limited to about 110°C by the risk of scaling, thus limiting the performance ratio at about 11 [20]. This results in a much higher energy consumption, which makes MSF a more expensive technique than MED. Precipitation can be reduced by applying acid or anti-scalants.
Multi-effect distillation (MED)	Reliable design, technological maturity, high quality of distillate produced, good operating records and high unit capacity are the main merits of MED technology. Cogeneration desalination plants which include MED combined with thermal or absorption heat pumps,	The main problems are related to corrosion and scaling of oversaturated compounds (such as $CaSO_4$), gain output ratio is generally very high

	and waste-heat steam generators or gas turbines show promising performance.	
Reverse Osmosis (RO)	High recovery factor, low energy consumption, low investment and total water cost are the main advantages of RO technology. Relatively small footprint and modularity enabling easy adaptation of process scale.	Some of the major problems in RO applications are fouling and concentration polarization phenomena. Concentration polarisation can be minimised by hydrodynamic means (such as an appropriate feed flow velocity, an adequate membrane module design and spacer as also turbulence promoters). Fouling can be reduced and controlled through a proper pre-treatment of the feed solution.
Electrodialysis (ED)	ED is competitive for brackish waters with up to 3000 ppm salt, while it is rarely used for seawater desalination. For water with low salt concentrations, ED/EDR is considered to be the most advantageous technique.	ED process is non-economical for waters with high salts concentrations
Membrane distillation (MD)	The main MD advantages are as follows: - theoretically complete rejection of non-volatile components, - Low operating temperature with respect to the distillation separation, with consequent possibility to utilize low-grade waste heat streams and/or alternative energy sources (solar, wind, or geothermal); - Low operating pressure, lower equipment costs and increased process safety - robust membranes -high system compactness - Less membrane fouling -Extremely low sensitivity to concentration polarisation phenomenon	Temperature polarization, membrane wetting, development of proper membranes and modules for MD application are the main drawbacks of MD.

Electrodialysis (ED) is another membrane process in commercial use for seawater or brackish water desalination. ED is an electrically driven membrane operation non-economical for waters with high salt concentrations [9], rarely used for seawater desalination but competitive for brackish

waters with up to 3000 ppm salt concentrations. For water with low salt content, ED/EDR is considered to be the most advantageous technique.

Recently, the thermally driven membrane process called membrane distillation (MD) has gained popularity due to some unique benefits associated with the process, such as the possibility to concentrate the seawater till around its saturation point without any significant flux-decline, to utilize low-grade waste heat streams and/or alternative energy sources (solar, wind, or geothermal), to reject theoretically 100% of non-volatile components[9]. Owing to these attractive benefits, MD might become one of the most interesting desalination techniques. It can overcome not only the limits of thermal systems (such as distillation) but also those of membrane systems (such as RO). Concentration polarization does not affect the driving force of the process significantly and therefore high recovery factors and high concentrations can be achieved in the operation, compared with the RO process. All the other properties of membrane systems (easy scale-up, easy remote control and automation, no chemicals, low environmental impact, high productivity/size ratio, high productivity/weight ratio, high simplicity in operation, and flexibility) are also present.

2.1.2. Membrane-based wastewater treatment

In addition to desalination, also wastewater treatment and reuse is a feasible solution and a sustainable alternative source of water, able to face the increasing municipal, industrial, and agricultural demands. Water reuse is a growing practice in many regions of the world, even in countries that are not typically considered to have problems with water scarcity but in which the continuous growth in population, in the standard of life, in tourist infrastructure and industrial development have increased water consumption and the stress on water supplies. Some governments have issued large-scale programs to recover and reuse treated municipal waste waters and rehabilitate marginal water sources (marginal water includes industrial, agricultural and municipal effluents as well as contaminated surface and well waters). Countries and regions in which water reuse is on the rise include the US, Western Europe, Australia and Israel. According to

the US Environmental Protection Agency's (EPA) 2000 Watershed Needs Survey, 2.6 billion gallons per day (bgd) (9.8 Gl/d) of recycling/reclaiming water are reused in the US[10], which is only the 7.4% of the total volume of wastewater produced (34.9 bgd =132.1 Gl/d). In accordance with a review of the Australian Academy of Technological Sciences and Engineering, a total of 166.2 Gl/y (43.91 billion gal/y) was reused in 2001–2002 in Australia[10]. According to Bixio et al.[11], there are more than 200 projects in Western Europe while many others are in an advanced planning phase. This is a large number considering that in the early 1990s municipal water reuse was limited to a few cases, mostly incidental, i.e., related to the proximity of the wastewater treatment plant to the point of use.

Today the uses of reused water include the irrigation of golf courses and lawns, irrigation of edible and non-edible agricultural crops, and indirect potable reuse, such as groundwater recharge. Industrial reuse includes use in cooling towers for boiler feed, and in the cooling cycles of power plants.

Some of the principal advantages in the use of reclaimed water are as follows:

To increase the use of wastewater for irrigation areas and crops that currently use fresh water. This saves fresh water for other water uses.

In some cases water reuse requires half of the energy currently required to bring imported water to the water district[10], therefore the cost of the water produced by the reuse technology is less than that of the other water supplies.

Improvement from the environmental view point because it reduces or eliminates the quantity of treated wastewater discharged to oceans and sensitive surface waters.

Widespread water reuse has also numerous obstacles, the main one being quality control to reduce the risk of human exposure, practices that vary considerably from region to region[11]. On the other hand, the true benefits and costs of many water reuse projects have never been properly

evaluated. Water recycling projects have the potentiality to reduce wastewater treatment and disposal costs, to decrease the discharge of pollutants to the environment and to provide high-quality water: all not easily quantified social benefits.

Both membrane and conventional activated sludge plants can be utilized for the treatment of wastewaters. A typical waste-water treatment plant usually involves four stages, called *primary*, *secondary*, *tertiary and*, *sometimes*, *quaternary treatment*:

First, the solids are separated from the wastewater stream;

In the secondary treatment (often also including nutrient removal) the dissolved biological matter is progressively converted into a solid mass by using indigenous, water-borne microorganisms. This treatment is characteristic of restricted agricultural irrigation (i.e. for not consumed uncooked food crops) and for some industrial uses such as industrial cooling (except for the food industry).

Finally, the biological solids are neutralized, then disposed of or re-used, and the treated water can be disinfected chemically or physically (for example by lagoons and micro-filtration). The final effluent can be discharged into water courses or it can be used for the irrigation of a golf course, green way or park. If it is sufficiently clean, it can also be used for groundwater recharge.

Quaternary treatment is a treatment producing a quality comparable to drinking water, often involving a "dual membrane" step to meet unrestricted residential uses and industrial applications requiring ultrapure water.

Since the early 70s, pressure-driven membrane separation processes (Microfiltration (MF) and Ultrafiltration (UF)), have been developed and suggested to replace secondary clarifications traditionally used in activated sludge treatment systems. The membrane allows total retention of the biomass regardless of its properties (size of floccules, age, etc.) and guarantees a very high quality of the treated water[12]. At present, the most interesting developments for membrane technologies are

related to the possibility of integrating various membrane operations with all the important benefits in the logic of the *Process Intensification*[13]. Some large installations use integrated membrane systems, combining MF or UF with Reverse Osmosis (RO) or Nanofiltration (NF) to achieve better quality water [14]. The use of MF and/or UF as pretreatment steps provides a better feed-water for the RO/NF membranes, with a lower turbidity and SDI and, therefore, with less potential fouling and more microbiology control. Fouling by suspended solids, colloidal material or ions dissolved in raw water is the major problem with RO systems, and pretreatment is the critical step for a successful RO plant. It has also to ensure that the quality of water fed to the RO module is high enough to avoid variability in the quality of itself. Traditional pre-treatment technologies, such as deep-bed media filters and physic-chemical systems, have serious limitations regarding the variable quality of the produced water. Long-term operating experiences prove that the use of Continuous Microfiltration (CMF), as a pre-treatment, produces a filtrate of consistent quality for RO. Numerous pilot plant studies and commercial facilities have demonstrated the technical and economical feasibility of reclaiming the effluent of municipal wastewater treatment plants through dual-membrane processes (such as CMF followed by RO or electrodialysis reversal (EDR)). The reasons why the trend is for Integrated Membrane Systems (IMS) are mainly feasibility, process reliability, plant availability, modularity, relative insensitivity in cases of raw water changes and lower operating costs. CMF and UF allow RO feed water quality to be better controlled, resulting in less frequent cleaning requirements for the RO membranes. In addition, CMF and UF increase the removal efficiency of undesired compounds. They seem to be very effective for particles and turbidity removal. Turbidity can be lowered to values below 0.1 NTU (nephelometric turbidity units) and TSS (total suspended solids) normally to lower than 1 ppm. Both CMF and UF are effective in removing bacteria, cysts and other microbiology contents. UF can also remove many viruses. Neither MF nor UF is very effective for removing disinfection by-products and dissolved substances in general, and have limited capability in removing organic matter. For this reason,

additional processes such as the addition of a coagulant or powder-activated carbon have to be used to enhance the effectiveness of membrane processes[14].

Table 3. Main advantages and drawbacks of membrane bioreactor compared to conventional activated sludge processes.

Advantages	**Drawbacks**
The main advantages of MBRs compared to conventional activated sludge systems are: -decreased sludge production; -higher and more consistent effluent quality as a result of membrane filtration. -The process can also be run at long sludge ages (>20 d), in favour of the development of slow-growing micro-organisms which led to better removal of refractory organic matter. Long sludge ages are not possible with conventional activated sludge systems because they produce sludge that does not settle well [15]. -Compactness (up to 5 times more compact than a conventional activated sludge plant) and optimal treated water quality.	The main disadvantages of MBR technology are: -relatively expensive to install and operate; -frequent membranes maintenance; -membranes are sensitive to some chemical agents and work in specific range of pressure, temperature and ph.

Membrane Bioreactor (MBR), a unit combining membrane filtration with biological treatment, is another effective membrane operation for wastewater treatment and recycling. It was introduced 30 years ago and currently is considered by the European Union as one of the best available technologies used to treat municipal and industrial waste water and one of the most effective processes to reach a high level of protection of the environment. The reactor is operated similarly to a conventional activated sludge process but without the need for secondary clarification and tertiary steps like sand filtration[12],[15]. Low-pressure membrane filtration (e.g., MF or UF), is used to separate effluent from activated sludge. A membrane bioreactor is a compact facility (up to 5 times more compact than a conventional activated sludge plant, the membrane module replacing the clarification tank) that produces significantly less excess sludge. On the other hand, however, the energy consumption can be significantly higher than that with a conventional activated sludge process, because of pumping. Feed water for MBR plants needs sufficient pre-treatment in order to

prevent the damage related to membrane fouling. Since the membrane is an absolute barrier for bacteria and in the case of UF also for viruses, the MBR process provides a considerable level of physical disinfection. The resulting high quality and disinfected effluent implies that MBR processes can be especially suitable for the reuse and recycling of wastewater.

Since the early MBR installations, the number of MBR systems has grown considerably; projected total European revenue for the MBR market was around 40 million euro in 2005 with a steady growth rate of 9%[15]. One key trend driving this continue growth was the use of MBR systems for decentralised treatment and water reuse. The majority of the currently operating and commissioned plants are of small- to medium size. The entry of membrane bioreactors into large-sized projects has been slow. It is only in the last few years that the use of MBRs for medium to large-scale domestic wastewater applications has begun to grow. The main factors that contributed to their development were the experience gained with pilot/small-scale projects, the decrease in the cost of membranes and the improvements in their performance.

2.1.3. Membrane-based vapor water capture

Owing to large industrial water withdrawals, which account for around 22% of global water consumption, the amount of evaporated water emitted each day by the chimneys or cooling towers of, for example, power plants and paper mills is enormous. Its recovery is not only an environmental concern to be addressed owing to greenhouse effects, but can be intended as a new water source[16]. The main traditional technologies for the capture of evaporated water by gaseous streams are: cooling with condensation[17], liquid and solid sorption[18] and cryogenic separation. Recently, membrane technologies have been introduced as suitable technologies for this new area of use. In the past, dense membranes[19,20] were proposed for the gas dehumidification. The results obtained confirmed the technical viability of gas dehydration with this technology, but the main

hurdle for its scaling up was related to the high pressure needed to promote the permeation of the water vapor through the membrane. Porous hydrophilic polymer membranes[21] were used instead as membrane-based dehumidification systems where the membrane operated as a contactor between the humid gas phase and a liquid-coolant phase (often water). A different principle, based on the so-called membrane condenser, has recently been proposed for the recovery of evaporated waste water from industrial gases[22,23,24,25].

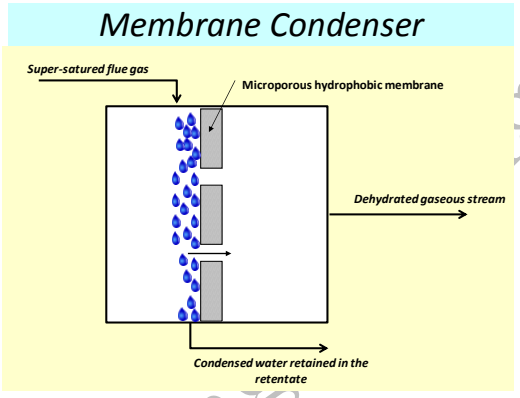


Figure 1. Membrane condenser scheme. Reprinted from "Clean-soil, Air, Water, 41, Brunetti A.; Santoro S.; Macedonio F.; Figoli A.; Drioli E.; Barbieri G., "Waste gaseous streams: from environmental issue to source of water by using membrane condensers", 1-9, Copyright (2013) with permission from Wiley".

Figure 1 schematizes the membrane condenser principle. The waste gaseous stream (e.g. flue gas) from an industrial plant at a certain temperature and, in most cases, water saturated, is fed to the membrane condenser kept at a lower temperature for cooling the gas up to a super-saturation state. The water condenses onto the membrane surface and the hydrophobic nature of the latter prevents the penetration of the liquid into the pores, letting the dehydrated gases pass through the membrane and retaining the liquid water at the retentate side. In comparison with other technologies,

the membrane condensers (Table 4) offer higher water recovery and are not affected by desiccant losses, corrosion phenomena typical of traditional condensers or desiccant units. Compared with the dense membrane technology, the latter requires a high pressure difference between the two membrane sides to promote the permeation of water vapor but allows the recovery of a very pure stream. On the contrary, the purity of the water recovered in membrane condensers can be affected by the possible condensation of contaminants – if present in the gaseous stream – but it is sufficient for cooling tower or boiler make up. However, further purifications would be needed to make it drinkable. In this context, membrane condensers can be considered also as a proper solution for pre-treating the flue gas streams that have to be fed to another membrane unit for CO_2 separation and whose performances are strongly affected by the presence of such contaminants as SO_x, NH_3, etc. The possibility of controlling, by opportunely tuning the operating conditions, the condensation of contaminants in the liquid water recovered in the retentate side of the membrane condenser could lead to two different options for its use: as a unit for water recovery, minimizing the contaminants content, or, as the pre-treatment stage in post-combustion capture, forcing most of the contaminants to be retained.

Table 4. Comparison between membrane condenser and traditional technologies for water vapour separation. Adapted from [24] with permission of Wiley.

	Liquid and solid sorption[19]	**Cooling with condensation**[18]	**Dense Membranes** [26]	**Membrane condensers** [24]
Water recovery	22-62 %	< 70 %	20-40 %	> 70 %
Water purity	>95%	Sufficient for cooling tower make up. Contaminants in the water	>95%	Sufficient for cooling tower make up Contaminants in the water
Maintenance and durability	Corrosion and salt crystals formation owing to salt desiccants presence and O_2 in the flue gas	Corrosion owing to the formation of a thin liquid layer of diluted acids and fly ashes forming deposits	Ashes removal and FGD necessary to avoid membrane damaging	Ashes removal to avoid membrane damaging
Environmental aspects	Increase of CO_2 emissions	Co-capture of SOx and NOx could	Clean operation	Clean operation

	Reduction of SO_x emission $CaCl_2$ losses	results in a environmental profit reducing the DENOx and FGD systems		
Investments costs	5.8 mln $ (2006) +200.000 $/year (2006) as operational costs	6.4 mln EURO (2011)	To be determined	To be determined
Economic viability	4.4 $/m^3	1.5-2 EURO/m^3	1.5 Euro/m^3 (WET regions) 10 EURO/m^3 (DRY regions)	1.5-2.5 Euro/m^3 (*)

*considering only costs related to energy requirements and membrane modules

2.2. Energy production and conversion

Nowadays, the necessity to diversify energy sources to assure supply and the increasing effort dedicated to the reduction of environmental problems have recently led to the development of clean technologies, designed to enhance both the efficiency and environmental acceptability of energy production, storage and use, in particular for power generation[27]. Among these technologies, the exploitation of light hydrocarbons is surely the main realistic energy source, since they allow both power generation and environmental-friendly fuel production, such as hydrogen.

2.2.1. Membrane reactors in pre-combustion capture and biomass conversion for hydrogen production

At present, 96% of hydrogen is directly produced from fossil fuels and about 4% is produced indirectly by using electricity generated through them[28]. The stream coming out from a reformer or a coal gasification plant contains around 50% hydrogen (on a dry basis) that must be recovered and between 40-45% CO that is usually reduced in an upgrading stage, producing more hydrogen at the same time. In traditional uses (Figure 2), the upgrading of reformate streams is performed by using

a multi-stage CO-shift process based on a series of catalytic reactors: the first, operating at high temperatures (HT-WGS) (about 350-400 °C) and taking advantage of the high reaction rate, converts a large part of the carbon monoxide giving hydrogen and CO_2; the other, operating at a low temperature (LT-WGS) (around 220-300 °C), refines the carbon monoxide conversion, thus allowing a lower final concentration of CO (less than 1% molar)[29]. This H_2 rich stream coming out from the last reactor is fed to a pressure swing adsorption (PSA) unit for H_2 separation from the other gases. The new utilization of H_2 as feed in fuel cells for mobile power sources requires the anode inlet gas to have a CO concentration lower than 10–20 ppm[30] in order to prevent catalyst poisoning with consequent drops in the fuel cell efficiency. Hence, the purification step of the H_2 produced from hydrocarbon must be very efficient to fulfil the fuel cell requirements. Because of this in some cases, another reaction unit is added for oxidizing CO in CO_2.

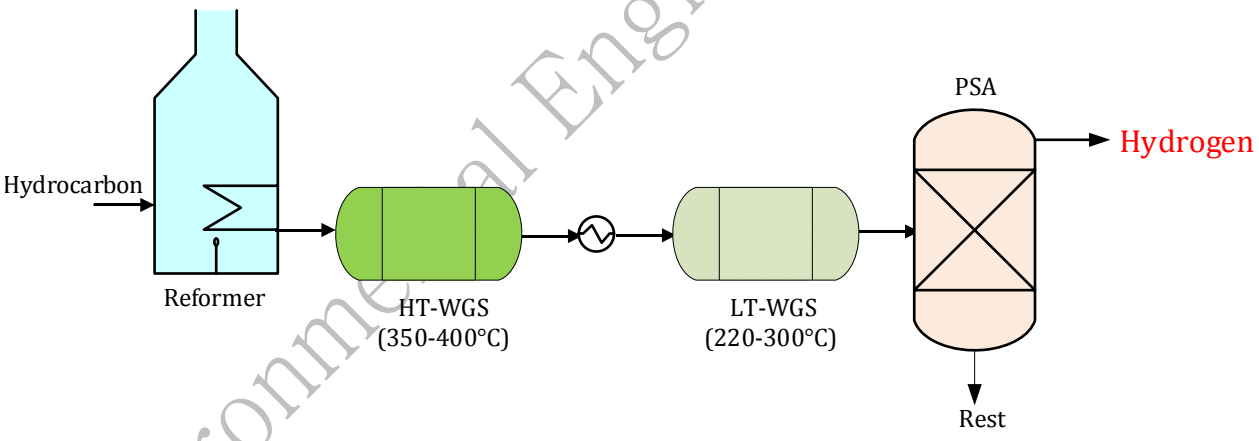


Figure 2. Scheme of the traditional plant for H_2 production from natural gas.

The enhancement of process efficiency, the lower environmental impact on one side and the reduction of the reaction/separation/purification stages, which means a lower footprint area occupied by the whole plant, less auxiliary devices required and reduction of the energetic load, are fundamental aspects to be taken into account in the redesigning of hydrogen production processes.

A promising approach for concretizing these technological aspects is the use of MRs, combining the reaction and H_2 separation by means of a selective membrane.

Many studies are now focused on the analysis of MR performances where light hydrocarbon reforming or water gas shift (WGS) reaction are carried out[31],[32],[33],[34],[35]. In these cases, the presence of the membranes, mostly Pd-based one, allows the recovery of a hydrogen rich stream which does not require further separation. Moreover, the removal of the H_2, reaction product, from the reaction volume shifts the reaction toward further conversion. This means the possibility of having an intensified process with a reduced plant size and higher yield. The traditional process can be thus redesigned as more compact and efficient (Figure 3) pursuing the logic of the Process Intensification strategy, with less reaction/ separation units than the conventional one (Figure 5). The synergic effects offered by MRs through combining reaction and separation in the same unit, their simplicity and the possibility of advanced levels of automation and control, offer an attractive opportunity to redesign industrial processes[36, 37, 38].

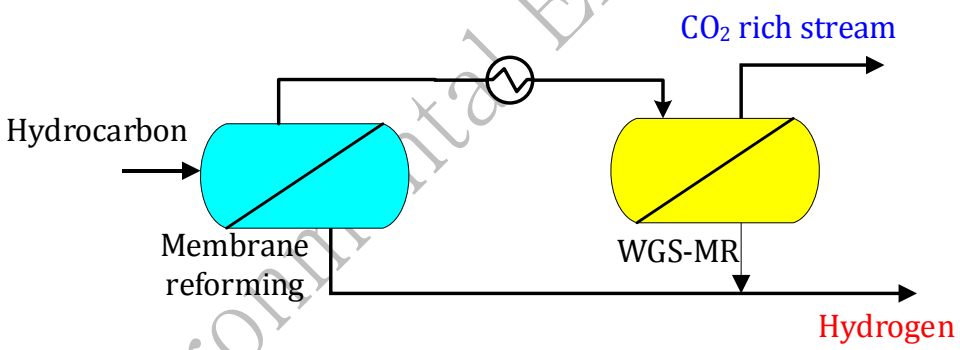


Figure 3. Scheme of the integrated membrane plant for hydrogen production from natural gas.

Additionally to the enhancement of conversion, recovery of pure/rich H2 stream, reduction of reaction/separation/purification units, the use of MR allows the attainment of a stream already concentrated and compressed in CO_2 (>80%), easily recoverable[39]. As can be seen in Figure 4 the

retentate stream of MR has always a higher CO_2 concentration with respect to the traditional reactor at each operating condition investigated and this has to be attributed to the hydrogen removal from reaction side. This means further reduction of energy consumption and footprint area occupied by the plant. In other words an intensified process.

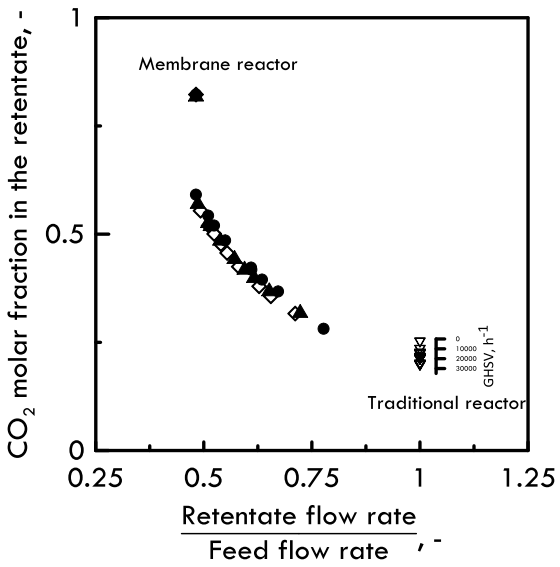
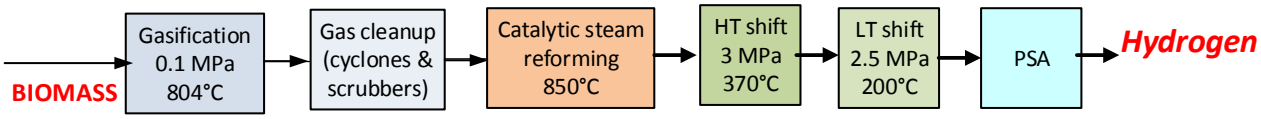


Figure 4. CO2 molar fraction in the retentate as function of retentate on feed flow rate ratio at different values of GHSV for membrane and traditional reactors..

The same approach and similar technology can be also adapted for biomasses exploitation. The hydrogen production from biomass is classified as a carbon neutral process because the CO_2 released during hydrogen production is consumed by a further biomass generation. At present, the contribution of biomass (including agricultural and forestry residues and municipal solid wastes) to the world's energy supply is around 10–14% [40]. There are various routes which can be taken to produce hydrogen from biomass; the most used is biomass gasification carried out at a much lower temperature (700-800 °C) than coal gasification. According to the operating conditions, the gasification can make syngas or a stream containing mainly CH_4.

(A)



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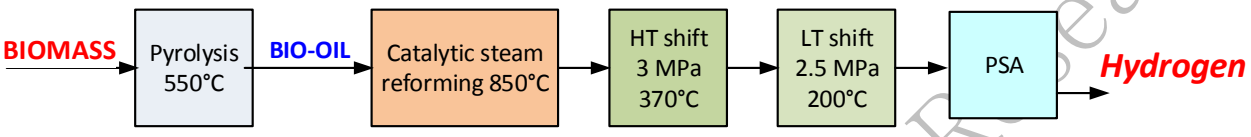

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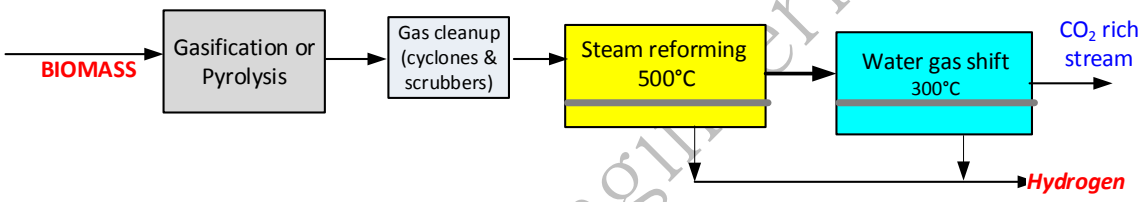

Figure 5. Scheme of plants for hydrogen production from biomass feedstock (A) conventional biomass gasification and (B) conventional biomass pyrolysis. (C) Innovative plant integrated by membrane reactors. Adapted from [41] with permission of Royal Society of Chemistry.

Figure 5A and B show two schemes of the conventional routes for hydrogen production from biomass, whereas Figure 5C shows a scheme of the intensified process for converting biomass into hydrogen[41]. Both considering gasification and pyrolysis, the number of stages necessary for conversion and/or for separation is significantly reduced. The presence of MRs for steam reforming and water gas shift reduces the four reaction stages plus a PSA unit in only two reactors able to produce hydrogen (CO free). Moreover, in both MRs the conversion is enhanced; therefore the

overall process yield is maximized. The reduction of the units number in the whole process makes it more adequate also for applications on medium-scale.

2.2.2. Gas separation and recovery

Today membrane technology for gas separation (GS) is a well-consolidated technique, in various cases competing with traditional operations. The separation of air components, H_2 from refinery industrial gases, natural gas dehumidification, separation and recovery of CO_2 from biogas and natural gas are some examples in which membrane technology is successfully used in industry [42,43]. For various years, membrane operations have been used for the separation of air components or oxygen enriched air for use in several fields, including chemical and related industries, the mechanical field, food packing and so forth. Currently, membranes dominate the fraction of the nitrogen market for uses with a productive capacity of less than 50 ton/day and relatively low purity (nitrogen 95-99.5%molar).

The greatest asset of membrane separation is simplicity. Gas mixture is fed to one side of the membrane, one or more components of the gas mixture preferentially permeate through the membrane, retaining the rest of the gaseous stream in the retentate (Figure 6). The driving force required for promoting the permeation is achieved either by compressing the feed gas or using a vacuum on the permeate side. Usually a one-stage process is not sufficient to produce high purity gases. Multi-stage gas separation[44] and membrane-hybrid processes[45] have been thus developed to this purpose.

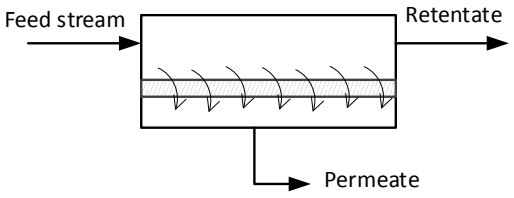

Figure 6. Scheme of membrane GS unit.

When compared with traditional technologies, such as absorption, adsorption and cryogenics, the operational simplicity and the modularity make membranes very attractive in applications where product demand is not constant. Whereas PSA requires the equipment for swinging pressure, cryogenic distillation must endure extreme temperatures and absorption requires huge amount of sorbent, the only equipment necessary for GS is the membrane and fans. There are almost no moving parts and the construction is fairly simple. The gaseous stream to be separated generally requires a compression, but this is much smaller than that necessary for PSA.

Table 5 summarizes a comparison among some of the main aspects to be taken into account in the choice of a separation technology. More details on these selection guidelines can be found in [46]. Membrane systems are extremely reliable with respect to the on-stream factors which can cause unscheduled shutdowns. The ease of control and the few auxiliary devices give them a fast response and they require short times for start up after variation. In addition owing to the modularity, membrane systems are highly capable of maintaining product purity even though the capacity is reduced down to 10% of the initial design value and exhibit a moderate ability to operate under variable feed quality conditions, either on a short- or long-term basis.

Table 5. Comparison among various technologies for gas separation by menas of some important design parameters. Partially adapted from[53] with permission of Elsevier.

	Membrane System	PSA	Cryogenic	Absorption

Ease of expansion	Very high (modularity)	Moderate	Very low	Moderate
By-product value	Moderate	Moderate	High	Moderate
Operating flexibility	Moderate	High	Low	Moderate
Response to variations	Instantaneous	Rapid (5-15 minutes)	Slow	Rapid (5-15 minutes)
Start up after the variations	Extremely short (10 minutes)	1 h	8-24 h	1 h
Turndown	Down to 10%	Down to 30%	Down to 30-50%	Down to 30%
Reliability	100%	95%	Limited	Moderate
Control requirement	Low	High	High	High

However, the selection of the suitable separation process should be driven by specific considerations, strictly related to the output to be obtained. The *composition of the feed* and its variability has a great effect on the selection of the separation process because it influences the performance, reliability and pre-treatment required. Membrane systems are suitable for a wide range of feed compositions, owing to the possibility of driving the process acting on different parameters such as feed and permeate pressure, temperature, and flow configuration. *Feed pressure and product flow rates* are best considered together when selecting a gas purification process because the three processes have drastically different economies of scale.

2.2.3. Membrane GS for CO_2 separation

One of the separations that more than other attracts the attention on the use of membranes is CO_2 capture. Power and hydrogen production, heating systems (for example, in the steel and cement industries) and natural gas and biogas purification, are examples of circumstances in which carbon dioxide is produced in huge (thousands of ton) streams. Although carbon dioxide separation from hydrogen and methane streams has long been used since the high value of these streams[47], [48], [49], [50], [51],

recent constraints and regulations on CO_2 emissions from power plants have forced researchers to focus on the separation of CO_2 from flue gas streams[52, 53,54, 55, 56, 57, 58, 59, 60]. As already mentioned, even though technologies such as adsorption, absorption, and cryogenic distillation[61] were the first to be considered suitable for this purpose, membrane technology is a valid alternative for carbon dioxide separation from the various aforementioned streams. One of the most important aspects in the selection of CO2 separation process is the economic value of the stream to be treated.

In biogas or natural gas the presence of CH_4, fuel with economic value, makes the range of operating conditions wider and includes feed pressure and vacuum on permeate, which can be used for separation. Considering that streams containing carbon dioxide coming from power plants or heating systems are waste streams with no economic value, no "profit" margin is involved in their treatment. A significant separation cost (no less than 20/25 US$/ton) would significantly affect the final cost (e.g., of the electricity)[52]. Therefore, the separation/capture process must consider these aspects in terms of energy demand and limit them as low as possible.

In addition, there are a number of issues associated with the capture of carbon dioxide from flue gases which limit the use of membranes. The concentration of carbon dioxide in flue gases is low, which means that large quantities of gases will need to be processed. The high temperatures of flue gases will rapidly destroy a membrane, so the gases need to be cooled to below 100℃, prior to membrane separation. Likewise, the membranes will need to be chemically resistant to the harsh chemicals contained within flue gases, or these chemicals will need to be removed prior to the membrane separation step. Additionally, creating a pressure difference through the membrane will require significant amounts of power, which will in turn lower the thermal efficiency of the power plant. The composition of flue gases greatly varies according to the fuel source, power plant and prior treatment. For instance, the flue gas from power plants and that from steel production plant exhibits a significant difference in CO_2 concentration. The use of membrane technology for CO_2 separation is, thus, also strictly related to the conditions of the stream to be treated. However, the

main role in its on large-scale use might be assigned to the membrane properties but also on the influence of the operating conditions on the whole process.

Many materials can be considered suitable for the separation of CO_2 from flue gas or methane-containing streams[62, 63, 64, 65, 66, 67, 68, 69], and many advances have been made in the maximization of their mass transport properties[70]. In this regard, an interesting parametric study on the impact of membrane materials and process operating conditions on carbon capture from humidified flue gas was performed[71]. For all cases, high membrane CO_2 permeance minimizes membrane area requirements, while high selectivity improves the CO_2 permeate concentration and reduces the energy needed for CO_2 purification. The benefits of greater selectivity are accentuated at higher feed-to-permeate pressure ratios, at the expense of increased energy cost. The advantages of higher permeance are most pronounced at lower pressure ratios. Therefore, the engineering design of a membrane separation unit for the recovery of CO_2 must thus take into account various factors. In our previous work[52], we developed a simple tool that uses "maps" to enable analysis of performance and the perspectives of membranes in CO_2 capture. These works analyzed the use of membrane gas separation in CO_2 processing with a general approach considering the effect and, eventually, the limitations offered by the main variables affecting the separation performance: the pressure ratio, the feed composition, and the mass transport properties (permeance and selectivity) of the membrane considered in the installation. As performed, the study was a useful guide for readers interested in CO_2 separation regardless from of the other gases present in the feed stream. It is thus suitable for flue gas separation as well as natural gas and biogas. Figure 7 shows the permeate concentration versus recovery for different values of CO_2 concentration in the feed at a pressure ratio of 1.5 and 5. At first observation, it appears that, for all the conditions considered, a very low recovery is achieved because the low pressure ratio strongly limits the driving force required for permeation. The permeate concentration is instead much more dependent on the feed composition, which defines the driving force together with the pressure ratio. At a pressure ratio of 1.5, a feed

stream containing a low percentage of CO_2 cannot reach high values of permeate concentration due to the insignificant driving force. As the fraction of CO_2 in the feed increases, the achievable permeate concentration also increases. The permeate concentration cannot exceed 16 % if the feed stream contains only 10 % CO_2, whereas a value of ca. 75 % can be achieved when the feed contains around 50 % CO_2. The strong limitation on the driving force does not allow increased effect of the membrane selectivity on the performance of the membrane unit. The low driving force is the rate determining step of the permeation and the use of a membrane with a very low value of selectivity (=30) or a membrane with extraordinary separation properties (=500) is equivalent for the final performance of the unit. The situation changes when a higher pressure ratio is utilized.

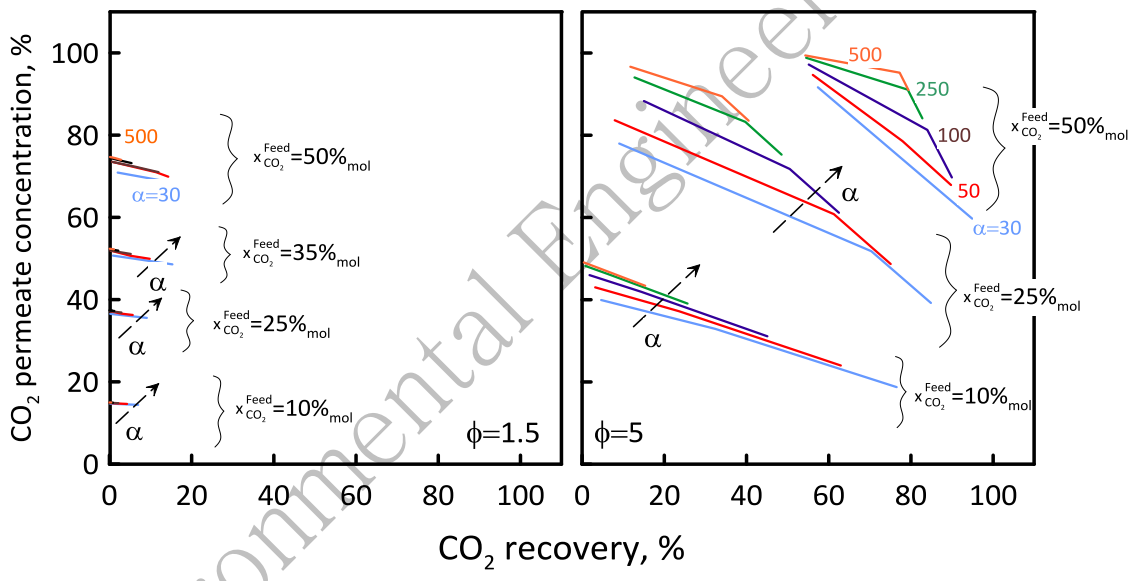

Figure 7. CO_2 permeate concentration as function of CO_2 recovery at various values of selectivity and CO_2 feed concentration. Pressure ratio 1.5; 5.

When the pressure ratio is 5, the performance of the system improves, particularly when the feed is not too diluted. In this case (also at a low CO_2 concentration in the feed), both recovery and permeate concentration can be significantly improved since the limiting effect of the diluted stream

on the driving force is compensated by the higher pressure ratio. Therefore, a stream with 10 % CO_2 in the feed can be concentrated at ca. 20 %, recovering ca. 75 % of the initial CO_2 with a membrane having a selectivity of just 30. Alternately, by using a membrane with a higher selectivity (250-500), a permeate concentration of 43-48 % can be achieved, recovering just less than 20 % of the CO_2 contained in the feed. The improvement offered by the higher pressure ratio in this case is even more evident at a higher CO_2 feed concentration.

On the basis of the above considerations, the selectivity of the membrane is fundamental for the final permeate concentration of the permeate stream. Its effect is limited when the permeation driving force is not sufficient; therefore, streams with low CO_2 concentration in the feed and/or low pressure ratio cannot achieve high permeate concentration level in one stage, even using membranes with extraordinary selectivity.

2.3. Raw materials depletion and reuse

In the last few decades mineral deficiency has become quite common all over the world, in part because of modern-day living. For example, the demand for lithium has already doubled over the past decade and it is expected to more than double over the next 10 years and the annual uranium requirements are projected to increase from 61,500 ton. in 1997 to 75,000 ton. in 2020. Moreover, simultaneously, for solving the problem of water shortage, desalination processes are spreading all over the world, as above described. Currently over 16,000 industrial desalination plants, with an average production rate of 65.2 million m^3/d, are operating worldwide[72]. By supplying water for municipal, tourist, agricultural and industrial use, desalination plants preserve and extend natural water resources freeing up water for agriculture, riverbed reclamation, recreational areas and forests. However, at the same time, these plants have negative impacts on the environment (such as CO_2

discharges from the energy consumed and highly concentrated brine as well as the solid wastes that have to be disposed of).

Open ocean, being composed of 96.7% of water and 3.3% of dissolved salts, is a reserve not only of water but also of chemical resources. It contains all elements from hydrogen to uranium even though seven elements (Na, Mg, Ca, K, Cl, S, and Br) account for around 93.5% of all the dissolved salts. Only a small fraction of the large variety of chemicals is currently extracted, principally table salt (sodium chloride) and the by-products (potassium chloride, magnesium salts and bromide salts).

The interest in mining the oceans is especially evident if we compare the amount of dissolved metal ions to the estimated reserves on land and to the total mass of minerals extracted today in the world (Table 6).

Table 6. Concentrations and estimated amounts of dissolved metal ions in the sea compared with the estimated land resources and with the total mass today extracted.

Element	**Concentration in seawater [g/L]**[A]	**Total oceanic abundance (tons)**[B]	**Mineral reserves on Land (tons)**[C]	**Production in 2014 (tons)**[D]
Cl	19.40	2.522×10^{16}	n.a.	n.a.
Na	10.80	1.404×10^{16}	n.a.	n.a.
Mg	1.29	1.677×10^{15}	2.20×10^{9} (from [73])	9.07×10^{5}
Ca	0.41	5.343×10^{14}	n.a.	n.a.
K	0.39	5.096×10^{14}	8.30×10^{9} (from 73)	n.a.
Br	0.070	8.749×10^{13}	Large	4.11×10^{5} (in the form of bromine)
Sr	0.00810	1.053×10^{13}	6.8×10^{6}	3.18×10^{5}
Li	0.00017	2.210×10^{11}	1.35×10^{7}	3.60×10^{4}
Ba	0.0000210	2.730×10^{10}	3.50×10^{8} (in the form of barite)	9.26×10^{6} (in the form of barite)
Mo	0.0000100	1.300×10^{10}	1.10×10^{7}	2.66×10^{5}
Ni	0.0000066	8.580×10^{9}	8.10×10^{7}	2.40×10^{6}
Zn	0.0000050	6.500×10^{9}	2.30×10^{8}	1.33×10^{7}
Fe	0.0000034	4.420×10^{9}	8.70×10^{10}	3.22×10^{9}
U	0.0000033	4.290×10^{9}	2.60×10^{6}–5.47×10^{6} (from [73])	6.65×10^{4} (from [73])
As	0.0000026	3.380×10^{9}	n.a.	4.60×10^{4} (in the

				form of arsenic trioxide)
V	0.0000019	2.470×10^9	1.50×10^7	7.80×10^4
Al	0.0000010	1.300×10^9	6.37×10^7	4.93×10^7
Cu	0.0000009	1.170×10^9	7.00×10^8	1.87×10^7
Se	0.0000009	1.170×10^9	1.20×10^5	n.a.
Mn	0.0000004	5.200×10^9	5.70×10^8	1.80×10^7
Cr	0.0000002	2.600×10^9	$> 4.80 \times 10^8$	2.90×10^7
Cd	0.0000001	1.430×10^9	n.a.	2.20×10^4

n.a.: not available.
[A] Seawater element concentrations are taken from [74] .
[B] Total oceanic abundance is calculated assuming a total ocean volume of 1.3×10^9 km^3.
[C] Mineral reserves are from USGS data[75] except for uranium reserves for which the values are given from [73]. The USGS[75] does not provide data for the world reserves of sodium and calcium. All land reserves are in terms of pure element, except for aluminum given in terms of smelter production and capacity. Detailed world arsenic reserves data are unavailable but thought to be at least 20 times world production [75].
[D] Mineral production data are from [75] except for uranium data, which is from [73]. In this case, the value reported is the total uranium consumption rather than the mineral production, which is about 2/3 of the total.

Table 6 lists seawater concentrations of some metal ions (in particular, the ones contained in higher concentration) and their total amounts assuming a total ocean volume of 1.3×10^9 km^3. The comparison of the total oceanic abundance of the various considered ions with their land reserves listed by the United States Geological Survey (USGS)[75] shows the presence of huge amounts of minerals in the sea, in most cases considerably larger than the estimated reserves on land. Moreover, the amount of minerals today extracted in the world is, in some cases, comparable to their estimated reserves on land (as it is happening, for example, for Al and to a lower extent also for Sr, Ni, Zn, Fe, Cu, Mn – see Table 6).

Moreover, when we consider the amount of water desalinated worldwide today (65.2 million m^3/day) and we suppose it is produced through reverse osmosis technology (recovery factor 45%, salt rejection 99.6%), the produced brine will contain, for some components, minerals in amounts comparable or higher than those today extracted (Table 7).

Table 7. Estimated amounts of mineral land resources compared with the total mass today extracted and with their concentration in brine.

Element	Mineral reserves on Land (tons)[A]	Production in 2014 (tons)[B]	Concentration in brine [ton/y][C]
Cl	n.a.	n.a.	9.22×10^8
Na	n.a.	n.a.	5.13×10^8
Mg	2.20×10^9 (from 73)	9.07×10^5	6.13×10^7
Ca	n.a.	n.a.	1.95×10^7
K	8.30×10^9 (from 73)	n.a.	1.86×10^7
Br	Large	4.11×10^5 (in the form of bromine)	3.20×10^6
Sr	6.8×10^6	3.18×10^5	3.85×10^5
Li	1.35×10^7	3.60×10^4	8.08×10^3
Ba	3.50×10^8 (in the form of barite)	9.26×10^6 (in the form of barite)	9.98×10^2
Mo	1.10×10^7	2.66×10^5	4.75×10^2
Ni	8.10×10^7	2.40×10^6	3.14×10^2
Zn	2.30×10^8	1.33×10^7	2.38×10^2
Fe	8.70×10^{10}	3.22×10^9	1.62×10^2
U	2.60×10^6–5.47×10^6 (from 73)	6.65×10^4 (from 73)	8.64×10^1
As	n.a.	4.60×10^4 (in the form of arsenic trioxide)	1.24×10^2
V	1.50×10^7	7.80×10^4	9.03×10^1
Al	6.37×10^7	4.93×10^7	4.75×10^1
Cu	7.00×10^8	1.87×10^7	4.28×10^1
Se	1.20×10^5	n.a.	4.28×10^1
Mn	5.70×10^8	1.80×10^7	1.90×10^1
Cr	$> 4.80 \times 10^8$	2.90×10^7	9.50
Cd	n.a.	2.20×10^4	5.23

n.a.: not available.
[A] Mineral reserves from USGS data [75] and from[73] already reported in Table 4.
[B] Mineral production data from [75] and from [75] already reported in Table 4.
[C] Brine element concentrations calculated assuming a total amount of desalinated water of 65.2×10^6 m^3/day produced through reverse osmosis technology with recovery factor 45% and salt rejection 99.6%.

Traditionally, the most concentrated ions in seawater (such as sodium chloride) are extracted from seawater by evaporation[73]. Ions such as Mg or K can subsequently be recovered by electrolytical processes[73]. These methods are not practical for low concentration ions and their main problem lies in the huge amounts of water that need to be processed.

The idea to reach a quasi-total exploitation of seawater, trying to recover all the water as desalted water and the ions as crystals, is in realty not a novel strategy.

In the Fifties and Sixties, Nelson and Thompson[76] carried out the first experimental work for the recovery both of fresh water and minerals from seawater by freezing. The advantages of their technology with respect to other desalination operations are related to minor corrosion, precipitation and incrustation problems. Its disadvantage is correlated to the difficulty to handle ice, which is mechanically hard to move and process. Therefore, this desalination and extraction technology never passed the experimental stage even though promising results have been obtained in recent years under the name of eutectic freeze crystallization [77].

The situation is completely different when evaporative and/or membrane operations (such as Membrane Crystallization) are utilized for the recovery of fresh water and salts from seawater.

Membrane crystallization (MCr) is an innovative operation combining membrane technology and crystallization process able to promote crystals nucleation and growth in a well-controlled pathway starting from under-saturated solutions. This technology uses evaporative mass transfer of volatile solvents through hydrophobic membranes in order to concentrate feed solutions above their saturation limit, thus attaining a supersaturated environment where crystals may nucleate and grow. According to the chemical–physical membrane properties and to the process parameters (temperature, concentration, flow rate, etc.), the solvent evaporation rate (and, as a consequence, super-saturation) might be regulated very precisely. The effect is the control of nucleation and growth rate (goals not easily achievable in conventional crystallization methods). Other advantages of MCr can be well clarified by comparing it with the most common and general principles of work of conventional crystallizers (such as, circulating-magma crystallizer). In a conventional crystallizer solvent evaporation and solute crystallization occur in the same location (i.e., the crystallization body) where the temperature gradients between the surface and the bulk of the body often compromise the suspension uniformity of the solid products. On the contrary, a membrane

crystallizer apparatus is characterized by the dissociation of solvent evaporation (occurring inside the membrane module) and the crystallization stage (performed in a separate tank on the retentate line). Thus, the produced crystals are expected to show improved size distribution and global quality. Secondly, the presence of the polymeric membrane in the crystallizing solution induces heterogeneous nucleation at super-saturation levels that would not be adequate for spontaneous nucleation in the bulk of the solution. Moreover, the membrane matrix acts as a selective gate for solvent evaporation, modulating the final degree and the rate for the generation of the super-saturation. Hence, the possibility of acting on the transmembrane flow rate, by changing the driving force of the process, allows one to modulate the final properties of the crystals produced both in terms of structure (polymorphism) and morphology (habit, shape, size, and size distribution)[78]. Furthermore, the generation of an extremely homogeneous super-saturation over the whole solution, owing to the numerous points for solvent removal (pores), allows the production of homogeneous distribution of initial aggregates which, in turn, will produce macroscopic crystals with uniform size distribution and controlled morphology[79] .

Finally, thanks to its intrinsic characteristic not to be limited by concentration polarization phenomena, MCr can be utilized for the simultaneously extraction of water and minerals from the brine of desalination plants thus minimizing their brine disposal problem, increasing their overall recovery factor and recovering the dissolved salts in the form of high-quality crystals [80] , [81]. In fact, the studies carried out by Drioli and co-workers [7, 8, **오류! 책갈피가 정의되어 있지 않습니다.**, 80], showed that high quality crystals of sodium chloride, CaCO3 and epsomite ($MgSO_4$ *$7H_2O$) can be obtained from the NF and/or RO brine streams of desalination plants.

3. Metrics for the analysis and redesign of industrial unit operations

To measure progress towards sustainability, much effort is being made to define indicators of the industrial process and, in particular their effect on environment, economy and society. Among these, the environmental indicators refer to the resources exploitation and the emission, effluents and waste related to the production, etc. Most of them, also known as metrics or indices, are calculated in the form of appropriate ratios allowing the comparison between different operations. Recently, various metrics were used for membrane operations taking into account the size, the weight and the yield of the plants. According to the unit operation considered, one is more suitable than another in the evaluation of the performance; therefore, in some cases all of them can be defined for an operation, in other cases only some of them. Table 8 summarizes the main metrics and some of the most important unit operations considered in this work for which these can be defined.

Table 8. Some of the most important metrics for Process intensification

	Equation	
Mass intensity	$MI = \frac{\text{Total inlet mass}}{\text{Reference product mass}}$	Eq. 1
Energy Intensity	$EI = \frac{\text{Total energy duty}}{\text{Reference product mass}}$	Eq. 2
Waste Intensity	$WI = \frac{\text{Total waste mass}}{\text{Reference product mass}}$	Eq. 3
Productivity/Footprint	$PF = \frac{\text{Reference product flow rate}}{\text{Footprint}}$	Eq. 4
Volume Index	$VI = \left.\frac{(\text{Reaction Volume})^{MR}}{(\text{Reaction Volume})^{TR}}\right\|_{\text{Set CO Conversion}}$	Eq. 5
Conversion Index	$CI = \left.\frac{(\text{Conversion})^{MR}}{(\text{Conversion})^{TR}}\right\|_{\text{Set Reaction Volume}}$	Eq. 6
Extraction index	$ExI = \frac{\text{Reference product recovered in the permeate}}{\text{Reference product available in the feed}}$	Eq. 7

Mass Intensity is defined as the ratio between the total mass entering the unit operation with respect to the total mass of reference product. The lower this value the better exploited is the raw material fed to the unit.

Energy Intensity is the ratio between the total energy duty involved in the unit operation with respect to the total mass of the reference product. Analogously to MI, the lower this value the better the energy exploitation in the unit.

Waste Intensity (or E Factor) draws attention to the quantity of waste that is produced for a given mass of product. It also exposes the relative wastefulness of different parts of the chemical processing industries that includes industries as diverse as petrochemicals, specialities and pharmaceuticals.

For Mass, Energy and Waste Intensities, lower values of these indicators are related to an intensified process. In the ideal situation they would approach value as low as possible.

The productivity/footprint ratio is very interesting for the Process Intensification objectives. Considering the same spatial area occupied by the units, this metric identifies the most productive scheme to get the targets. The higher the index is the more compact and efficient the unit operation will be.

The Volume Index is an important parameter in installing new plants. Future plants must be characterized by little sizes and high productivities: the VI is an indicator of the modularity of a unit and, specifically for MRs, it compares the MR reaction volume with that of a traditional reactor (TR), necessary to achieve a set conversion. VI ranges from 0 to 1. A low VI means that the reaction volume, required by an MR for reaching a set CO conversion, is much lower than that required by a TR. As a consequence, the catalyst weight necessary in MR is significantly reduced.

The capability of reaching a conversion higher than a TR, exceeding the TR equilibrium limits, is a typical property of an MR. The Conversion Index, defined as the ratio between the conversion

achieved in an MR and that of a TR, for a set reaction volume, provides an evaluation of the gain in terms of conversion and its use is particularly indicated when the feed mixture also contains reaction products. A high CI implies a relevant gain in terms of conversion achieved in an MR with respect to that of the conventional reactor, with the same reaction volume, meaning better raw material exploitation and lower wastage.

In MR technology, the quantification of H_2 recovered with respect to that totally extractable from the feed is an important issue. The Extraction Index defined as the ratio between H_2 permeated through the membrane with respect to that totally fed to the reactor, gives an indication about the limitations of an MR in the achievement of a complete conversion. If the hydrogen is the permeating species, as in the case study considered, EI takes into account the hydrogen fed as H_2 molecules and the one contained in the feed stream in other chemicals (e.g., H_2O).

3.1. Membranes-based desalination systems

Metrics that well allow comparing performance of membrane and thermal desalination systems are mass intensity, energy intensity and waste intensity.

In Figure 8, mass intensity (MI), energy intensity (EI) and waste intensity (WI) for a seawater reverse osmosis desalination system utilizing conventional pre-treatment (and indicated with SWRO) are compared with the value that these indices reach in a thermal desalination plant (MSF). Considering the same feed flow rate for all the two analysed desalination systems, Figure 8 clearly indicates a better performance of membrane with respect to thermal desalination systems, both in terms of productivity (i.e., high amount of fresh water produced) and in terms of environmental impact (lower volume of discharged brine and lower energy consumption).

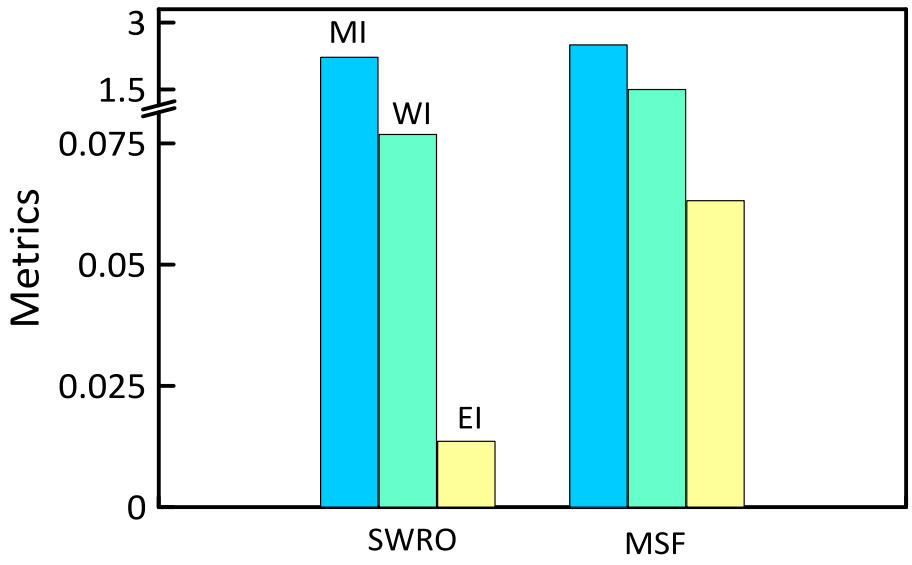

Figure 8. Mass intensity (MI [kg kg-1]), Waste intensity (WI [kg kg-1]), and Energy intensity (EI [MJ kg-1]) for thermal and non-thermal desalination systems (RO recovery factor=45%, MSF recovery factor 40%).

MI, EE and WI also provide a useful evaluation of various membrane-based desalination systems. An example can be found in Figure 9 where the above-cited indices estimated for a SWRO process are compared with those (i) of an SWRO plant utilizing MF and NF as RO pre-treatment (indicated with MF+NF+RO), and (ii) of an SWRO plant utilizing membrane pre-treatment and MCr as post-treatment of RO brine (indicated with MF+NF+(RO+MCr)). The results achieved confirm that the recourse to membrane pre-treatment improves the efficiency of RO and the presence of MCr unit also reduces significantly the brine disposal problem.

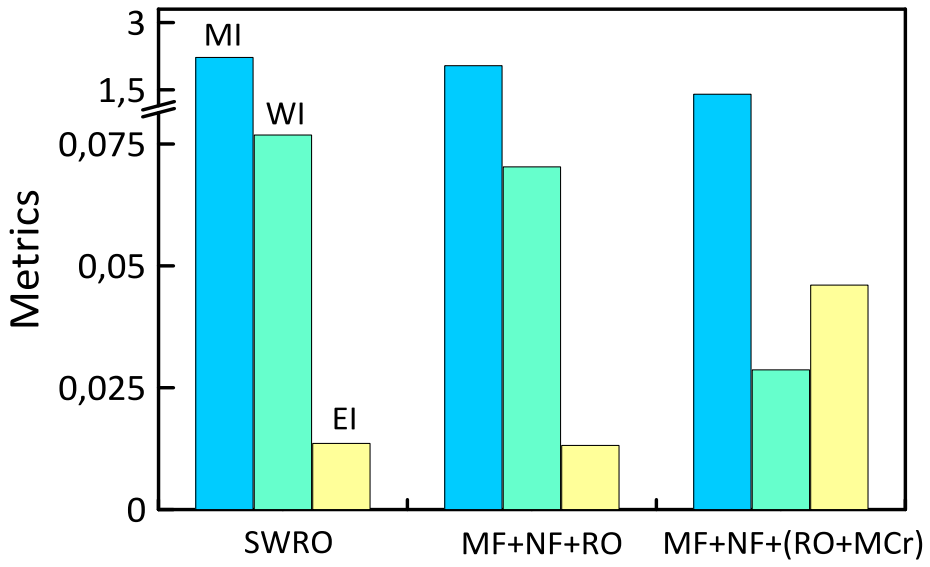

Figure 9. Mass (MI [kg kg-1]), Waste (WI [kg kg-1]), and Energy (EI [MJ kg-1]) intensity for various membranes desalination systems.

These indices can also help during the designing phase for individuating the most convenient process design. For example, in a membrane-based desalination process with NF as RO pre-treatment, there are two different brine streams, one for NF and one for RO. Then, MCr can be utilized for the exploitation of either NF brine, or RO brine or both. Figure 10 shows the indices for these three different situations. The lowest (i.e., best) value of MI for the desalination process with MCr on NF brine (indicated with MF+(NF+MCr)+RO) with respect to that with MCr on RO brine (indicated with MF+NF+(RO+MCr)) is due to the higher brine flow rate of NF than RO. Taking into account that MCr is not limited by concentration polarization phenomena, higher its feed flow rate, higher it will be the amount of fresh water that it can produce. However, the energy consumption (and the energy efficiency) of the system will also be higher due to the higher flow rate which has to be heated. These trends will be, of course, accentuated in a desalination system with MCr units concentrating both NF and RO brine streams (indicated with MF+(NF+MCr)+(RO+MCr)). The latter will have, on the other hand, the great advantage of minimizing the environmental impact of the whole desalination plant proved by a WI approaching 0.

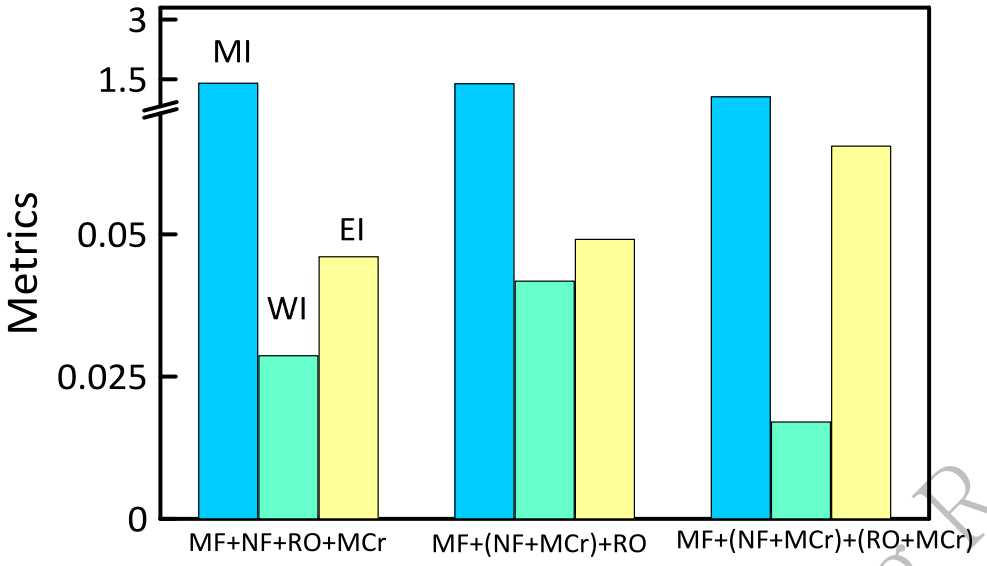

Figure 10. Mass (MI [kg kg-1]), Waste (WI [kg kg-1]), and Energy (EI [MJ kg-1]) intensity for various membranes-based desalination systems with MCr for the concentration of brine: (RO+MCr) is for the process with MCr on RO brine, (NF+MCr) is for the process with MCr on NF brine, (NF+MCr) +(RO+MCr) is for the process with MCr on NF and RO brine.

3.2. Membrane condensers

As already mentioned, the membrane condenser is a suitable and innovative unit operation for recovering H_2O from humidified waste gaseous streams and condensed liquid water is, thus, the reference product of this operation. Therefore, the experimental results [24] analyzed in terms of Mass and Energy Intensities, takes into account the H_2O recovered in the retentate (Eq. 2) as a valuable product with respect to the total mass fed for the former, the power required by the system (Eq. 3) for the latter.

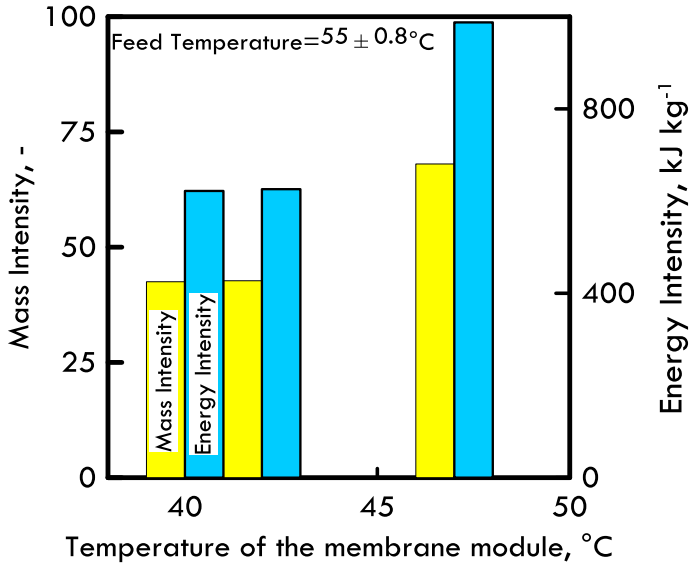

Figure 11. Mass an Energy intensities as a function of membrane module temperature. Data adapted from [24] with permission from Wiley.

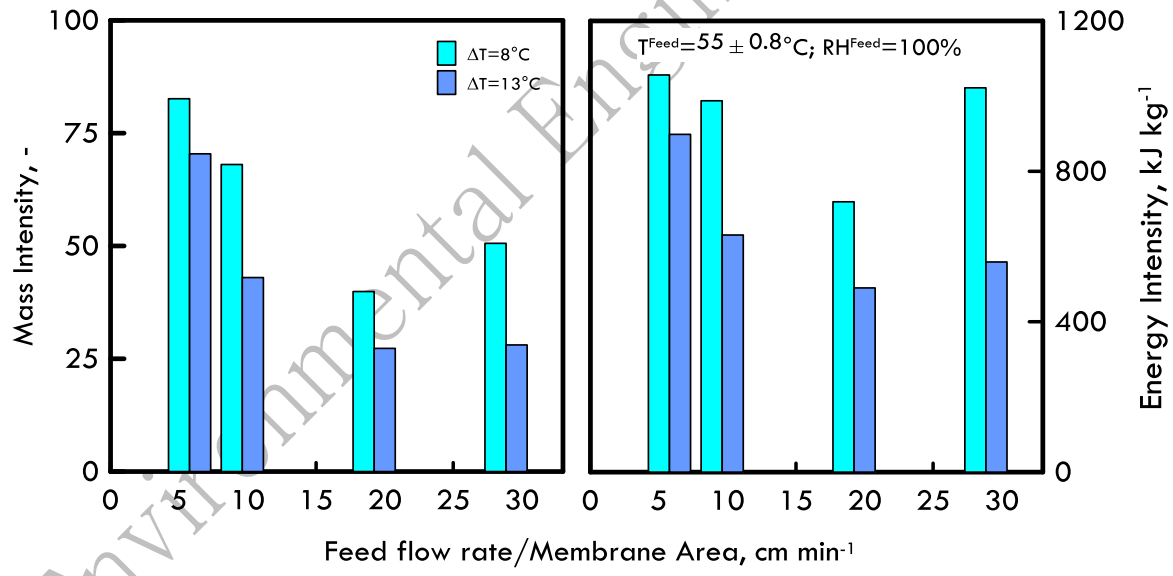

Figure 12. Mass and energy intensities as a function of feed flow rate/membrane area ratio at different values of temperature difference between feed and module.. Data adapted from [24] with permission from Wiley.

Figures 11 and 12 show an example on how the mass and energy intensity are influenced by the main variables determining the system performance, they being, in the case of membrane condenser, membrane module temperature and feed flow rate.

Mass intensity reduces in direct proportion to the lower temperature of the module and, thus, to the higher temperature reduction with respect to the feed. This is strictly connected to the greater amount of water recovered in the retentate (Figure 11). Analogously, the energy intensity follows the same trend, indicating that the process is more convenient for a high T. Observing both indices, the process appears more "intensified" when a significant T between the temperature of the feed and that of the module is imposed. The alternative point of view offered by metric evaluation with respect to conventional performance analysis is quite evident with EI evaluation. Actually, if, on one hand, in fact, the energy duty necessary to keep the module at the lower temperature is greater, on the other one, the amount of H_2O recovered is significantly higher with respect to that recovered at the higher module temperature where, on the contrary, less energy is required for cooling the system.

As detailed in [24], another determining parameter for membrane condenser performance is the ratio $Q^{Feed}/A^{Membrane}$. At a high value of this ratio it corresponds an under-dimensioned module with respect to the feed flow rate to be treated and, as a consequence, the water recovery is lower than that achieved for the lowest values of this ratio. However, analyzing the results in terms of metrics (Figure 12) the mass and energy intensities tend to a reduction at higher $Q^{Feed}/A^{Membrane}$ ratios. In particular, the mass intensity seems to reach a plateau which has a lower value at the lowest T whereas for Energy Intensity in all the cases a minimum is achieved. This behavior can be explained considering that at low T the rate determining step for the water recovery is the temperature difference between the feed and the module. On the contrary, for a high T, the process is controlled by the $Q^{Feed}/A^{Membrane}$ which becomes the limiting factor. As it can be clearly

deduced, the use of these two metrics allows the identification of two zones of operation where it can be more convenient to operate in order to intensify the process.

3.3. Membrane reactors

For MRs, some specific indices were introduced in the literature, taking into account, among the several advantages connected to their use, the one related to the conversion improvement, which means better exploitation of raw material, the recovery of upgraded species, the plant size reduction. In the following the upgrading stage of syngas streams for hydrogen production carried out in a Pd-Ag membrane reactor is taken as an example to highlight the main aspect put in light by metrics analysis[82].

Most likely, for this kind of MR, the mass intensity is defined as the ratio between total mass entering the reactor and the total H_2 (reference product) fed to the MR and produced by the reaction, whereas, the energy intensity relates the total energy involved to the same denominator. Both indices are determined by the conversion and the composition of the feed stream.

The ideal values of MI and EI are the ones at the reactor equilibrium conversion, referred as TREC for TR, and MREC for MR[83].

The ratios of MI and EI provide an indication on the distance of the actual performance from the ideal one. An example of metrics dependence on the main variable affecting MR performance is shown in Figure 13 where it is well evident the difference between the actual and ideal value. While the metrics calculated at the equilibrium increase with temperature, the ones describing the actual performance show high values at low temperatures with a decreasing behaviour. This has to be mainly attributed to the dependence of both indices on the conversion and to the fact that WGS is an exothermic reaction. In actual conditions, a low temperature implies a slow kinetics which antagonizes the positive thermodynamic effect on the reactor performance and thus induces a low

conversion. As the temperature increases, the metrics also increase owing to the favourable kinetics, and specifically for the MR, the improved permeation rate that further promotes the conversion.

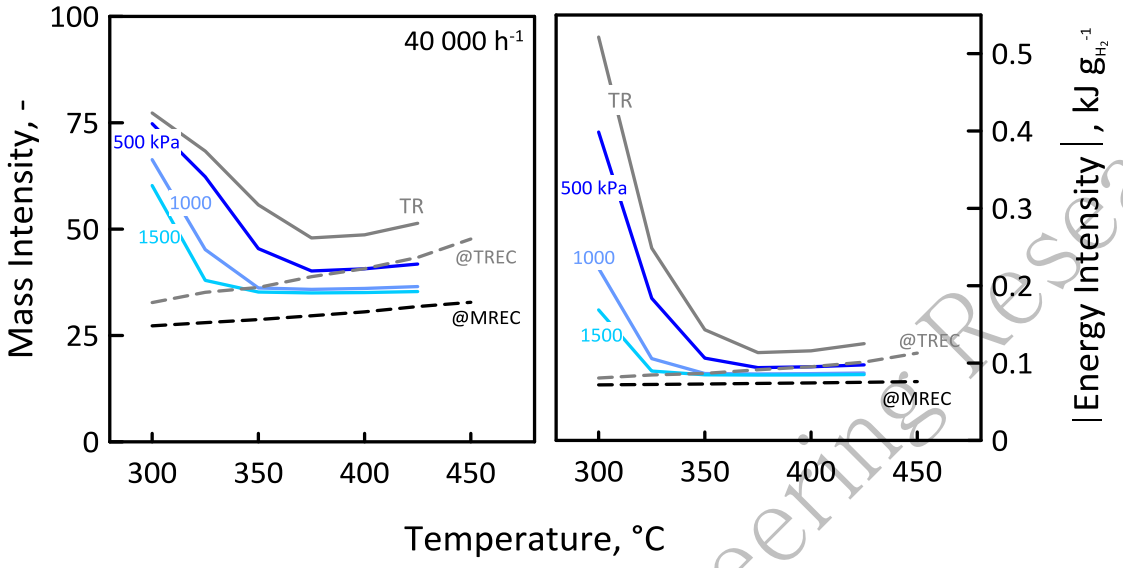

Figure 13. Mass Intensity and Energy Intensity as function of the temperature for different values of reaction pressure at 40000 h^{-1}. Dashed lines: values calculated at TREC or MREC (@ 1500 kPa).

At a glance, Figure 14 gives a phase diagram of the mass intensity and energy intensity ratios referred to the TREC, the zones where the process is more intensified. As explained this happens as the mass and energy intensity ratios are much higher. In the blue area, both parameters have the most desired values: MI and EI ratios higher than one, achievable only by the MR, since mass intensity and energy intensity ratios are higher than that at TREC. When the variables fall in this area, the MR is more intensified than any TR also at its equilibrium state. The second zone, in grey, is the locus of all the possible values for TR and MR obtained under TREC condition. As the temperature and the pressure increase, the values tend to the intensified zone. As the MR is proposed as a suitable alternative to the whole upgrading stage of syngas, it is interesting to compare the gain offered by this innovative technology in terms of size reduction and thus Volume

Index, which, in this case, compares the reaction volume required by an MR and the one necessary to the whole traditional process, for achieving the same conversion (Figure 15). As expected, the reaction volume required by MR results always lower than the one of the whole traditional process, further decreasing as feed pressure increases. This relevant difference has to be mainly attributed to the bigger amount of catalyst required by the low temperature stage of the traditional process due to the low kinetics of the CuO-ZnO. At 350°C and 5 bar, the MR reaction volume is around 80% of the one of the Traditional process and it drastically reduces only to 24% at 15 bar. Moreover, by increasing the temperature, this value is still reduced passing form 64% at 5 bar to ca. 18% at 15 bar, owing to the H_2 permeation promotion.

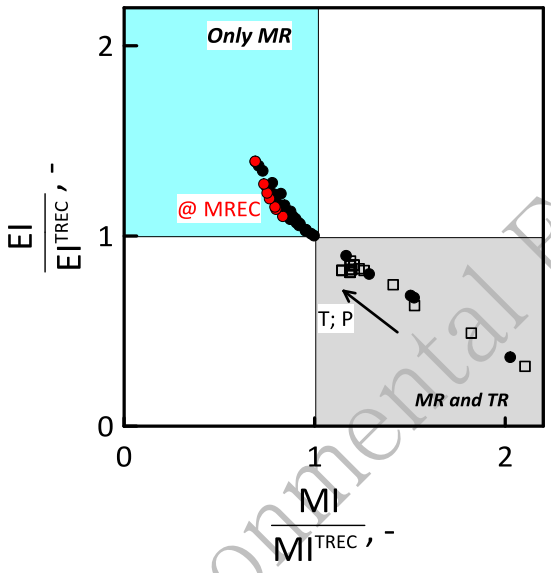

Figure 14. Energy Intensity ratio referred to the TREC as a function of Mass Intensity ratio referred to the TREC for all the operating conditions.

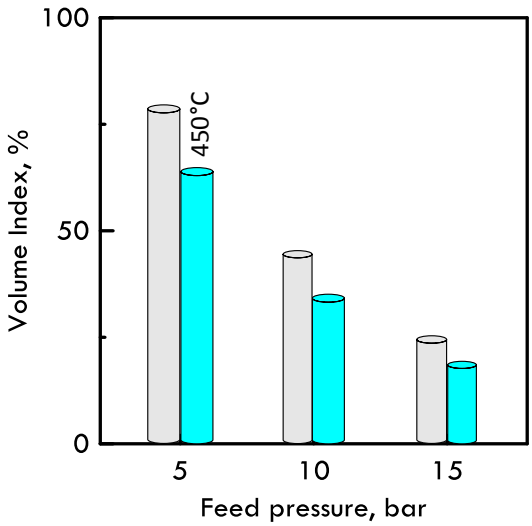

Figure 15. Volume Index as a function on feed pressure at 350 (grey bars) and 450°C (blue bars) . GHSV=40000 h^{-1}.

The advantage offered by MR in terms of conversion is indicated by Conversion Index, defined as the ratio between the conversion achieved in an MR and that of a TR, for a set reaction volume.

Also this index provides an immediate indication of the system performance and its dependence on the main operating parameter. Since MR is a pressure-driven process, the higher the feed pressure the higher the CI, as is shown in Figure 16. It is clearly shown how the MR can get a conversion more than 2 times greater than the one achievable by a TR with the same catalyst amount. This advantage is obviously function of pressure and temperature since both, positively acting on H2 permeation, shift the conversion toward further conversion.

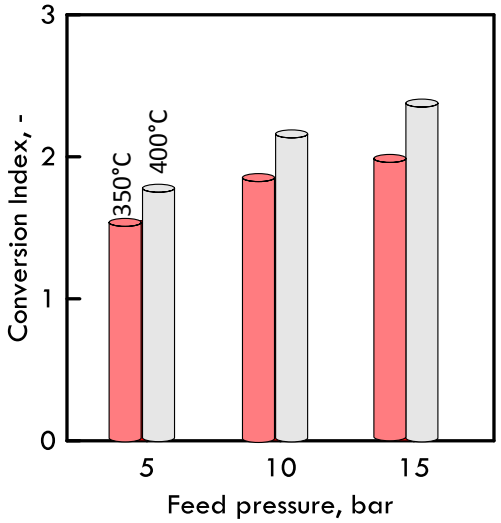

Figure 16. Conversion Index as a function on feed pressure at 350 (pink bars) and 400°C(grey bars). GHSV=20000 h-1

The amount of reference product recovered by the membrane unit can be quantified in terms of Extraction Index. It takes into account the reference product, in this case hydrogen, fed as molecule and that which is contained in the feed stream in other chemicals (e.g., H_2O). As defined, it is determined by the membrane properties, feed molar ratio and conversion achieved in the MR, at set operating conditions. In particular, EI increases with the temperature as well as the feed pressure, owing to the positive effect on the permeation.

Figure 17 shows an example of extraction index dependence on feed pressure when a syngas mixture is fed to the module. The highest EI measured is 71.5% at 15 bar and 400°C, which means that 71.5% of the hydrogen totally available in the feed, as molecule and also as reactant, was recovered as pure stream in the permeate side. This highlights the significant extractive capability of the MR that, thus, assures a good exploitation of the reactants.

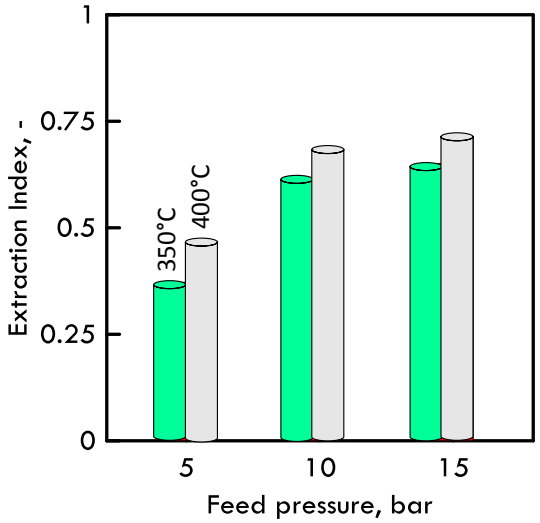

Figure 17. Extraction Index as a function on feed pressure at 350 (green bars) and 400 °C (grey bars). GHSV=40000 h^{-1}.

3.4. Membrane gas separation

3.4.1. Single stage

H_2 separation from binary mixtures with e.g. polyimide hollow fibres membrane module can be considered as a case study for showing an example of possible comparison between traditional separation technologies, like PSA and cryogenic, in terms of metrics. More details on the membrane units considered can be found in[84]. The performances of the membrane system compared with those of the PSA and Cryogenic systems show interesting results (Figure 18). The installation area required by the membrane systems is always lower than that of the other two separation operations, implying a significantly higher productivity footprint ratio. However, H_2 recovery and purity obtained with the membrane operation are lower or comparable with those of the other two systems; therefore the mass intensity is higher. It must be noticed that the membrane systems considered in these calculations operate at 50°C. However, at a higher temperature, the membrane permeance increases; therefore a higher recovery can be expected. Moreover, the results presented for the PSA

and cryogenic systems consider the treatment of a refinery off-gas, where the amount of hydrogen in the feed is (50-75%) higher than that used for membranes (30%)[85].

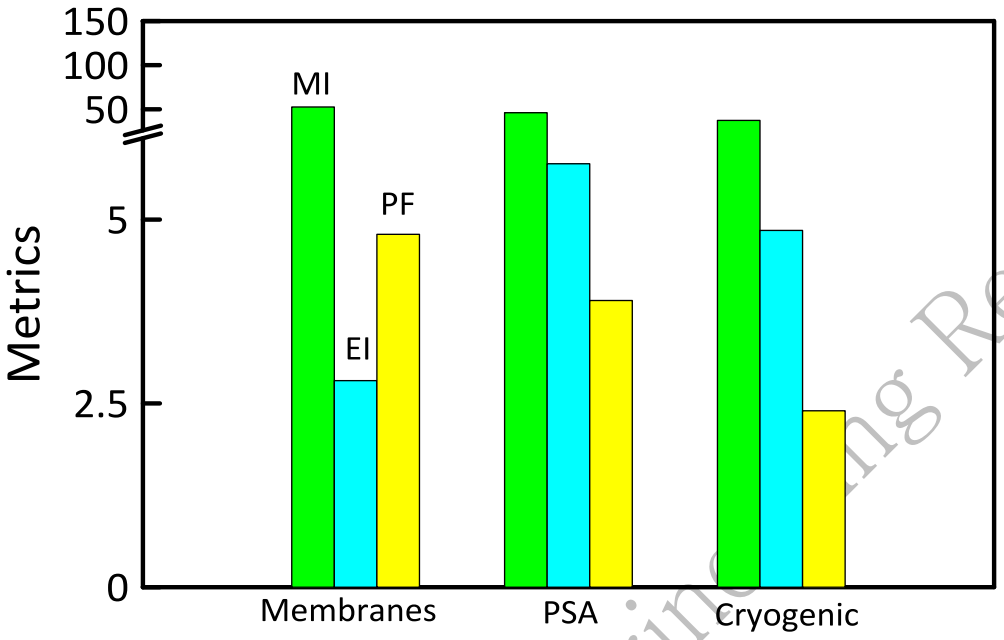

Figure 18. Mass Intensity (MI [kg kg-1]), Energy Intensity (EI [MJ kg-1]) and Productivity/Footprint ratio for various gas separation systems. The data reported for PSA and cryogenic refers to[86].

3.4.2. Multistage cascade system

In a recent paper[87], process schemes based on membrane-integrated systems have been proposed for biogas separation, introducing also the evaluation of overall performance of the whole system by process metrics, which provide an alternative point of view in the evaluation of the plant performance. Four process schemes were considered and Figure 19 schematizes one of them. Without going too much into the details on various schemes and single units performance, which can be found in[87], Table 9 gives an indication on the comparison of the various schemes. The quite

similar values of Mass and Energy Intensities of the four schemes indicate that the exploitation of energy and mass of the various systems with respect to the final recovery of CH_4 and CO_2 is comparable among the various schemes. The difference is much more relevant in terms of Productivity/Footprint, which means that the area of installation occupied by the membrane units to achieve a set productivity is significantly lower than the membrane units required by the other scheme solutions. This result evidences the importance of defining these indices owing to the complementary information acquired which might constitute a useful indication during the design phase, specifically for the choice of the most proper technology for a certain application.

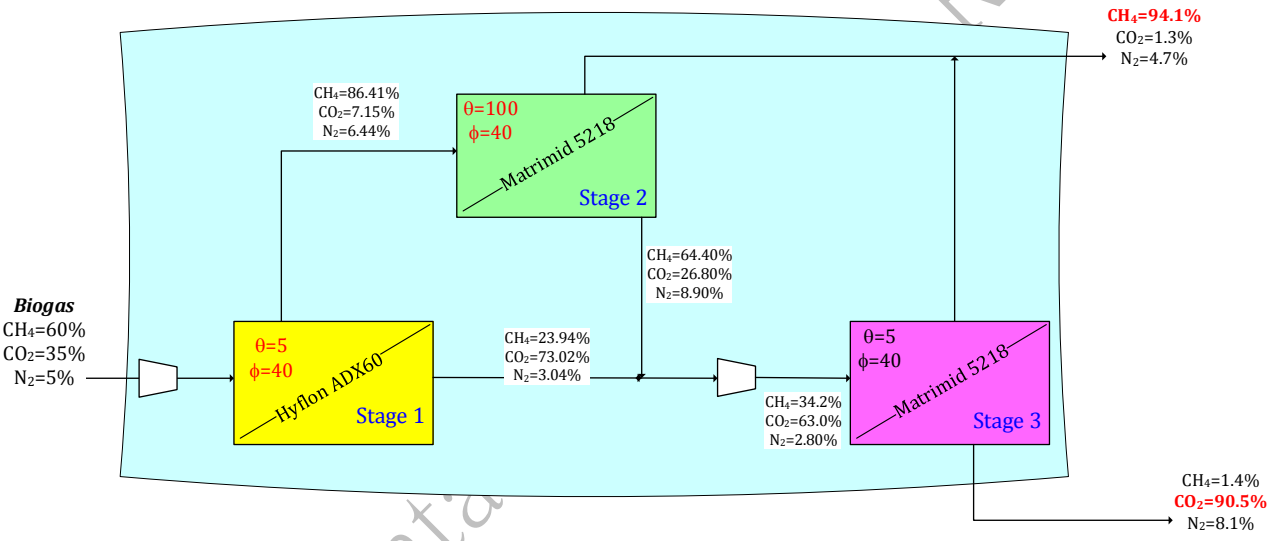

Figure 19. Scheme of biogas separation by membrane GS system. Reprinted from "International Journal of Greenhouse Gas Control, 35, Brunetti A.; Santoro S.; Macedonio F.; Figoli A.; Drioli E.; Barbieri G., "Process Intensification for Greenhouse Gas Separation from Biogas: More Efficient Process Schemes based on Membrane-Integrated Systems", 18-29, Copyright (2015) with permission from Elsevier".

Table 9. Process Intensification metrics for four options of scheme suitable for biogas separation.

	Scheme 1		Scheme 2		Scheme 3		Scheme 4	
	CO_2	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2	CH_4
Mass Intensity, kg kg^{-1}	1.82	2.94	1.82	2.94	1.92	2.78	1.92	3.33
Energy Intensity, kJ kg^{-1}	1,299	2,083	1,282	2,632	1,351	2,000	1,351	2,381
Productivity/Footprint, kg m^{-2} h^{-1}	0.37	0.6	0.19	0.09	1.55	2.28	0.38	0.21

4. Conclusions and future perspectives

To discuss the role of membrane operations for re-designing industrial applications, the introduction of new metrics for quantifying and comparing membrane performance with that of traditional operations has been suggested and is necessary. This work provided an analysis of some processes referring to some new indices introduced and related to Process Intensification strategy. These metrics allow the introduction of a non-conventional and complementary analysis of membrane unit performance, consisting in easy and useful indices able to give an immediate idea of the eventual gain offered by a membrane system and to allow also a better understanding of the application limits of membrane systems to obtain a determined quality target of a process. They provide useful information about the raw material exploitation, energy efficiency, waste production, volume and footprint reductions, supplying indications on when a process can be defined as more "intensified" than another.

In the membrane reactor case study, the comparison showed that membrane reactor resulted always more material and energy intensive than a traditional reactor, particularly at a high feed pressure indicating that membrane reactor requires less material as feed and makes available more energy in producing the same amount of H_2. The membrane reactor resulted always more intensified than a traditional reactor operated in similar conditions and exceeded also the ideal performance achievable by a traditional reactor, at a temperature higher than 350°C. Metrics for membrane reactor demonstrated, in line with the process intensification strategy, the advantages of this technology in terms of better exploitation of raw materials (reduction up to 40%), higher energy efficiency (up to 35%), lower reaction volume (up to 85% less than a traditional unit).

As in the case of membrane gas separation and membrane condensers, the metrics were not only useful in the comparison with traditional operations, but also resulted in an interesting approach for the selection of the most suitable operating conditions allowing the process to be intensified. For

instance, in various schemes proposed for biogas separation by membrane units, the differences in terms of Productivity/Footprint allowed the identification of which scheme would be more productive occupying less installation area with respect to the others, and this constituted additional useful information in the designing phase.

For water desalination and raw material reuse, the metrics are useful (i) for the comparison between traditional and membrane operations, (ii) during project design for evaluation of different possible operative schemes, and (iii) for the individuation of the most sustainable process. In fact, the lower mass and energy intensity of SWRO with respect to a conventional MSF plant clearly confirm what already common, which is its higher recovery factor and lower energy consumption that in turn justify the lower desalted water cost of SWRO with respect to MSF. Moreover, the lower waste intensity of SWRO underlines the lower environmental impact of the membrane with respect to the thermal plant. A further "sustainability" of the desalination plant for what concerns the reduction in the amount of discharged brine can be achieved through the utilization of MCr units where WI approaches zero. Therefore, it is important to underline that the use of metrics, together with conventional parameters (such as energy consumption, recovery factor and cost) can help in the choice of the most economically profitable process and at the same time with the least environmental impact.

In the end, this manuscript aimed to give a point of view not only on the potentialities of some membrane operations, but on the approach to be used for a proper evaluation of their performance and comparison with conventional units. All the metrics reported above can in fact be easily extended to the other types of unitary operation as a useful tool for the evaluation of pros and cons during the design phase of a new plant where the membrane operation would replace the traditional ones.

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