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The Status and Perspectives of Sustainable Membrane Materials, Membrane (Bio)reactors, and Membrane Distillation Processes

Francesca Russo[1], Rosalinda Mazzei[1], Adele Brunetti[1], Alessandra Criscuoli[1], and Alberto Figoli[1,*]

[1]*Institute on Membrane Technology (CNR-ITM), Via P. Bucci 17c, 87036 Rende (CS), Italy*

[*]Author to whom any correspondence should be addressed; Alberto Figoli: e-mail: a.figoli@itm.cnr.it

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Abstract

Membrane technology is recognized to be unique in many industrial sectors. This technology contributes significantly to sustainable development promoted by the principles of Green Chemistry and Process Intensification Strategy (PI). It has become a successful alternative technology that led to significant benefits concerning the conventional separation techniques, such as ease of processability, flexibility, and small footprints making them the preferred choice in many fields of interest. In this overview, the vision for the future development of membrane operations is evidenced and it is based on the improvement of existing membrane processes for specific applications, such as hydrogen production, food sector, and distillation, by using membrane reactors, bioreactors, and membrane distillation (MD) processes, respectively. Furthermore, to enhance the sustainability throughout the lifecycle of membrane products, the exploitation of new solvents and biopolymers platforms that have great potential to replace hazardous solvents or petroleum-based materials for more sustainable membranes in different geometries is presented and discussed.

Keywords

Sustainable membrane materials; membrane reactors; hydrogen production; membrane bioreactors; membrane distillation

1. State-of-the-Art

Membrane science is currently considered one of the best sustainable technologies in the global industry [1]. It exhibits significant dependence upon the concepts of green chemistry and Progress Intensification Strategy for achieving technological changes, such as recycling of waste, waste minimization, pollution control, more efficient usage of resources, changing production processes, energy recovery, lower footprint, and ease of scalability [2]. Membrane demand tends to follow overall economic activity; thus, a strong correlation exists between membrane consumption per capita (including membrane modules, systems, and additional equipment) and the global gross domestic product (GDP) per capita. The membrane growth in an emerging market is expected to increase from 5.4 billion USD in 2019 to 8.3 billion USD by 2024 [3]. Due to its intrinsic characteristics of efficiency and operational simplicity, high selectivity and permeability for the transport of specific components, this technology represents an interesting answer to the environmental damage caused by the increase in production and consumption of the resources, rapid industrialization and population growth. Membrane technology offers, in fact, interesting opportunities in the design, operation, and optimization of systems in different sectors such as waste treatment, water purification, health-pharmaceutical-medical, food and biotechnology, organic material separation, gas separation, pollution control, and recovery and recycling of chemicals. The main advantages of this technology over the traditional processes (such as distillation, absorption, etc.) include lower environmental impact due to lower energy consumption, low investment and operating costs, easy scalability, and small footprints.

In the last years, significant progress has been made in the preparation of sustainable membranes in different configurations, such as flat sheet, hollow fibers, nanofibers, or spherical ones, according to Green Chemistry design, and many research projects in this area are also in progress [4–7]. One of the most important subject issues of sustainable membrane preparation is the elimination of fossil-based materials and the replacement of hazardous materials and toxic polar aprotic solvents such as N-methyl-pyrrolidone (NMP), dimethylacetamide (DMAc), and dimethylformamide (DMF) with eco-friendly solvents. The solvent represents the major component of the casting solution during the membrane preparation procedure. It can solubilize the polymer at a certain temperature, high chemical affinity with the polymer to determine membrane properties and high affinity toward the nonsolvent to control the phase inversion process [8]. The priority of the sustainable membrane using green solvents or biopolymers is the preservation of the membrane structure without compromising performance. **Figure 1** shows the key metrics for the future development of environmentally friendly materials for greener membrane preparation. They include environment and health assurance, efficiency and prevention, circularity, and cost reduction following the principles of green chemistry. Reducing volatile organic compounds (VOC) levels, carbon footprint, and reducing waste from more renewable resources are all drivers of environmental progress and human health assurance. The national and local VOC regulations, the 'Registration, Evaluation, Authorisation and Restriction of Chemicals' (REACH) legislation published by the European Chemicals Agency (ECHA) together with the necessity of product's carbon footprint raise the requirements to change many solvents and polymers. These guidelines may require significant research investments for both raw material suppliers and membrane manufacturers. Life Cycle Assessment (LCA) should be the right tool to quantify the impact of a prepared membrane as well as the used solvent throughout the "cradle-to-grave" approach that follows the life cycle from fabrication to application use and disposal. The term "disposal" highlights the necessity to use renewable resources from biomass, bio-solvents and bio raw materials, to facilitate membrane recycling for a more circular economy and environmental protection. Currently, these materials are limited, not due to the unavailability of biomass, but due to the lack of adequate process capacities. The biorefinery concept needs to be further developed in Europe to enable the transition from a fossil-based carbon-intensive economy to a totally circular and bio sourced solutions. Limiting the use of toxic solvents or fossil-based polymers increases the transition to less hazardous alternatives at reasonable costs when possible.

Figure 1: Metrics that favor the development of greener membrane preparation

The potentialities of membrane operations according to PI are well established in the literature [1,2]. In the sustainability scenario, membrane reactors (MRs) as well as bioreactors and/or membrane distillation play a significant role in the operation of new membrane units. Today, the MRs constitute a solution for several processes thanks to the combination of reaction and separation in the same unit, their simplicity, automation, and control of the system [9]. MRs can be involved in the petrochemical industry, energy conversion, and/or hydrogen production. Hydrogen is recognized as the new energy vector since the energy contained in the molecule can be efficiently converted to electric energy in fuel cells. Its purity requirements depend on the final use, and, therefore, different separation /purification technologies can be applied. Inspired by nature, and in particular by biological membranes, membrane bioreactor (MBR) is an intensified process that combines biocatalysis with a separation step, based on a membrane process [10]. Besides, thanks to the membrane versatility, MBRs can be easily integrated with other membranes (e.g. pervaporation for biodiesel production, reverse osmosis for water treatment, etc.) and non-membrane processes, well responding to the development of green processes following the logic of PI which aims at the development of new solutions in terms of competitiveness, product quality, novelty, and environmental compatibility.

Membrane distillation (MD) is an emerging thermal-driven technology. Through this process, it is possible to promote the transport of vapors and volatile molecules through microporous membranes, using a difference in vapor pressure as the driving force. High separation efficiencies are obtained, with high-purity water produced starting from different feeds (wastewater, seawater, etc.), when working both as a single membrane operation and in integration with other membrane processes (e.g., reverse osmosis) [11]. This work aims to put in evidence: 1. the contribution of some membrane operations, such as membrane reactors, as well as bioreactors and membrane distillation, and their future perspectives for sustainable development in different sectors of interest (there are no ties between them, but reported as examples of fields where sustainable solutions are needed in the next future) and 2. how membranes themselves can be prepared in a more sustainable way (greener solvents). Both aspects are, in fact, crucial for sustainable development based on the use of membrane operations. In particular, to highlight the effect of different greener solvents on membrane formation, a detailed description is reported and compared to the traditional ones. Besides the crucial solvent role in membrane stability and performance, the new trend toward the use of biopolymers for membrane preparation will be described. The future direction of membranes in processes such as membrane reactors, bioreactors, and membrane distillation, are also highlighted, with new membrane systems based on green metrics.

2. New Chemical Platforms for Polymeric Membranes

2.1. Conventional Solvents and Polymers for Membrane Preparation

The common toxic, polar aprotic solvents such as NMP, DMAc, and DMF are still frequently employed in membrane preparation, even though their classification as CMR substances (carcinogenic, mutagenic, or toxic to reproduction substances) has meant that, under hazardous substance legislation, substitution solvents becomes obligatory. The amide solvents were classified as toxic for reproduction and may damage the unborn child. They also cause eye, skin, and respiratory irritation. For many years, their toxicity was suspected. In 2011 NMP was added to the candidate list as a substance of very high concern (SVHC) and a proposal was made in 2018 to classify it as a substance subject to authorization (8th Recommendation for inclusion in Annex XIV). Then, the restriction on inclusion in Annex XIV was postponed until notification in May 2020. A proposal for restriction on DMF and DMAc has already been submitted. The planned date for adopting the Annex XVII amendment for DMAc was the first quarter of 2021 **[11]**. The DMAc was also classified by the European Commission as an SVHC substance and registered under REACH in October 2021 due to its reproductive toxicity **[12]**. Generally, a temporary period of two years before the application of the proposed restrictions is required, to ensure the transition to new chemicals and proper communication throughout the supply chain at the industrial level. Common polymers such as poly (vinylidene fluoride) (PVDF), polyethersulfone (PES), polysulfone (PSF), and cellulose acetate (CA) are often used in the preparation of membranes. Traditional polymers provide many advantages in terms of mechanical, chemical, and thermal stability. They have good processability for producing membranes with high efficiency of the process. PES is one of the polymers of the sulfone family; it is a kind of excellent polymer for its easy processability at room temperature and its high solubility in different polar aprotic solvents **[13,14]**. Fluorine polymers involve thermoplastic and elastomeric materials ranging from semi-crystalline to amorphous state such as poly (tetrafluoroethylene)-PTFE and poly (vinylidene fluoride)-PVDF. Currently, halogenated solvents like chloroform, tetrahydrofuran (THF), and dichloromethane (DCM) are also used for the producing of dense membranes via the evaporation-induced phase separation (EIPS) technique. The halogenated solvents are probably carcinogenic to humans, according to the World Health Organization IARC evaluations **[15]** with a strong environmental impact of their VOC emission and hence the high risk of worker exposure. In this regard, the European restriction according to the REACH regulation limited the use of toluene, benzene, chloroform, and DCM with specific options.

2.2. Green Solvents for Polymeric Membranes Preparation

Bio-based solvents are obtained through the chemical or physical transformation of plant-based feedstocks, which include sugar, starch, oils, and lignocellulose from forestry, crops, and organic waste. They have non-toxic, carbon-neutral, and environmentally friendly properties. Nelson traced the first high-level classification of green solvents in 2003 **[16]** with a list of 659 solvents. Recently, Wypych **[17]** published a datebook of green solvents that collects data sheets for a range of solvents. Those that have been declared to be 'green' are predominantly oxo-hydrocarbons (cyclic and acyclic alcohols, esters, carbonates, and ethers) with some hydrocarbons and those containing other heteroatoms. Even though green solvents are becoming more common in membrane preparation, their use in biopolymeric membrane preparation is still limited. The appropriate solvent-polymer systems can be also identified by the solubility parameters in terms of dispersive parameter (δd), polar parameter (δp), and hydrogen bonding parameter (δh). By controlling the the mutual diffusion, the thermodynamic and kinetic aspects of membrane formation, membrane morphology, as well as performance, can be precisely controlled for the required membrane applications. Currently, a series of solvents alternate to conventional organic solvents for membrane preparation have been developed, e.g. bio-based polar aprotic solvents, ionic liquids (ILs), deep eutectic solvents, etc. **[18]**. The most relevant ester and carbonate are methyl acetate, ethyl acetate, glycerol triacetate, ethyl lactate, γ-valerolactone (GVL), methyl 5-dimethylamino-2-methyl-5-oxopentanoate (Polarclean), dimethyl carbonate (DMC) and glycerol carbonate. In the group of ethers, the relevant green solvents are cyclopentyl methyl ether, isosorbide dimethyl ether, 2,5-dimethylfuran, 2-methyltetrahydrofuran (2MHT), ethylene glycol monomethyl ether, ethylene glycol dimethyl ether and dihydrolevoglucosenone (Cyrene®) **[19,20]**. A specific distribution of solvents with key properties and safety applied to polymer membranes is reported below. The recent works on greener solvents for membrane preparation are reported in **Table 1**.

2.2.1. Non-Toxic Polar Aprotic Solvents

The solvents referred to in this section are identified as alternatives to traditional toxic solvents with a less toxic profile. The new generation of NMP solvent is the N-butyl pyrrolidone (Tamisolve NxG), which is a water-based polyurethane mixture that is considered biodegradable, non-reprotoxic solvent with high miscibility in water. Due to its high boiling point (240 °C), it is suitable for the preparation of polymeric membranes via NIPS, VIPS, and TIPS techniques. TamiSolve NxG has been used, for the first time, for the preparation of PVDF membranes via NIPS by Marino *et al.* **[21]** and Russo *et al.* **[5]**. These membranes varied from microfiltration (MF) to ultrafiltration (UF) applications. In another work, Saïdi *et al.* **[22]** used MF PVDF membranes prepared using Tamisolve NxG for direct contact membrane distillation (DCMD) and Crystallization (Cr) demonstrating performance comparable to commercial PVDF membranes. The preparation of membranes with this solvent was also demonstrated for the preparation of sulfonated polyether ether ketone (PEEK-WC) and poly(ethersulfone) (PES) membranes. The DMSO is also a substitute for classic polar aprotic solvents (DMAc, DMF, and NMP) for its high ability to dissolve a wide range of polymers due to its amphipathic nature and high polarity. It is derived by the oxidation of dimethyl sulfide and it is considered a renewable and non-toxic solvent for a recent study in vitro **[23]**. DMSO can be used for producing different polymer membranes such as PVDF, PES, polyimide, and cellulose **[24,25]** in flat sheet configuration. Furthermore, DMSO can be mixed well with acetone to produce PVDF nanofiber membranes by electrospinning technique **[26]**. Arkema Chemical Company produced a new upgraded solvent like DMSO EVOL™ improving smell without changing its properties. Marino *et al.* **[27]** used this type for producing PES membranes via VIPS method. The range of pore size was modulated by adding different concentrations of polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG) as pore formers. They obtained a water permeability between 2000 to 13200 $Lm^{-2}h^{-1}bar^{-1}$.

Table 1: Emerging solvents for PES and PVDF membrane preparation. Reprinted from [28] with the publisher's permission.

Membrane	Solvent				Membrane preparation technique	Membrane geometry	Ref.
	Name	Molecular weight	Boiling point	Solubility in water			
		g/mol	°C	(20 °C)			
PVDF	Triethyl phosphate (TEP)	182.15	215	Completely miscible	NIPS	Flat sheet	[29]
							[30]
							[31]
							[32]
						Hollow fiber	[33]
					VIPS-NIPS	Flat sheet	[34]
					Dry-jet wet-spinning method	Hollow fiber	[35]
PVDF	N-buthyl pirrolidone (Tamisolve)	141.21	241	Completely miscible	NIPS	Flat sheet	[5,22]
					VIPS-NIPS	Flat sheet	[21]
PVDF	Glycerol triacetate (TRIACETIN)	218.21	258	Slightly miscible	TIPS	Hollow fiber	[36]
PVDF	Triethylene glycol diacetate (TEGDA)	234.25	286	Completely miscible	TIPS	Flat sheet	[37]
PES	methyl-5-(dimethylamino)-2-methyl-5-oxopentanoate (Polarclean)	187.8	278-282	Completely miscible	VIPS-NIPS	Flat sheet	[38]
PES					NIPS	Hollow fiber	[14]
PVDF					VIPS-NIPS	Flat sheet	[39]
					N-TIPS	Hollow fiber	[40]
					TIPS		[41]
PVDF	Maleic acid dibutyl ester (DBM)	228.28	281	Not miscible	TIPS	Flat sheet	[42]
PVDF	Dibutyl sebacate	314.46	178-179	Not miscible	TIPS	Flat sheet	[43]
PVDF	Propylene carbonate	102.09	240	Completely miscible	TIPS	Flat sheet	[43]
PVDF	γ-Butyrolactone (γ-BL)	86.09	204-205	Completely miscible	TIPS	Flat sheet	[43]
PES	γ-Valerolactone (GVL)	100	207	Completely miscible	NIPS	Flat sheet	[44]
PES	Dimethyl isosorbide (DMI)	174.2	250	Completely miscible	VIPS-NIPS	Flat sheet	[13]
PVDF				Completely miscible	VIPS-NIPS	Flat sheet	[13]
PES	Dihydrolevoglucosenone (Cyrene^{TM})	128.13	227	Completely miscible	VIPS-NIPS	Flat sheet	[28,45]
PVDF				Completely miscible	VIPS-NIPS	Flat sheet	[28]
PES	Dimethyl sulfoxide (DMSO)	78.13	189	Completely miscible	NIPS	Flat sheet	[24]
							[46]
							[47]
							[48]
					VIPS-NIPS		[49]
							[27]
							[50]
					CCD		[25]
PVDF					NIPS	Flat sheet	[31]
							[51]
					Electrospinning	Nanofibers	[26]
PES	1-ethyl-3-methylimidazolium dimethylphosphate ([EMIM]DEP)	236.21	-	Completely miscible	NIPS	Flat sheet	[52]
						Hollow fiber	[53]
PES	1,3-dimethylimidazolium dimethyl phosphate ([MMIM]DMP)	222.18	-	Completely miscible	NIPS	Flat sheet	[53]
PES	1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF6])	284.18	-	Completely miscible	NIPS	Flat sheet	[54]
PVDF	Sulfobetaine-based DES solvents	-	-	Partial miscibility	NIPS	Flat sheet	[4]

NIPS: nonsolvent induced phase separation; VIPS: vapor induced phase separation; TIPS: thermally induced phase separation method; CCD: combined crystallization and diffusion.

Triethyl Phosphate (TEP) is a good alternative to toxic solvents. It has a high boiling point (215 °C) and high miscibility in water for potential preparation of membranes via phase inversion. PVDF has a great affinity with this solvent, but the dope solution for membranes presents high viscosity with respect to the solution with NMP with the possibility to obtain membranes without the presence of macrovoids in the structure **[55]**. The literature pointed out the potential of this solvent for flat membranes using a different phase inversion method. Marino *et al.* **[29,34]** produced PVDF membranes via NIPS and VIPS with the evaluation of pore former agents such as PVP and PEG. The resulting membranes were also applied in the membrane (MD) distillation process. They obtained asymmetric structure and pore in the range of UF via the NIPS method while by coupling VIPS with NIPS, membrane symmetric and bicontinuous morphology were prepared in the range of MF. The same result was also observed by Shih *et al.* **[56]**. They evidenced that TEP is a weak solvent for PVDF, which had allowed the minority presence of a nonsolvent to induce phase inversion. Consequently, liquid-liquid demining occurs at an early stage and macrovoids cannot develop. Zhao *et al.* **[57]** demonstrated the possibility of preparing PVDF hollow fibers with TEP using Pluronic F127 particles as additives via nonsolvent and thermally induced phase separation (N-TIPS). The results showed the surface pore structure of membranes without the formation of mechanically weak macrovoids. Hybrid membranes, like PVDF/GO, PVDF/TiO_2, and poly(vinylidene fluoride-co-chlorotrifluoroethylene) (PVDF-co-CTFE) can be prepared as well **[58]**.

2.2.2. Waste Valorization Solvents

Methyl 5-(dimethylamino)-2-methyl-5-oxopentanoate (Rhodiasolv®PolarClean) is a biodegradable solvent (97% after 18 days) reducing the carbon footprint. It is derived by the valorization of 2-methylglutaronitrile (MGN) which is a byproduct in the hydrocyanation of butadiene used to manufacture adipodinitrile (ADN). It has a boiling point of 280 ˚C and a freezing point of -60 ˚C. For the first time, Hassankiadeh *et al.* **[41]** prepared hollow fibers by using Polarclean as a solvent via the N-TIPS method. It was found that PolarClean associated with additives (PEG, PVP, and glycerol) induces porous structure and formation of β polymorphs in membranes, resulting in high-water permeability. This was recently confirmed by the work of Tocci *et al.* **[59]**. For the second time, Jung *et al.* **[60]** prepared PVDF membranes in flat sheet configuration via NIPS and TIPS methods. The membranes obtained a permeability exceeding 2000 $Lm^{-1}h^{-1}$ bar^{-1} with an average pore size of 40-50 nm. Recently, the PVDF copolymer in Polarclean was used for producing membranes via the VIPS process by Russo *et al.* **[39]**. Based on the water permeability and rejection tests, carried out using a methylene blue dye, the prepared membranes showed that they could be used in MF and UF applications. Polarclean is also employed in the preparation of PSF, PES, and cellulose **[55]** membranes by the production, for the first time, of porous Matrimid® 5218 membranes **[61]**.

PES Hollow fibers were also produced by Ursino *et al.* **[14]**. The pore structures of PolarClean/PES hollow fibers were from finger-like two sponge-like structures with a pore size ranging from 0.04 μm to 0.4 μm by varying the additives, polymer concentration, and bore fluids. The cost evaluation of the green solvent PolarClean, employed for making PES hollow fiber membranes for full-scale production was also performed. The final cost of membranes (lower of 4 €/m^2), was evaluated considering also the manpower and OPEX (energy, water, water-solvent disposal, and rental) and not only the solvent price.

2.2.3. Bioderived Solvents

Dihydrolevoglucosenone (Cyrene™) solvent is bioderived from two steps of conversion of cellulose via levoglucosenone (LGO). It was developed by Circa Group and Sherwood *et al.* **[45]** from York University. It shows a similar dipolarity to NMP, DMF, and sulpholane. It presents a boiling point of 227 ˚C, high-water solubility, and solvency capacity for different polymers such as PES, PVDF, and Cellulose acetate for membrane preparation. Marino *et al.* proposed, for the first time, Cyrene™ **[28]** for PVDF and PES membrane preparation, obtaining various membrane morphologies (from the sponge-shaped structure to the finger-shaped structure) by varying the exposure time to humidity (from zero to five minutes). This result was reached without the presence of any additives. In addition, the porosity, as well as the pore size, was modulated by varying the polymer concentration. The PES membranes prepared with Cyrene™ by using PVP were tested for water filtration. The results confirmed the high porosity of membranes with similar performances to membranes using NMP **[62]**.

Another polar aprotic solvent that is a popular bioderived platform chemical from lignocellulosic biomass is γ-Valerolactone (GVL). Its production follows two synthetic pathways: one via the production of hydroxymethylfurfural to levulinic acid and the second via furfural from hemicellulose **[63,64]**. GVL is soluble in water and presents a high boiling point of 208 °C. It is stable at room temperature; at 100 °C can react with water to form 4-hydroxyvaleric acid (4-HVA) **[65]**. This represents a limit for the application of membrane at high temperatures.

GVL together with glycerol derivatives such as monoacetin, diacetin, triacetin, and glycerol, were used for nanofiltration membrane preparation by Rasool and Vankelecom **[44]**. Thermodynamic aspects in terms of affinity for different types of polymers, i.e., PES, polyimide, and cellulose, were analyzed and the membranes prepared via NIPS were characterized by morphological analysis. This work demonstrates also that the price of the GVL ranged from $2/kg to $100/kg, which is not that high by comparison with conventional solvents, i.e., NMP (80-150$/kg), DMF (130-$200/kg), DMAc ($35-100/kg), and THF ($50-100/kg). In this study, the 2-methyl tetrahydrofuran (2-MeTHF) was also used as a co-solvent, representing a renewable alternative to tetrahydrofuran (THF). The physical properties are the boiling point of 80 °C and melting point of -136 °C. It has a lower miscibility in water and higher stability than THF. It is synthesized from xylose and glucose **[66]**. This solvent was recently used for NF membrane preparation. An initial approach was developed by Chuang *et al.* **[67]** that used 2-MeTHF for polybenzimidazole (PBI) NF membranes obtaining good separation performances with mixed dyes.

The bio-based platform chemical such as dimethyl isosorbide (DMI) is considered sugar-based and it is a very promising substitute for widely used dipolar aprotic solvents. It can be produced from isosorbide via the platform molecule-sorbitol and recently the synthesis was also modified via dimethyl carbonate (DMC) chemistry by Aricò *et al*. [68]. Russo *et al*. [13] proposed DMI, for the first time, for polymeric membranes. The research showed that DMI could be used as a solvent for two of the most widely used polymers in the membrane technology, such as PVDF and PES [13]. The phase inversion technique was also examined in connection to the kinetic parameter of viscosity and the thermodynamic parameter of the ternary phase diagram. The influence of the molecular weight of PVDF and the humidity action in the preparation were also examined without the presence of additives. The results confirmed high values of water permeability for both PVDF and PES membranes, from 6300 to 15000 $Lm^{-2}h^{-1}bar^{-1}$.

Other potential bio-based solvents are methyl lactate, ethyl lactate, and N,N-dimethyl lactamide (DML or AGNIQUE AMD 3L from BASF company) [69,70]. Methyl lactate and ethyl lactate are considered biodegradable and miscible in water. Recently, Rasool *et al*. [71] prepared cellulose acetate membranes using methyl lactate for nanofiltration application. DML is used in the cosmetic, pharmaceutical products, and chemical industries for its green profile. It is biodegradable, from lactic acid by microbial fermentation. It has a boiling point, melting point, and flash point of 223°C, -2°C, and 109°C, respectively. This solvent is an excellent candidate for PES membranes in flat sheet configuration. Gronwald and Weber [69] produced PES membranes via NIPS for NF application using AGNIQUE AMD 3L. The study evidenced the high solubility of the polymer/solvent system by using the Hansen theory. The results of membrane tests evidenced ultra-high-water permeability, about 610 $Lm^{-2}h^{-1}bar^{-1}$. Recently, AGNIQUE AMD 3L was also studied by Uebele *et al*. [70] for producing PES hollow fibers via the NIPS technique and with the use of low molecular weight PEG as a hydrophilic additive. The effect of the solvent on the dope solution and the membrane properties due to the changing in bore fluids at different water/solvent ration was investigated. The results showed a less stable thermodynamic polymer/solvent system that confirmed the necessity of less nonsolvent to induce phase separation. This can positively affect the wet-spinning process and promote the use of a humidified air gap in the preparation of the membrane.

2.2.4. Organic Carbonates

Organic carbonates are esters of carbonic acid, including a carbonyl functional group attached to two alkoxy groups [58]. Different kinds of organic carbonates such as dimethyl carbonate (DMC), propylene carbonates (PC), ethylene carbonate (EC), and 1,2-Butylene carbonate (BC) are presently on the market and useful for producing membranes more sustainably. They are soluble in water with different boiling points: 90 °C for DMC, 242 °C for PC, 248 °C for EC, and 238 °C for BC. A systematic study on the solubility of carbonate solvents with different polymers was conducted by Rasool *et al*. [72]. Polymers used were PES, PVDF, PSF, PAN, polyimide and cellulose. The screening was conducted considering the affinity for polymer and the energy difference between polymer and solvent. Cellulose was the only polymer that can be dissolved in these solvents. The work also produced membranes using a mixture of solvents with carbonates.

2.3. Biopolymers for Membranes

The approach of preparing biopolymer membranes from renewable resources served as a starting point for an effort to reduce the use of fossil-based materials, health hazards, environmental issues, and solid waste processing. Biopolymers have a low carbon impact, high biocompatibility, biodegradability, and biocompatibility [73,74]. Their properties show good flexibility but low strength in terms of durability and physical stability, which are still the weak points today. The future challenges of working entirely with biopolymer-based membranes in water treatment and gas separation include 1-the improvement of mechanical properties, 2- the extension of the aging time, and 3- the promotion at an industrial scale [75,76]. The most popular biopolymers can be classified as biopolymers from plants (cellulose CA etc.), from animals (chitosan CHT), from microorganisms (Polyhydroxyalkanoates (PHAs)), from synthesis raw materials, that include polycaprolactone (PCL), polylactic acid (PLA), poly(vinyl alcohol) (PVA), poly(ethylene-co-vinyl alcohol) (EVOH), polyglycolic acid (PGA) [74]. Chitosan (CHT) is a biodegradable and hydrophobic polymer with cationic properties in terms of ability to trap metals or dyes in waste water treatment. It also presents thermal stability [77]. PVA is a synthetic polymer with semi-crystalline molecular structure. It is biodegradable and biocompatible and high solubility in water and high processability to spin, to coagulate and orient of nanofibers. Pervez and Stylios [78] used the PVA polymer for reducing the viscosity of dope solution of CHT for electrospun nanofibers preparation. The PVA nanofibers have also good adhesive properties for adsorption of organic compound in the air and oil/water separation [79]. PHAs are considered as potential linear homo and co-polyesters derived from microbial fermentation of different sources of biomass. They are characterized by hydrophobicity, optical purity, high processability and biocompatibility without toxic effect. For these properties, they can be used for drug carriers and delivery systems [80]. PLA is a thermoplastic polyester, which has excellent properties such as high processability, water resistance, biocompatibility, biodegradability and permeability properties. It presents high solubility in different organic solvents, high melting point temperature (in the range of 170 and 180 °C) with a Tg from 50 to 65°C, depending on the degree of crystallinity. It is produced by lactic acid polymerization or ring-opening polymerization of cyclic lactide [81]. It can exist in different forms, such as L isomer -lactic acid, D isomer-lactic acid or a combination of both isomers. The thermal properties of PLA, as well as the grade of crystallization, can be influenced by the percentage of D- to L-PLA. Recently, PLA found large application in pervaporation and gas separation, respect to other biopolymers, thanks to its lower degradation rate and good mechanical and chemical properties [7,74,82–84]. Recently, Galiano *et al*. [83] employed ethyl lactate to produce PLA membranes via E-NIPS. The resulting membranes were produced using an evaporative time of 7 min and showed great potential to separate methanol/methyl tert-butyl ether via a pervaporation process.

2.4. Future Research and Perspectives on the Use of Green Solvents and Biopolymers for Membrane Preparation

Based on the overall trend toward Green Chemistry metrics, the future of membrane preparation will be dependent on the use of sustainable solvents and/or biopolymers, in order to protect both the environment and consumers, and reduce waste generation and energy consumption. At this stage, the number of publications on the use of green solvents and biopolymers in membrane preparation has continued to increase since 2007 as reported in **Figure 2**.

This work offers companies the opportunity to partner with research to access broader sustainability expertise.

The following perspectives are indicative of future developments:

- Besides the green solvents that recently were utilized, other bio-based or customized solvents from green platforms can be considered for producing polymeric membranes.
- The scalability of the membrane production must be addressed. The transition toward green solvents in large-scale industrial applications is essential for the bio-economy. Cost analysis need to be considered. This aspect depends on the purity, quality and the use of the solvent. The concepts of recycling, circular economy and "zero waste" play a fundamental role in this panorama [44]. The recyclability and reusability of the solvents during membrane manufacturing should be investigated in order to decrease the overall cost.
- The future projects primarily focus on the study and development of novel, highly sustainable membranes. These membranes are based on a combination of biopolymers and green solvents derived from biomass. Their tunable morphology and pore size enable their use in various fields of application. Another important aspect is the waste disposal of a membrane system **(Figure 3)**. In the context of circular economy, the potentials of reutilizing polymers (solid waste) derived from the end of life of the membrane cover important aspects for overviewing a totally sustainable and green membrane production [85,86].

3. Membrane Reactors

3.1. Membrane Reactors for Hydrogen Production

The utilization of membrane reactors (MR) constituted by membranes exhibiting high selectivity toward hydrogen is a promising technology for making hydrogen production processes. Generally speaking, MRs are multifunctional reactors, which combine in the same unit reaction and separation [87] The membrane divides the reactor into reaction and permeate zones and can have different functions, also combined acting as separator, distributor, and contactor, with catalytic properties **(Figure 4)**.

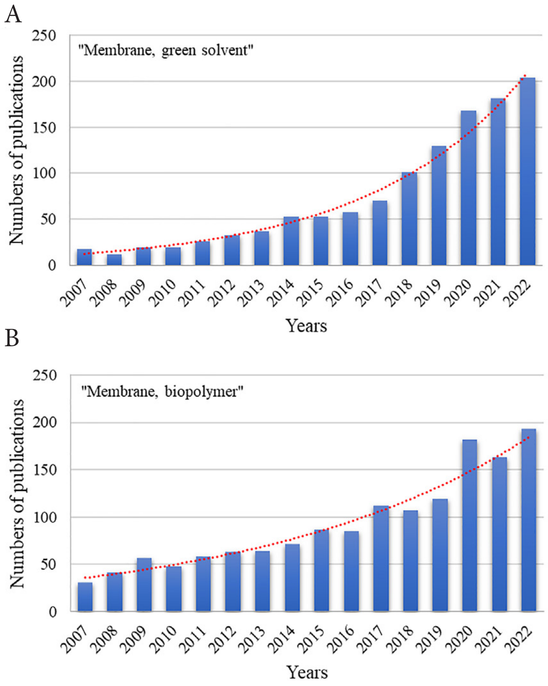


Figure 2: The number of publications from 2007 to 2022 was obtained from the Web of Science by combining (A) "membrane" and "green solvent" and (B) "membrane" and "biopolymer."

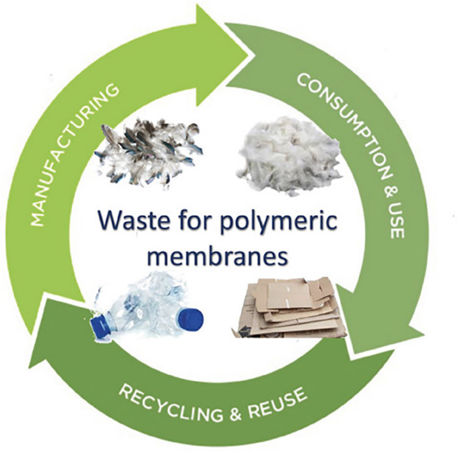


Figure 3: The concept of waste reutilization in polymeric membrane preparation. Adapted from [85].

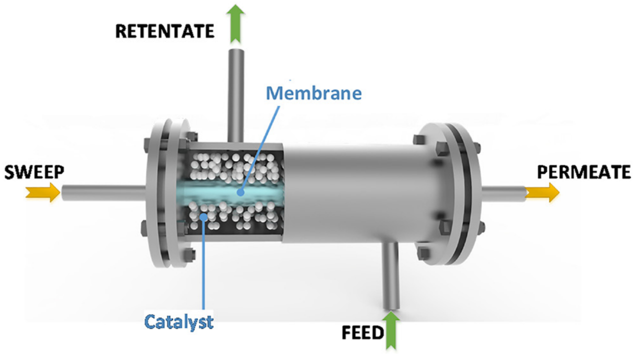


Figure 4: Packed bed MR. Reprinted from [88] with permission from the publisher.

In the production of H_2, most membranes used in MRs are highly selective toward hydrogen. This allows for the selective removal of H_2 from the reaction volume under the effect of a driving force, which is a function of the species' partial pressures on both sides of the membrane. This driving force can be created by applying a pressure difference, such as compressing the feed or applying a vacuum on the permeate side, or by using an inert sweep gas on the permeate side to reduce the hydrogen partial pressure. Among these options, the first one is more advantageous as it enables the recovery of pure H_2 as a permeate stream. The removal of hydrogen from the reaction volume has several advantages, including enhanced conversion, reduced secondary reactions, and recovery of a concentrated rich stream. In particular, removing a product from the reaction volume allows for greater conversion, even exceeding the thermodynamic equilibrium conversion of a traditional reactor (TREC). Additionally, reaction pressure can positively affect reactor performance, independent of thermodynamic limits attributed to mole number variations. An increase in pressure on the feed side corresponds to a higher driving force for hydrogen permeation, resulting in greater removal of hydrogen from the reaction volume and thus greater conversion. Dense inorganic Pd-based membranes and ceramic membranes (such as silica and zeolite) can be used in hydrogen production, depending on the role of the membrane. Pd-based membranes exhibit perm-selective transport governed by a solution-diffusion mechanism. Their main advantage is their infinite selectivity toward H_2, allowing for a pure H_2 permeate stream in MRs without further downstream separation **[89]**.

However, the high cost is actually one of the main problems that limit their diffusion at an industrial level. Currently, several works are presenting new composite membranes consisting of a thin Pd-based layer deposited, with different techniques, on porous supports that can be ceramic or stainless steel. In this way, the Pd content is reduced as well as the related cost **[90]**. Another drawback is the inhibition or poisoning effects that some species such as carbon monoxide or sulfur can exert on the membrane, reducing the permeating flux.

Meso- and micro-porous membranes, such as alumina, silica, titania, zirconia, and zeolites, are not affected by poisoning and are more affordable than metallic membranes. However, they have finite selectivity toward H_2, requiring further downstream separation to purify their permeate stream.

MRs can have various configurations. The most commonly used is the fixed-bed membrane reactor with a tube-in-tube configuration, where the membrane is the inner tube and the catalytic bed is packed in the annulus or core. An emerging technology is the fluidized-bed MR, where a typical configuration consists of a membrane immersed in a catalytic bed operated in a bubbling or turbulent regime **[91,92] (Figure 5)**. This configuration offers advantages such as higher catalyst effectiveness and enhanced mass and heat transfer rates compared to a packed bed MR, resulting in a more uniform temperature profile. However, maintaining the minimum fluidization velocity to keep the catalyst bed in suspension can impose limitations on space velocity and contact time conditions.

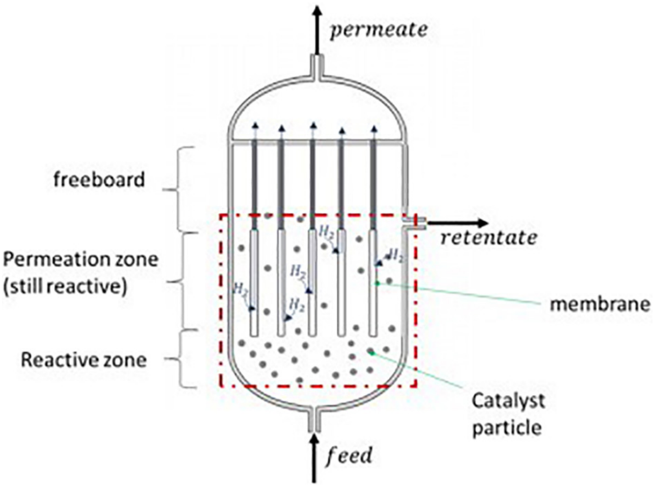


Figure 5: Schematic of a fixed-bed membrane reactor. Reprinted from **[93]**.

Membrane microreactors or micro membrane reactors are a recent evolution of MRs; they can be distinguished as microreactors reinforced by membrane separation/purification or membrane reactors miniaturized into a characteristic size of 1-1000 µm, which combine the advantages of both MRs and microreactors, leading to a greatly intensified operation unit **[94–96] (Figure 6)**. Micro-MRs including hydrogen separation function can be suitable for various applications such as hydrogen production from water gas shift reaction, methanol steam reforming reaction, on-board fuel processing for portable fuel cells, methanol dehydrogenation **[94,97,98]**.

3.2. Hydrogen from Light Hydrocarbons or Biomass: Traditional Process and Future Perspectives

Membrane reactors are today becoming an innovative solution for biomass conversion significantly improving the process, reducing the number of the units involved, enhancing the yield, and reducing the energetic load as well as the presence of auxiliary devices.

Currently, about 96% of hydrogen production comes from fossil fuels. In the coming years, the main challenge will be to increase the production of blue H_2, derived from biomass or bioprocesses. Identifying innovative technologies that are suitable for blue hydrogen production and can also improve traditional processes for better exploitation of fossil fuels, such as light hydrocarbons, is an important step toward developing intensified processes.

Steam reforming and coal gasification are the most important and commonly used processes for hydrogen production. Steam reforming is an endothermic, catalytic process carried out at temperatures between 700-900°C using a nickel-based catalyst. Hydrogen production from coal is typically carried out at 30 bars and 800-900°C with steam, producing gaseous products such as CO, CO_2, H_2, and a small amount of methane. When feed pressure is increased to 60 bars, methane becomes the major product. The syngas stream exiting these reaction stages is usually upgraded in another reaction stage, consisting of a water gas shift reaction to reduce CO content and increase H_2 yield. This reaction is conventionally carried out in two fixed-bed adiabatic reactors connected in series, followed by a separation unit to recover hydrogen from the rest of the gaseous stream. Today, membrane reactors are considered a valid alternative to these conventional processes [2,99–101]. As aforementioned, the presence of a hydrogen-selective membrane allows a hydrogen-rich (or pure, depending on the type of membrane used) stream to be recovered, not requiring a further separation [2]. For the WGS reaction, Barbieri and coworkers [2,9,88,102–113] demonstrated that a single MR operating in the high-temperature range can obtain better performance than the traditional process in a wide range of operating conditions, implying a reduction of two reactions and one purification stage in only one unit. The CO conversion achieved in the MR was greater than that achievable by the entire traditional process and the reaction volume required by MR was always lower than the one of the whole traditional process [97–103,114]. Using an MR directly in the steam reforming of light hydrocarbons can result in better performance, higher conversions, higher yields, and recovery of a pure/rich hydrogen stream compared to using a conventional reactor. Process intensification, with reduced reaction volumes, higher conversion, and milder operating temperatures, can translate into lower energy consumption, reduced plant footprint, enhanced exploitation of raw materials, and fewer reaction/separation/purification units. In other words, an intensified process.

Promising results obtained at the laboratory scale have encouraged some larger-scale applications. Table 2 summarizes some of the most important industrial patents related to this application in recent years [107,115]. For example, MRT Inc. [116] has developed a proven technology based on a patented fluidized-bed MR for high-purity hydrogen production. The process combines hydrocarbon reforming, shift conversion, and hydrogen purification in a single step. Shell Oil Company [117] has patented a process and apparatus for producing pure hydrogen by steam reforming. This process integrates steam reforming and shift reactions to produce pure hydrogen with minimal CO production and virtually no CO in the hydrogen stream. It also provides for CO$_2$ capture by sequestration, uses a steam reforming MR, and is powered by heat from a heater convection section.

Various prototypes were developed also in the framework of various EU-funded projects. As an example, in the framework of the DEMCAMER project (GA 262840) [118], a fixed-bed membrane reactor with 33 Pd-based membranes of 22-23 cm long (OD 10 mm – ID 7 mm) was designed and built for producing 5 Nm^3/h (grade 3.0) of pure hydrogen in a water gas shift membrane reactor (Figure 7).

Hydrogen production from biomass involves various unit operations for conversion, clean-up, compression, upgrading, and purification of the hydrogen-containing stream. Replacing traditional reactors with membrane reactors can significantly reduce the number of stages required for conversion and/or separation (Figure 8). This reduction in the number of units and system complexity could lead to the development of decentralized systems for hydrogen production, including on-site production for hydrogen fueling stations for fuel-cell vehicles or direct links to fuel cells for home-based energy production [2]. Synergistically combining different energy sources, such as fossil or renewable fuels, and solar or wind energy, along with the improvement and/or development of new fuel conversion technologies, will enable optimal exploitation of these sources to produce hydrogen in a renewable way (Figure 9).

Table 2: Most relevant pilot scale membrane reactor patents or installations all around the world. Reprinted from [115] with the publisher's permission.

Company	Country	H$_2$ produced	H$_2$ purity [%]	Reformer details	T [°C]	Catalytic process	Ref.
Power & Energy Inc.	USA	160 Nm^3/h	97 - 99.9999999	Radial Micro Channel membrane reactor	-	Methane steam reforming	[119]
Pall Co.	USA	47 Nm^3/h	> 99	Composite Pd-based membrane reactor	600	Natural gas steam reforming	[120]
MRT Ltd.	Canada	15-50 Nm^3/h	> 99.999	Membrane reactor's HydRecTM	450	Natural gas/renewable steam reforming	[116]
Shell Oil Company	USA	Up to 1500 40 Nm^3/h	High purity	Metal membrane reactor	450-550	Natural gas steam reforming	[117]
Tokyo Gas Company Ltd.	Japan	≥ 40 Nm^3/h	> 99.99	Composite Pd-based membrane reactor	495-540	Natural gas steam reforming	[121]
KT—Kinetics Technology S.p.A	Italy	20 Nm^3/h	99.9	Pd, Pd-Ag membrane reactors	500-650	Natural gas steam reforming	[122]
Linde-Engineering (Linde Group)	Germany	100 - 400000 Nm^3/h	99.9999	-	600-650	Natural gas steam reforming	[123]
REB Research & Consulting Co.	USA	0.018 Nm^3/h	> 99.9999	Micro membrane reactor	200-700	Methane, Methanol, Ethanol steam reforming & Ammonia cracking	[124]

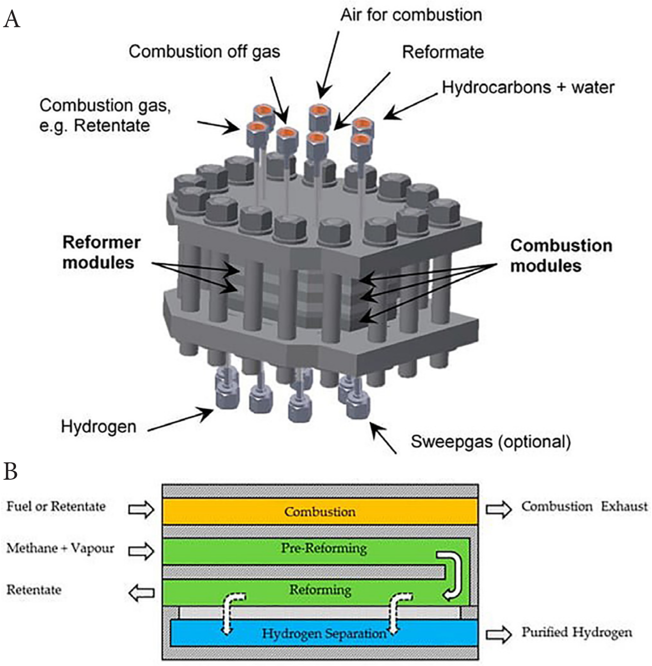


Figure 6: (A) Schematic representation of the modular membrane reactor system with reformer and combustion modules, with inlets and outlets for reaction gases; (B) rough scheme of the combination of the three functionalities (combustion for heat supply, reforming and hydrogen separation) of a fully integrated methane steam reformer in one module. Reprinted from [114].

Figure 7: Picture of the prototype reactor for the WGS process where the placement of the WGS-MR is highlighted. Reprinted from [118].

4. Membrane Bioreactors

4.1. Membrane Bioreactors Fundamentals

In MBR, the membrane can act as a separation unit, or it can have the dual role of the catalytic and separation unit, as it can also be the site where the reaction takes place [125]. In the latter case, the biocatalyst is immobilized within the membrane pores and the resulting reactor is called a biocatalytic membrane reactor (BMR). Depending on the membrane material and the final application, different biocatalyst immobilization methods can be used, which are summarized in Figure 10.

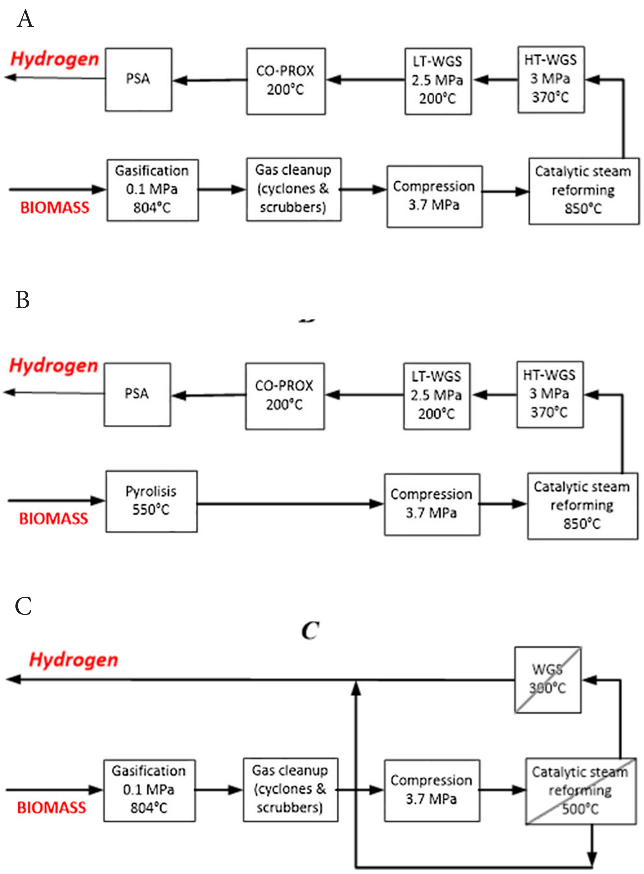


Figure 8: Scheme of plants for hydrogen production from biomass feedstock (A) conventional biomass gasification and (B) conventional biomass pyrolysis. (C) Innovative plant integrated by membrane reactors. Reprinted from [2] with permission from the publisher.

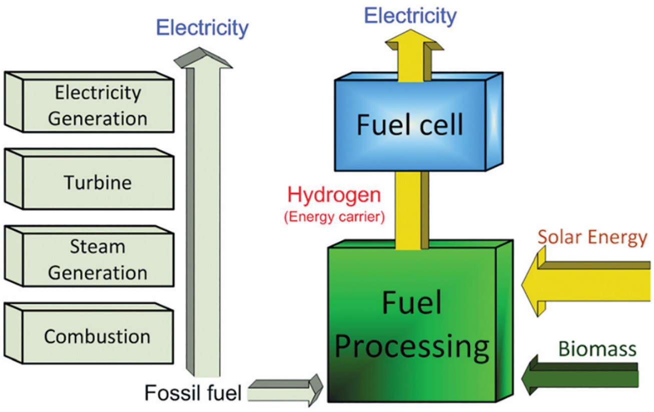


Figure 9: Scheme of a new vision of fuel conversion: a fuel processing unit integrated with PEMFC for producing electricity. Reprinted from [2] with permission from the publisher.

Biomolecule immobilization can be random, which is generally used for membrane reactor development, or site-specific, which is mostly used for the production of biosensors. To solve problems related to enzyme recovery and membrane regeneration, the integration of nanoparticles as immobilization support for the biomolecules and membrane process is increasingly applied **(Figure 10)**. The NPs used can be organic [126] or inorganic, and in the latter case, iron NPs are more frequently used because they can be easily recovered by applying an external magnetic field [127].

Based on the position of the membrane in the reactor, it is also possible to distinguish between side-stream or submerged configurations **(Figure 11)**, the latter being most commonly used for water treatment which is more suitable for fouling control. In both systems, the biocatalyst can be free or immobilized and the strategy for feed supply and product recovery can be either continuous and/or intermittent.

The different compartments created by the membrane allow the development of heterogeneous (organic/water) / multiphasic (liquid/gas) reaction systems [128,129], in which the biocatalytic membrane has the additional task of keeping the different phases in contact and/or dispersing them. In these systems, the phases can be separated by the membrane, as in the case of membrane-based solvent extraction processes, or dispersed in each other, as in membrane emulsification processes [130] **(Figure 12)**.

4.2. Application of MBR/BMR at Industrial Level

In recent years, MBR technology has attracted exponential interest from the scientific community as well as municipal and industrial wastewater treatment industries due to its advantages over conventional methods, such as smaller footprint, high effluent quality, lower sludge production, low energy consumption, complete separation of hydraulic retention time (HRT) and solids retention time (STR), easy scale-up, etc. The significant increase in the number of both large (≥ 10,000 m^3/d) and super-large scale (≥ 100,000 m^3/d) water treatment plants worldwide is further evidence of the increasing application of this technology, which began with the first plant in China (Beijing Wenyu River plant) with a capacity of 100 m^3/d and continues to grow there (more than 200 plants) and around the world [131]. The Henriksdal wastewater treatment plant in Stockholm [132] is one of the largest in the world (250,000 m^3/d) and it currently serves approximately one million people. In 2040 it will have a treatment capacity of 864,000 m^3/d thanks to an upgrade [132,133].

The following paragraphs focus primarily on the use of MBR and BMRs that employ enzymes as catalysts, with an emphasis on their application in non-conventional sectors (e.g. pharmaceutical, food, etc.), as a promising strategy to promote process intensification. In the aforementioned sectors, such as food, pharmaceutical, and biofuel production, there is a plethora of studies on the use of this technology [134–136], but the industrial applications are rare **(Table 5)** and not at the same level as water treatment, as they are not driven by the growing scarcity of water and increasingly stringent norms about the development of green processes. The main problems are related to the trade-off between enzyme loading and specific activity, the use of enzyme covalent immobilization that does not allow enzyme replacement, the need for membrane cleaning with aggressive substances that deactivate the enzyme, and the low biomolecule stability [137].

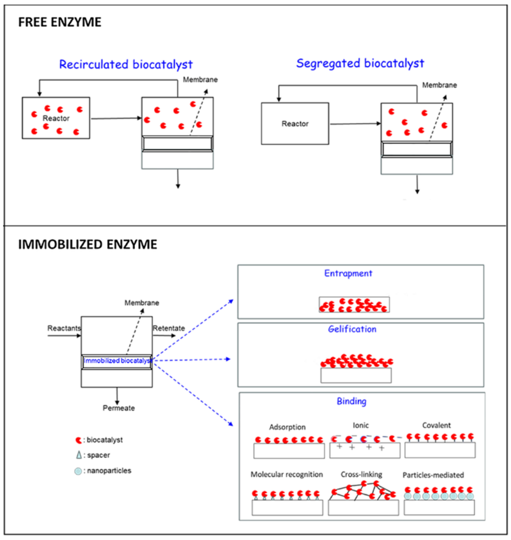


Figure 10: MBR configurations with free and immobilized biocatalyst and immobilization techniques.

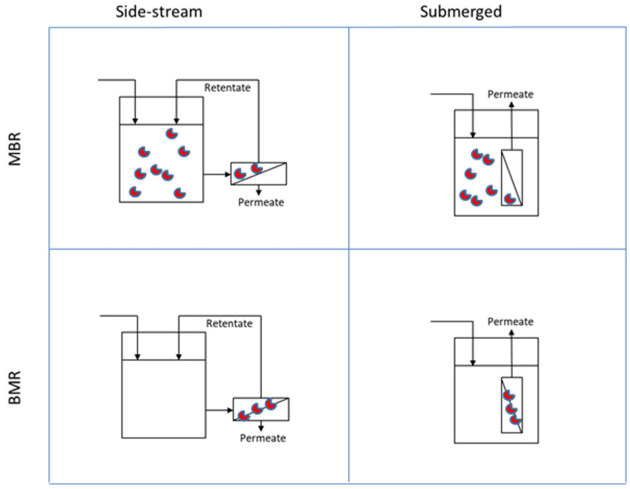


Figure 11: Schematic representation of MBRs in side-stream and submerged configuration.

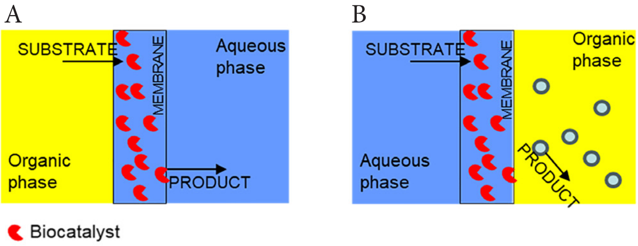


Figure 12: Schematic representation of MBRs conjugated with: (A) membrane-based solvent extraction; (B) membrane emulsification process to permit catalysis and product extraction.

4.3. Innovative Strategies to Overcome Main Limits

In recent years, several interesting solutions have been proposed, which seem very promising to overcome the limitations related to enzyme reuse and membrane regeneration.

Advances in *in situ* characterization of the immobilized enzyme have made it possible to optimize its distribution within membrane pores to avoid excessive accumulation on the membrane and resulting steric hindrance. An innovative technique for *in situ* detection of membrane-immobilized enzymes was developed by the ITM-CNR research group **[136,137]** and integrates membrane-based enzyme immunolocalization with SEM and TEM. Specifically, after enzymatic membrane immobilization, biocatalytic membranes were thinly sliced and hybridized with specific labeled antibodies that were easily detected using TEM and SEM. This allowed the enzyme spatial visualization after the immobilization and the possibility to optimize its distribution.

Membranes used for enzyme immobilization are not specifically designed for this purpose but are generally modified by various techniques to create functional groups that can bind enzymes. The goal of this modification is to introduce functional groups on the membrane surface and in the membrane pores without affecting the properties of the membrane and thus the transport through it. Surface modification of membranes can be done in several ways: grafting, etching, and coating **[138]**.

An innovative approach is to combine multiple materials, integrating materials with different properties at different geometrical scales. In this strategy, the advantages of one support can be combined with those of another to develop hybrid membranes that have high chemical resistance (required for wet chemistry and covalent binding of enzyme) and high affinity for enzyme attachment ensuring easy reuse of enzymes **[139]**.

Within this strategy, the conjugations of magnetic nanoparticles to immobilize enzymes and membrane is a very innovative system. It consists of immobilizing enzymes on nanoparticles (pectinase **[138]** xylanase **[140]**, phosphodiesterase **[141]**), dispersed on the membrane surface by an external magnetic field, leading to the formation of a biocatalytic hybrid membrane.

This approach allows the biomolecule to be recovered as needed and the membrane to be regenerated at the end of the process. The strategy is also particularly useful for membrane fouling in continuous reaction processes, as it allows selective catalyst removal for cyclic membrane cleaning or backflushing, without affecting enzyme activity. An increasing and promising trend is also the combination of MBR with other membrane processes, which allows pretreatment of the effluent but may also allow control of the enzymatic reaction and membrane fouling in separated steps **[127,142]**. The use of extremophilic enzymes resistant to harsh conditions (e.g. high temperature, high pressure, etc.) is another strategy to increase the stability of the biocatalyst and the conversion once immobilized. One example is the immobilization of the thermostable phosphotriesterase from *S. solfataricus* on different polymeric membranes **[130,143]**, which allowed to increase in the stability of the immobilized enzyme to more than ten months compared to the free enzyme.

4.4. MBR Applications in Non-conventional Sectors

Since the use of MBR in water treatment has been described in many reviews **[138,144,145]** this part will mainly focus on enzyme membrane reactors and their use in non-conventional sectors. The analysis of a patent survey on the applications of MBRs **[145]** shows that the sectors most interested in their use are: food **[134]** and pharmaceutical **[146,147]**, although also biofuel sector is growing exponentially, as recently reviewed by Mazzei *et al*. **[137]**.

In the food sector, the main applications of MBR **(Table 3)** are: 1) in milk and whey treatment to produce milk for intolerant or allergic people; 2) in fruit juice production to decrease stream viscosity and mitigate membrane fouling; 3) in starch hydrolysis to produce sugars syrup, cyclodextrins and functional oligosaccharides, and 4) in oil treatment 5) in wine production and 6) in beer making **(Table 3)** to improve the production process and quality of the final product.

Table 3: MBRs and BMRs application fields, configurations, and biocatalysts used in the food sector.

Application field	Aim	Biocatalyst	Main MBR configuration	Ref.
Milk and whey treatment	- Production of milk with low-lactose content - Protein hydrolysis for allergic people - Production of diet milk	- Lactase - Pepsin - Lipase	FB in MBR	**[137,148–152]**
Fruit juice production	- Decrease the high viscosity given by pectin and mitigate fouling - Galacturonic acid production (food additive)	Pectinase	- FB in MBR - BMR	**[153–155]**
Starch hydrolysis	- Production of cyclodextrin - Production of oligosaccarides	- Amylase - Pullulanase - Transferase	- FB in MBR - BMR	**[156,157]**
Oil treatment	- Production of high-added value lipids compounds, diet food, cheap butter substitutes	Lipase	-BMR and MBR in multiphase systems	**[158,159]**
Wine making	- Must fermentation - Aroma enhancement	Yeasts	Fermentation with FB in MBR	**[160–163]**
Beer making	- Production of "green beer"	Yeasts	Fermentation with FB in MBR	**[164]**

FB: free biocatalyst

The most common configuration is with a free biocatalyst integrated with the membrane separation step, and the most commonly used membranes are polymeric since extreme pH and temperature are not used to maintain food quality, for which ceramic membranes are generally preferred. In Fruit juice production, although both MBR configurations are used, the biocatalyst status is more often immobilized to limit fouling by pectin on the membrane surface.

Some examples of MBRs and BMRs in the food sector are also on an industrial scale. One of the first was developed by Centrale del Latte (Milan Italy) and Snamprogetti S.p.a. (Italy) for the production of low-lactose milk using immobilized lactase in polymeric membranes, which could produce 10 tons per day **[165]**. The same team developed another BMR with immobilized b-galactosidase to produce galactooligosaccharides (nutraceuticals) from the wasted lactose **[166]**. The system was capable of producing about 9.0 tons of food additives per day.

Another industrial-scale example in the food sector is the system developed by Mitsubishi to produce a low-calorie sweetener (precursor of aspartame) **[167]**. In this system, a bacterium (*Brevibacterium flavium*) was used free in the reactor, while UF membranes were used to compartmentalize the biocatalyst and to separate the product. Other examples of industrial use of MBR can be found in the pharmaceutical sector, where the main objective is the production of **(Table 4)**, vitamins, antibiotics, anti-inflammatory drugs, intermediates for drug synthesis, and functional aminoacids. **Table 5** lists some characteristics of the above systems. In the system developed by Degussa AG, acylases from various sources were used to produce L-aminoacids (180-240 tons per year) in combination with a 0.5-square meter hollow fiber polyamide membrane (10 kDa). The same system was also used on a technical scale with various enzymes (fumarase, aspartase, etc.) to produce proteinogenic and non-proteinogenic amino acids. In another system commercialized by Degussa AG, two different enzymes (formate dehydrogenase and leucine dehydrogenase) were used simultaneously along with two co-factors, retained by the membrane. It produced 200 tons of L-leucine per year, which passed though the membrane with CO_2 and could be easily separated from the reaction mixture without further purification.

A BMR for industrial production of the intermediate diltiazem (a coronary vasodilator and calcium channel blocker) was developed by Tanabe Seyaku and Sepracor Inc (USA). The system was a multiphasic system in which the membrane was biocatalytic and also had the role of keeping in contact with the organic phase in which the substrate was present and the aqueous phase in which the product was extracted. The enzyme was immobilized by entrapment on PAN hollow fiber membranes (1440 m^2) and was able to produce 75 tons of drug per year.

Table 4: MBRs and BMRs application fields, configurations, and biocatalysts used in the pharmaceutical sector.

Products	Biocatalyst	Main MBR configuration	Ref.
Vitamins	Nitrilase/ amylase	FB in MBR	**[168]**
Antibiotics	Acylase (e.g. penicillin G)	FB in MBR	**[169,170]**
Anti-inflammatory drugs	Lipase	BMR in multiphase systems	**[171]**
Intermediates for the synthesis of drugs	Lipase Dehydrogenase	-BMR in multiphase systems - FB in MBR	**[172]**
Production of functional aminoacids L-aminoacids	Acylase, Dehydrogenase, Lipase, transferase	-BMR in multiphase systems - FB in MBR	**[173]**

Other examples of MBRs are on a small scale, such as those used to produce rhinovirus protease inhibitors, ACE inhibitors, and drugs to prevent osteoporosis. In these systems, there is no need to increase productivity because it is strictly related to a specific market requirement. Compared to the chemical industry, the productivity is extremely low, but the advantages resulting from higher selectivity and higher enantiomeric excess, make MBR technology a preferred system compared to conventional production processes.

4.5. Challenges and Future Perspectives on the Use of MBR and BMR in Non-conventional Sectors

Despite the potential of these technologies in all the sectors studied in terms of process intensification, sustainability, and bio-based approach compatible with the development of an environmentally friendly process, much remains to be done to implement the systems on an industrial scale, as has already been observed with MBR in water treatment. The major drawbacks that have hindered the development of MBR and BMR at the industrial scale in the food, pharmaceutical, and biofuel sectors are the low stability of the enzymes and membrane fouling. To solve these issues, new insights into enzyme immobilization, development of new membrane materials, and reactor technology must considered.

- Innovative strategies, some of which have been described in previous sections, seem to be very promising in addressing the main technology drawbacks and could be very interesting if thoroughly researched, such as the design of multiple support materials with different properties at a geometrical scale, could improve membrane chemical resistance and compatibility with enzymes during immobilization (e.g. the conjugation of biofunctionalized magnetic nanoparticles coupled with membrane processes to selectively remove the biocatalyst when needed.

- The use of extremophile enzyme to be immobilized on membranes, which due to the increased tolerance to high temperature can improve enzyme activity/stability as well as productivity.

- The introduction of integrated membrane processes, before the enzyme membrane reactor, to decrease membrane fouling and remove denaturing agents for the immobilized enzymes.
- The introduction of *in situ* characterization techniques on immobilized enzymes, to improve their distribution on membrane surface and then the conversion.
- The development of new enzyme immobilization techniques on membranes, based on nature simulation by enzyme compartmentalization.

The simple application of the above strategies will be possible if a continuous integration between membrane science, genetic engineering, and chemical engineering is considered simultaneously.

5. Membrane Distillation

5.1. Membrane Distillation for the Treatment of Desalination Brines

Water is a key element for daily life and is becoming a major concern for many countries worldwide. In fact, while the available sources of fresh water are limited, water consumption is rapidly increasing due to both the continuous population growth and the high number of industrial activities. Moreover, the climate change experienced in the last decades, further aggravated the scenario, causing drought in new areas and thus contributing to the fresh water sources depletion. One of the adopted solutions to face the problem of water scarcity is to desalinate seawater. Actually, desalination plants are mainly based on the use of reverse osmosis (RO) membranes which are able to be selectively permeated by the fresh water while retaining salts. However, being the driving force obtained by pressurizing the seawater (in order to overcome the osmotic pressure), RO is limited to water recovery factors up to 50%. This means that RO produces also another stream, called brine, in which salts are concentrated and which has to be treated/disposed of somehow. The common practice was to re-inject the brine into the sea or into deep wells or to discharge it into sewage and/or to locate it in evaporation ponds **(Figure 13)**. These methods led, in time, to serious impacts on the environment and new approaches are today needed for making desalination plants more sustainable **[174,175]**.

A possible option could be to use MD to treat the produced brine. MD employs microporous and hydrophobic membranes, often in polypropylene (PP), polyvinylidene fluoride (PVDF), or polytetrafluoroethylene (PTFE). **Table 6** summarizes the main features of membranes used in MD. MD is typically applied to purify aqueous feeds, like wastewater coming from industry or water contaminated by heavy metals **[176–192]**.

The hot feed (typical temperatures are in the range of 40°C - 80°C) is kept in contact with one side of the membrane without pressurizing it. The hydrophobicity of the membrane material prevents the passage of the liquid through the micropores while water vapor and volatiles can permeate them thanks to a difference of vapor pressure created at the two membrane sides. All non-volatiles are kept in the feed side. Depending on how the driving force is established, different MD configurations can be obtained, like Direct Contact Membrane Distillation (DCMD), Air Gap Membrane Distillation (AGMD), Vacuum Membrane Distillation (VMD), and Sweep Gas Membrane Distillation (SGMD). In **Table 7**, the sketches of the MD configurations, together with their main characteristics, are reported. Since MD is based on a difference of vapor pressure as a driving force, osmotic limitations are not present in the process, and high-concentrated feeds, like the brine produced by RO, can efficiently be treated. In this way, the RO brine becomes a source of additional fresh water. Moreover, its volume can significantly be reduced, thus a lower amount of brine has to be managed after the process **(Figure 14)**.

Table 5: Examples of MBR and BMR technology in the pharmaceutical industry.

Reactor	Biocatalyst	Application	Company	Space-time yield g/L day	Tons per year	Ref.
MBR	acylase	L- aminoacids production	Degussa AG	-	180-240	**[193]**
	dehydrogenase	L- aminoacids production	Degussa AG	42.5	200	**[194]**
	lipase	(S)- 3-acetylthioisobutyrate production	DMS-Adeno, Tanabe		> 100	**[195]**
	dehydrogenase	rhinovirus protease inhibitor	Pfizer	560	-	**[196]**
	Recombinant *E.coli*	L- aminoacids production	Degussa AG and research center Juelich	19.2	-	**[197]**
BMR	lipase	Production of diltiazem intermediate (coronary vasodilator and calcium channel blocker	Sepracor Tanabe Seyaku (Mitsubishi Tanabe Pharma Corporation)	125*	75	**[198]**
	lipase	Production of drugs for osteoporosis prevention	Novo Nordisk	-	-	**[199]**
	transferase	Metabolite for potassium channel	Pfizer	-	-	**[200]**

*g/m^{2}day

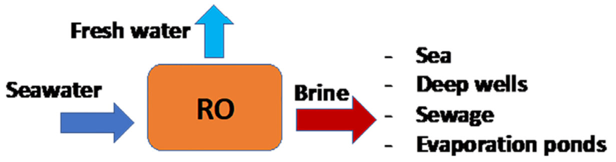


Figure 13: Traditional methods for handling the brine produced in desalination plants.

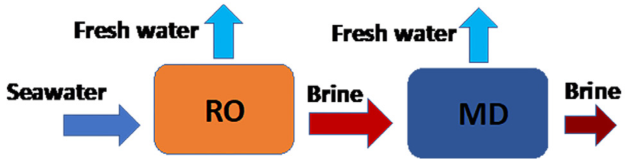


Figure 14: The coupling of RO with MD.

If compared with the traditional RO unit, the integrated RO–MD units lead to important improvements in the overall performance in terms of water recovery factor, quality of the produced water, and brine reduction, the only weak point being the higher energy consumption due to the thermal demand of MD. Nevertheless, typical operating temperatures in MD can be reached by using waste heat or renewable energies, with a consequent reduction of the associated energy consumption. In **Figure 15**, the performance of RO is compared to that of an integrated RO-MD system for two case studies, starting from a seawater concentration of 39 g/L **[201,202]**. In one case, the DCMD configuration was chosen, while in the other case the VMD configuration was applied. Whatever the MD configuration, a significant reduction of the produced brine (80%), together with a 2-fold increase of the fresh water production was obtained. It is worthy to mention that MD can also be applied to approach the Zero Liquid Discharge (ZLD) goal, by pushing the water removal from the RO brine up to its oversaturation. In this way, salt crystals can nucleate, grow and can be recovered as valuable products **(Figure 16)**. The MD unit working under these conditions is called Membrane Crystallizer (MCr) **[203–205]**.

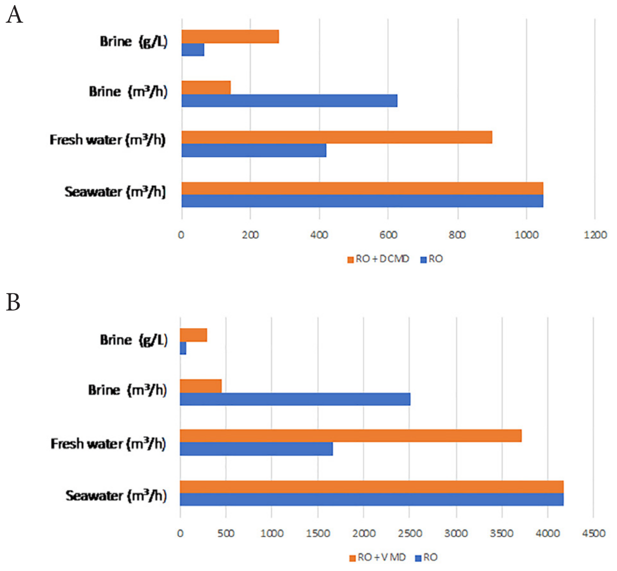


Figure 15: Comparison of the performance on single and integrated RO units. (A) RO vs RO + DCMD. (B) RO vs RO + VMD. The data in the figure are from **[201]** and **[202]**.

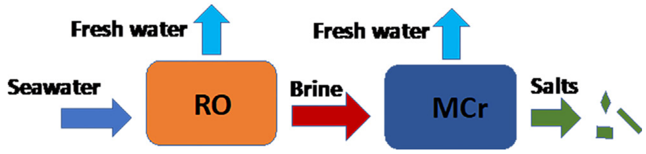


Figure 16: The coupling of RO with MCr.

Table 6: Main features of membranes used in MD.

Membrane	Microporous and hydrophobic
Contact angle	90° - 140°
Pore size	0.1 - 0.5 µm
Porosity	70 - 80%
Thickness	60 - 200 µm

5.2. Future Research and Perspectives on MD Applications

MD is a promising operation for the increase of the freshwater recovery factor and the sustainable management of brine in desalination plants. Nevertheless, its implementation at a large scale is still dependent on a series of issues to be solved/improved, like the need for membranes stable in time, the increase of the trans-membrane flux, and the reduction of thermal energy consumption. Membranes in MD must keep their hydrophobic character in long-term runs in the presence of high salt concentrations. The low fouling tendency must also be ensured for an efficient performance. Different research activities are in progress, like the development of superhydrophobic membranes obtained by appropriate surface treatments, the preparation of hydrophilic-hydrophobic membranes to reduce the heat and mass transfer resistances, thus increasing the flux, the use of electrospinning to obtain membranes with more open structure and the development of novel membranes with localized heating **[206–213]**. In particular, the tuning of membrane surface properties, such as roughness, surface charge, pore size, and surface functional groups is under study. The presence of nanoparticles/specific coatings on the surface able to be heated by solar light or by electrical heating is another type of membrane surface modification in progress, to enhance the temperature at the liquid-membrane interface, thus reducing the temperature polarization and increasing the flux. New module designs are also studied to reduce both heat and mass transport resistances, as well as fouling, by acting on the fluid dynamic and the direction of the hot stream in a way that limits the impact on the pressure drops inside the modules **[214–217]**. The issue of thermal energy consumption is being addressed by realizing MD modules with internal heat recovery, where the heat of condensation is used to pre-heat the feed, and by coupling MD units to solar panels or by using geothermal energy **[218–222]**. The integration of different MD configurations **[223,224]** is also another possible solution under investigation. In this respect, preliminary studies focused on the coupling of a DCMD unit with an AGMD one to heat the retentate and with a VMD unit to increase the permeate production. **Figure 17** summarizes the main research activities in progress to improve the MD performance.

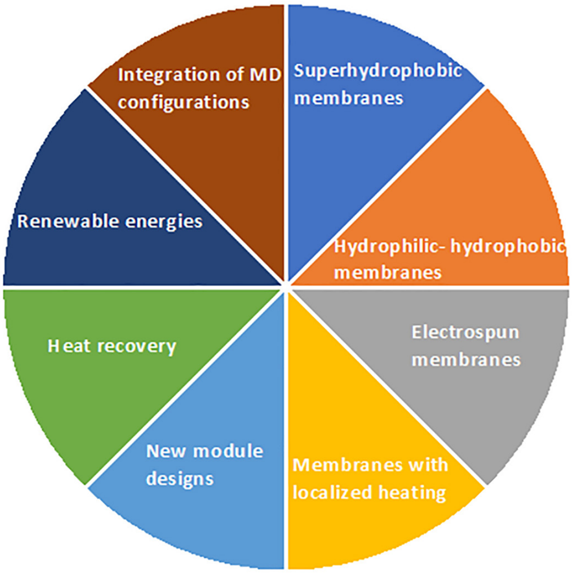
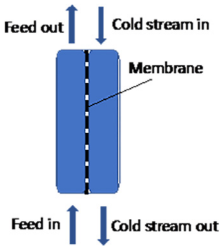
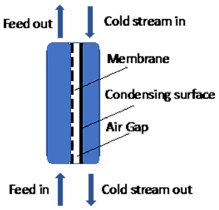
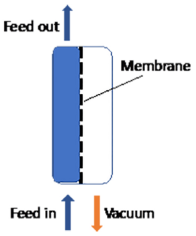
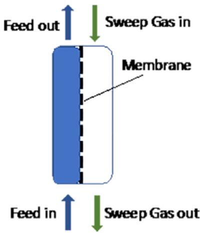


Figure 17: Main research activities in progress.

6. Conclusions and Outlook

Based on the overall trend toward Green Chemistry metrics, the future of membrane engineering will be dependent on the use of intensified processes, pursuing a redesign of traditional processes as more compact and efficient. Furthermore, the new materials for membrane manufacturing pose a challenge at different levels of the industry. The implementation of green solvents, as well as biopolymers, in the preparation of the membranes, is a strategy for producing immediate results of sustainable development and will have an obvious impact on the processing industries. Greener alternatives are being used for their excellent chemical stability, non-flammability, and for their physical properties, such as complete solubility in water, high boiling point, and low molecular weight. This option will positively affect human health through uncomplicated and safe handling compared to conventional solvents. This study not only provides a useful reference for the preparation of membranes using new greener solvents and polymeric materials but also ideas for new trends in membrane reactors, (bio-) reactors, and MD application. Membrane operations will respond to these needs, and will further expand their application in the coming years.

Table 7 : Main MD configurations.

Configuration	Scheme	Main characteristics
DCMD		A colder aqueous stream is sent at the permeate side. Condensation inside the module in the permeate stream. Heat loss by conduction. No heat recovery inside the module.
AGMD		Condensation inside the module on a condensing surface. Additional resistance is offered by the air gap. Heat recovery inside the module by using the feed also as a cold stream.
VMD		Vacuum applied at the permeate side. High fluxes and high risk of membrane wetting. Condensation outside the module. No heat recovery inside the module.
SGMD		Sweep gas sent at the permeate side. Condensation outside the module. No heat recovery inside the module.

Authors' Contributions

F.R.: investigation, data curation, some conceptualization, and writing (original draft preparation); **R.M.:** investigation, data curation, some conceptualization, and writing (original draft preparation and review); **A.B.:** investigation, data curation, some conceptualization and writing (original draft preparation and review); **A.C.:** investigation, data curation, some conceptualization and writing (original draft preparation, review and editing); **A.F.:** conceptualization, investigation, supervision, data curation, and writing (review and editing).

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Conflicts of Interest

The authors declare no conflicts of interest.

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References

[1] Muralidhara HS. Challenges of membrane technology in the XXI century. In: Cui ZF, Muralidhara HS, editors. Membrane Technology, Elsevier; 2010, p. 19–32.

[2] Drioli E, Brunetti A, Di Profio G, Barbieri G. Process intensification strategies and membrane engineering. Green Chemistry 2012;14:1561–72. https://doi.org/10.1039/c2gc16668b.

[3] Membranes market global forecast to 2024. MarketsandMarkets n.d. https://www.marketsandmarkets.com/Market-Reports/membranes-market-1176.html (accessed June 8, 2022).

[4] Russo F, Tiecco M, Galiano F, Mancuso R, Gabriele B, Figoli A. Launching deep eutectic solvents (DESs) and natural deep eutectic solvents (NADESs), in combination with different harmless co-solvents, for the preparation of more sustainable membranes. Journal of Membrane Science 2022;649:120387. https://doi.org/10.1016/j.memsci.2022.120387.

[5] Russo F, Marino T, Galiano F, Gzara L, Gordano A, Organji H, *et al*. Tamisolve® NXG as an alternative non-toxic solvent for the preparation of porous Poly (vinylidene fluoride) membranes. Polymers 2021;13:2579. https://doi.org/10.3390/polym13152579.

[6] Dong X, Lu D, Harris TAL, Escobar IC. Polymers and solvents used in membrane fabrication: a review focusing on sustainable membrane development. Membranes (Basel) 2021;11:309. https://doi.org/10.3390/membranes11050309.

[7] Iulianelli A, Russo F, Galiano F, Desiderio G, Basile A, Figoli A. PLA Easy Fil – White-based membranes for CO2 separation. Greenhouse Gases: Science and Technology 2019;9:360–9. https://doi.org/10.1002/ghg.1853.

[8] Wang HH, Jung JT, Kim JF, Kim S, Drioli E, Lee YM. A novel green solvent alternative for polymeric membrane preparation via nonsolvent-induced phase separation (NIPS). Journal of Membrane Science 2019;574:44–54. https://doi.org/10.1016/j.memsci.2018.12.051.

[9] Brunetti A, Drioli E, Barbieri G. Energy and mass intensities in hydrogen upgrading by a membrane reactor. Fuel Processing Technology 2014;118:278–86. https://doi.org/10.1016/j.fuproc.2013.09.009.

[10] Giorno L, Mazzei R, Drioli E. Biological membranes and biomimetic artificial membranes. Comprehensive Membrane Science and Engineering 2010:1–12. https://doi.org/10.1016/b978-0-08-093250-7.00055-4.

[11] EU Commission proposes REACH restriction on uses of DMF n.d. https://product.enhesa.com/162874/eu-commission-pro.

[12] ECHA. Registry of restriction intentions until outcome n.d. https://echa.europa.eu/registry-of-restriction-intentions/-/dislist/details/0b0236e18244cd73 (accessed January 18, 2024).

[13] Russo F, Galiano F, Pedace F, Aricò F, Figoli A. Dimethyl isosorbide as a green solvent for sustainable ultrafiltration and microfiltration membrane preparation. ACS Sustainable Chemistry & Engineering 2019;8:659–68. https://doi.org/10.1021/acssuschemeng.9b06496.

[14] Ursino C, Russo F, Ferrari RM, De Santo MP, Di Nicolò E, He T, *et al*. Polyethersulfone hollow fiber membranes prepared with Polarclean® as a more sustainable solvent. Journal of Membrane Science 2020;608:118216. https://doi.org/10.1016/j.memsci.2020.118216.

[15] IARC. IARC Monographs on the Identification of Carcinogenic Hazards to Humans Questions and Answers 2019. https://monographs.iarc.who.int (accessed December 27, 2021).

[16] Nelson WM. Green Solvents for Chemistry: Perspectives and Practice. Oxford University Press; 2003.

[17] Wypych A, Wypych G. Databook of green solvents. Toronto: ChemTec Publishing; 2014.

[18] Takkellapati S, Li T, Gonzalez MA. An overview of biorefinery derived platform chemicals from a cellulose and hemicellulose biorefinery. Clean Technol Environ Policy 2018;20:1615–30. https://doi.org/10.1007/s10098-018-1568-5.

[19] Clark JH, Hunt A, Topi C, Paggiola G, Sherwood J. Sustainable Solvents: Perspectives from Research, Business and International Policy. The Royal Society of Chemistry; 2017. https://doi.org/10.1039/9781782624035.

[20] Zou D, Jeon SM, Kim HW, Bae JY, Lee YM. In-situ grown inorganic layer coated PVDF/PSF composite hollow fiber membranes with enhanced separation performance. Journal of Membrane Science 2021;637:119632. https://doi.org/10.1016/j.memsci.2021.119632.

[21] Marino T, Russo F, Criscuoli A, Figoli A. TamiSolve® NxG as novel solvent for polymeric membrane preparation. Journal of Membrane Science 2017;542:418–29. https://doi.org/10.1016/j.memsci.2017.08.038.

[22] Saïdi S, Macedonio F, Russo F, Hannachi C, Hamrouni B, Drioli E, *et al*. Preparation and characterization of hydrophobic P(VDF-HFP) flat sheet membranes using Tamisolve® NxG solvent for the treatment of saline water by direct contact membrane distillation and membrane crystallization. Separation and Purification Technology 2021;275:119144. https://doi.org/10.1016/j.seppur.2021.119144.

[23] Verheijen M, Lienhard M, Schrooders Y, Clayton O, Nudischer R, Boerno S, *et al*. DMSO induces drastic changes in human cellular processes and epigenetic landscape in vitro. Sci Rep 2019;9:4641–4641. https://doi.org/10.1038/s41598-019-40660-0.

[24] Evenepoel N, Wen S, Tilahun Tsehaye M, Van der Bruggen B. Potential of DMSO as greener solvent for PES ultra- and nanofiltration membrane preparation. Journal of Applied Polymer Science 2018;135. https://doi.org/10.1002/app.46494.

[25] Wang B, Ji J, Chen C, Li K. Porous membranes prepared by a combined crystallisation and diffusion (CCD) method: Study on formation mechanisms. Journal of Membrane Science 2018;548:136–48. https://doi.org/10.1016/j.memsci.2017.11.005.

[26] Russo F, Ursino C, Avruscio E, Desiderio G, Perrone A, Santoro S, *et al*. Innovative Poly (vinylidene fluoride) (PVDF) electrospun nanofiber membrane preparation using DMSO as a low toxicity solvent. Membranes (Basel) 2020;10:36. https://doi.org/10.3390/membranes10030036.

[27] Marino T, Galiano F, Simone S, Figoli A. DMSO EVOL™ as novel non-toxic solvent for polyethersulfone membrane preparation. Environmental Science and Pollution Research 2018;26:14774–85. https://doi.org/10.1007/s11356-018-3575-9.

[28] Marino T, Galiano F, Molino A, Figoli A. New frontiers in sustainable membrane preparation: Cyrene™ as green bioderived solvent. Journal of Membrane Science 2019;580:224–34. https://doi.org/10.1016/j.memsci.2019.03.034.

[29] Marino T, Blefari S, Di Nicolò E, Figoli A. A more sustainable membrane preparation using triethyl phosphate as solvent. Green Processing and Synthesis 2017;6:295–300. https://doi.org/10.1515/gps-2016-0165.

[30] Nejati S, Boo C, Osuji CO, Elimelech M. Engineering flat sheet microporous PVDF films for membrane distillation. Journal of Membrane Science 2015;492:355–63. https://doi.org/10.1016/j.memsci.2015.05.033.

[31] Chang H-H, Chang L-K, Yang C-D, Lin D-J, Cheng L-P. Effect of solvent on the dipole rotation of poly(vinylidene fluoride) during porous membrane formation by precipitation in alcohol baths. Polymer 2017;115:164–75. https://doi.org/10.1016/j.polymer.2017.03.044.

[32] Tao M, Liu F, Ma B, Xue L. Effect of solvent power on PVDF membrane polymorphism during phase inversion. Desalination 2013;316:137–45. https://doi.org/10.1016/j.desal.2013.02.005.

[33] Abed MRM, Kumbharkar SC, Groth AM, Li K. Ultrafiltration PVDF hollow fibre membranes with interconnected bicontinuous structures produced via a single-step phase inversion technique. Journal of Membrane Science 2012;407–408:145–54. https://doi.org/10.1016/j.memsci.2012.03.029.

[34] Marino T, Russo F, Figoli A. The formation of polyvinylidene fluoride membranes with tailored properties via vapour/non-solvent induced phase separation. Membranes (Basel) 2018;8:71. https://doi.org/10.3390/membranes8030071.

[35] Chang J, Zuo J, Zhang L, O'Brien GS, Chung T-S. Using green solvent, triethyl phosphate (TEP), to fabricate highly porous PVDF hollow fiber membranes for membrane distillation. Journal of Membrane Science 2017;539:295–304. https://doi.org/10.1016/j.memsci.2017.06.002.

[36] Rajabzadeh S, Maruyama T, Sotani T, Matsuyama H. Preparation of PVDF hollow fiber membrane from a ternary polymer/solvent/nonsolvent system via thermally induced phase separation (TIPS) method. Separation and Purification Technology 2008;63:415–23. https://doi.org/10.1016/j.seppur.2008.05.027.

[37] Cui Z, Hassankiadeh NT, Lee SY, Woo KT, Lee JM, Sanguineti A, *et al*. Tailoring novel fibrillar morphologies in poly(vinylidene fluoride) membranes using a low toxic triethylene glycol diacetate (TEGDA) diluent. Journal of Membrane Science 2015;473:128–36. https://doi.org/10.1016/j.memsci.2014.09.019.

[38] Marino T, Blasi E, Tornaghi S, Di Nicolò E, Figoli A. Polyethersulfone membranes prepared with Rhodiasolv®Polarclean as water soluble green solvent. Journal of Membrane Science 2018;549:192–204. https://doi.org/10.1016/j.memsci.2017.12.007.

[39] Russo F, Ursino C, Sayinli B, Koyuncu I, Galiano F, Figoli A. Advancements in sustainable PVDF copolymer membrane preparation using Rhodiasolv® polarclean as an alternative eco-friendly solvent. Clean Technologies 2021;3:761–86. https://doi.org/10.3390/cleantechnol3040045.

[40] Jung JT, Wang HH, Kim JF, Lee J, Kim JS, Drioli E, *et al*. Tailoring nonsolvent-thermally induced phase separation (N-TIPS) effect using triple spinneret to fabricate high performance PVDF hollow fiber membranes. Journal of Membrane Science 2018;559:117–26. https://doi.org/10.1016/j.memsci.2018.04.054.

[41] Hassankiadeh NT, Cui Z, Kim JH, Shin DW, Lee SY, Sanguineti A, *et al*. Microporous poly(vinylidene fluoride) hollow fiber membranes fabricated with PolarClean as water-soluble green diluent and additives. Journal of Membrane Science 2015;479:204–12. https://doi.org/10.1016/j.memsci.2015.01.031.

[42] Cui Z, Cheng Y, Xu K, Yue J, Zhou Y, Li X, *et al*. Wide liquid-liquid phase separation region enhancing tensile strength of poly(vinylidene fluoride) membranes via TIPS method with a new diluent. Polymer 2018;141:46–53. https://doi.org/10.1016/j.polymer.2018.02.054.

[43] Su Y, Chen C, Li Y, Li J. PVDF membrane formation via thermally induced phase separation. Journal of Macromolecular Science, Part A 2007;44:99–104. https://doi.org/10.1080/10601320601044575.

[44] Rasool MA, Vankelecom IFJ. Use of γ-valerolactone and glycerol derivatives as bio-based renewable solvents for membrane preparation. Green Chemistry 2019;21:1054–64. https://doi.org/10.1039/c8gc03652g.

[45] Sherwood J, De bruyn M, Constantinou A, Moity L, McElroy CR, Farmer TJ, *et al*. Dihydrolevoglucosenone (Cyrene) as a bio-based alternative for dipolar aprotic solvents. Chem Commun 2014;50:9650–2. https://doi.org/10.1039/c4cc04133j.

[46] Sadeghi I, Aroujalian A, Raisi A, Dabir B, Fathizadeh M. Surface modification of polyethersulfone ultrafiltration membranes by corona air plasma for separation of oil/water emulsions. Journal of Membrane Science 2013;430:24–36. https://doi.org/10.1016/j.memsci.2012.11.051.

[47] Sun W, Chen C, Li J, Lin Y. Ultrafiltration membrane formation of PES-C, PES and Ppesk polymers with different solvents. Chinese Journal of Polymer Science 2009;27:165. https://doi.org/10.1142/s0256767909003790.

[48] Tsehaye MT, Wang J, Zhu J, Velizarov S, Van der Bruggen B. Development and characterization of polyethersulfone-based nanofiltration membrane with stability to hydrogen peroxide. Journal of Membrane Science 2018;550:462–9. https://doi.org/10.1016/j.memsci.2018.01.022.

[49] Thuyavan YL, Anantharaman N, Arthanareeswaran G, Ismail AF. Impact of solvents and process conditions on the formation of polyethersulfone membranes and its fouling behavior in lake water filtration. Journal of Chemical Technology & Biotechnology 2016;91:2568–81. https://doi.org/10.1002/jctb.4846.

[50] Arthanareeswaran G, Starov VM. Effect of solvents on performance of polyethersulfone ultrafiltration membranes: Investigation of metal ion separations. Desalination 2011;267:57–63. https://doi.org/10.1016/j.desal.2010.09.006.

[51] Wang Q, Wang Z, Wu Z. Effects of solvent compositions on physicochemical properties and anti-fouling ability of PVDF microfiltration membranes for wastewater treatment. Desalination 2012;297:79–86. https://doi.org/10.1016/j.desal.2012.04.020.

[52] Kim D, Salazar OR, Nunes SP. Membrane manufacture for peptide separation. Green Chemistry 2016;18:5151–9. https://doi.org/10.1039/c6gc01259k.

[53] Kim D, Vovusha H, Schwingenschlögl U, Nunes SP. Polyethersulfone flat sheet and hollow fiber membranes from solutions in ionic liquids. Journal of Membrane Science 2017;539:161–71. https://doi.org/10.1016/j.memsci.2017.06.001.

[54] Lakshmi DS, Cundari T, Furia E, Tagarelli A, Fiorani G, Carraro M, *et al*. Preparation of polymeric membranes and microcapsules using an ionic liquid as morphology control additive. Macromolecular Symposia 2015;357:159–67. https://doi.org/10.1002/masy.201400214.

[55] Xie W, Li T, Tiraferri A, Drioli E, Figoli A, Crittenden JC, *et al.* Toward the next generation of sustainable membranes from green chemistry principles. ACS Sustainable Chemistry & Engineering 2020;9:50–75. https://doi.org/10.1021/acssuschemeng.0c07119.

[56] Shih HC, Yeh YS, Yasuda H. Morphology of microporous poly(vinylidene fluoride) membranes studied by gas permeation and scanning electron microscopy. Journal of Membrane Science 1990;50:299–317. https://doi.org/10.1016/s0376-7388(00)80627-4.

[57] Zhao J, Chong JY, Shi L, Wang R. Explorations of combined nonsolvent and thermally induced phase separation (N-TIPS) method for fabricating novel PVDF hollow fiber membranes using mixed diluents. Journal of Membrane Science 2019;572:210–22. https://doi.org/10.1016/j.memsci.2018.11.015.

[58] Zou D, Nunes SP, Vankelecom IFJ, Figoli A, Lee YM. Recent advances in polymer membranes employing non-toxic solvents and materials. Green Chemistry 2021;23:9815–43. https://doi.org/10.1039/d1gc03318b.

[59] Tocci E, Rizzuto C, Macedonio F, Drioli E. Effect of green solvents in the production of PVDF-specific polymorphs. Industrial & Engineering Chemistry Research 2020;59:5267–75. https://doi.org/10.1021/acs.iecr.9b06701.

[60] Jung JT, Kim JF, Wang HH, di Nicolo E, Drioli E, Lee YM. Understanding the non-solvent induced phase separation (NIPS) effect during the fabrication of microporous PVDF membranes via thermally induced phase separation (TIPS). Journal of Membrane Science 2016;514:250–63. https://doi.org/10.1016/j.memsci.2016.04.069.

[61] Russo F, Castro-Muñoz R, Galiano F, Figoli A. Unprecedented preparation of porous Matrimid® 5218 membranes. Journal of Membrane Science 2019;585:166–74. https://doi.org/10.1016/j.memsci.2019.05.036.

[62] Nguyen Thi HY, Nguyen BTD, Kim JF. Sustainable fabrication of organic solvent nanofiltration membranes. Membranes (Basel) 2020;11:19. https://doi.org/10.3390/membranes11010019.

[63] Clarke CJ, Tu W-C, Levers O, Bröhl A, Hallett JP. Green and sustainable solvents in chemical processes. Chemical Reviews 2018;118:747–800. https://doi.org/10.1021/acs.chemrev.7b00571.

[64] Alonso DM, Wettstein SG, Dumesic JA. Gamma-valerolactone, a sustainable platform molecule derived from lignocellulosic biomass. Green Chemistry 2013;15:584. https://doi.org/10.1039/c3gc37065h.

[65] Granatier M, Schlapp-Hackl I, Lê HQ, Nieminen K, Pitkänen L, Sixta H. Stability of gamma-valerolactone under pulping conditions as a basis for process optimization and chemical recovery. Cellulose 2021;28:11567–78. https://doi.org/10.1007/s10570-021-04243-5.

[66] Watanabe K. The toxicological assessment of cyclopentyl methyl ether (CPME) as a green solvent. Molecules 2013;18:3183–94. https://doi.org/10.3390/molecules18033183.

[67] Chuang W-Y, Young T-H, Chiu W-Y, Lin C-Y. The effect of polymeric additives on the structure and permeability of poly(vinyl alcohol) asymmetric membranes. Polymer 2000;41:5633–41. https://doi.org/10.1016/S0032-3861(99)00818-6.

[68] Aricò F, Aldoshin AS, Tundo P. One-pot preparation of dimethyl isosorbide from d-sorbitol via dimethyl carbonate chemistry. ChemSusChem 2016;10:53–7. https://doi.org/10.1002/cssc.201601382.

[69] Gronwald O, Weber M. AGNIQUE AMD 3L as green solvent for polyethersulfone ultrafiltration membrane preparation. Journal of Applied Polymer Science 2019;137. https://doi.org/10.1002/app.48419.

[70] Uebele S, Johann KS, Goetz T, Gronwald O, Ulbricht M, Schiestel T. Poly(ether sulfone) hollow fiber membranes prepared via nonsolvent-induced phase separation using the green solvent Agnique®AMD3 L. Journal of Applied Polymer Science 2021;138. https://doi.org/10.1002/app.50935.

[71] Rasool MA, Van Goethem C, Vankelecom IFJ. Green preparation process using methyl lactate for cellulose-acetate-based nanofiltration membranes. Separation and Purification Technology 2020;232:115903. https://doi.org/10.1016/j.seppur.2019.115903.

[72] Rasool MA, Pescarmona PP, Vankelecom IFJ. Applicability of organic carbonates as green solvents for membrane preparation. ACS Sustainable Chemistry & Engineering 2019;7:13774–85. https://doi.org/10.1021/acssuschemeng.9b01507.

[73] Galiano F, Briceño K, Marino T, Molino A, Christensen KV, Figoli A. Advances in biopolymer-based membrane preparation and applications. Journal of Membrane Science 2018;564:562–86. https://doi.org/10.1016/j.memsci.2018.07.059.

[74] Russo F, Galiano F, Iulianelli A, Basile A, Figoli A. Biopolymers for sustainable membranes in CO2 separation: a review. Fuel Processing Technology 2021;213:106643. https://doi.org/10.1016/j.fuproc.2020.106643.

[75] Burger C, Hsiao BS, Chu B. Nanofibrous materials and their applications. Annual Review of Materials Research 2006;36:333–68. https://doi.org/10.1146/annurev.matsci.36.011205.123537.

[76] Silva SS, Rodrigues LC, Fernandes EM, Reis RL. Fundamentals on biopolymers and global demand. Biopolymer Membranes and Films 2020:3–34. https://doi.org/10.1016/b978-0-12-818134-8.00001-8.

[77] Sanmugam A, Vikraman D, Karuppasamy K, Lee JY, Kim H-S. Evaluation of the corrosion resistance properties of electroplated chitosan-zn(1-x)cu(x)o composite thin films. Nanomaterials (Basel) 2017;7:432. https://doi.org/10.3390/nano7120432.

[78] Pervez MN, Stylios GK. An experimental approach to the synthesis and optimisation of a 'green' nanofibre. Nanomaterials (Basel) 2018;8:383. https://doi.org/10.3390/nano8060383.

[79] Wang X, Chen X, Yoon K, Fang D, Hsiao BS, Chu B. High flux filtration medium based on nanofibrous substrate with hydrophilic nanocomposite coating. Environmental Science & Technology 2005;39:7684–91. https://doi.org/10.1021/es050512j.

[80] Braunegg G, Lefebvre G, Genser KF. Polyhydroxyalkanoates, biopolyesters from renewable resources: Physiological and engineering aspects. Journal of Biotechnology 1998;65:127–61. https://doi.org/10.1016/s0168-1656(98)00126-6.

[81] Nofar M, Sacligil D, Carreau PJ, Kamal MR, Heuzey M-C. Poly (lactic acid) blends: Processing, properties and applications. International Journal of Biological Macromolecules 2019;125:307–60. https://doi.org/10.1016/j.ijbiomac.2018.12.002.

[82] Jamian WNR, Hasbullah H, Mohamed F, Salleha WNW, Norazana I, Ali RR. Biodegradable Gas Separation Membrane Preparation by Manipulation of Casting Parameters. Chemical Engineering Transactions 2015;43:1105–10. https://doi.org/10.3303/CET1543185.

[83] Galiano F, Ghanim AH, Rashid KT, Marino T, Simone S, Alsalhy QF, *et al*. Preparation and characterization of green polylactic acid (PLA) membranes for organic/organic separation by pervaporation. Clean Technologies and Environmental Policy 2018;21:109–20. https://doi.org/10.1007/s10098-018-1621-4.

[84] Iulianelli A, Russo F, Galiano F, Manisco M, Figoli A. Novel bio-polymer based membranes for CO2/CH4 separation. International Journal of Greenhouse Gas Control 2022;117:103657. https://doi.org/10.1016/j.ijggc.2022.103657.

[85] Goh PS, Othman MHD, Matsuura T. Waste reutilization in polymeric membrane fabrication: a new direction in membranes for separation. Membranes (Basel) 2021;11:782. https://doi.org/10.3390/membranes11100782.

[86] Adamczak M, Kamińska G, Bohdziewicz J. Application of waste polymers as basic material for ultrafiltration membranes preparation. Water 2020;12:179. https://doi.org/10.3390/w12010179.

[87] Drioli E, Giuseppe B, Brunetti A, editors. Membrane Engineering for the Treatment of Gases: Volume 1: Gas-separation Issues with Membranes. The Royal Society of Chemistry; 2017. https://doi.org/10.1039/9781788010436.

[88] Brunetti A, Caravella A, Fernandez E, Pacheco Tanaka DA, Gallucci F, Drioli E, *et al*. Syngas upgrading in a membrane reactor with thin Pd-alloy supported membrane. International Journal of Hydrogen Energy 2015;40:10883–93. https://doi.org/10.1016/j.ijhydene.2015.07.002.

[89] Brunetti A, Caravella A, Drioli E, Barbieri G. Membrane reactors for hydrogen production. In: Drioli E, Barbieri G, Brunetti A, editors. Membrane Engineering for the Treatment of Gases : Gas-separation Issues Combined with Membrane Reactors, The Royal Society of Chemistry; 2017, p. 1–29.

[90] Liguori S, Kian K, Buggy N, Anzelmo BH, Wilcox J. Opportunities and challenges of low-carbon hydrogen via metallic membranes. Progress in Energy and Combustion Science 2020;80:100851. https://doi.org/10.1016/j.pecs.2020.100851.

[91] Habib MA, Harale A, Paglieri S, Alrashed FS, Al-Sayoud A, Rao MV, *et al*. Palladium-alloy membrane reactors for fuel reforming and hydrogen production: a review. Energy & Fuels 2021;35:5558–93. https://doi.org/10.1021/acs.energyfuels.0c04352.

[92] Gallucci F, Fernandez E, Corengia P, van Sint Annaland M. Recent advances on membranes and membrane reactors for hydrogen production. Chemical Engineering Science 2013;92:40–66. https://doi.org/10.1016/j.ces.2013.01.008.

[93] Ongis M, Di Marcoberardino G, Manzolini G, Gallucci F, Binotti M. Membrane reactors for green hydrogen production from biogas and biomethane: A techno-economic assessment. International Journal of Hydrogen Energy 2023;48:19580–95. https://doi.org/10.1016/j.ijhydene.2023.01.310.

[94] Kolb G. Review: Microstructured reactors for distributed and renewable production of fuels and electrical energy. Chemical Engineering and Processing: Process Intensification 2013;65:1–44. https://doi.org/10.1016/j.cep.2012.10.015.

[95] Garcia G, Arriola E, Chen W-H, De Luna MD. A comprehensive review of hydrogen production from methanol thermochemical conversion for sustainability. Energy 2021;217:119384. https://doi.org/10.1016/j.energy.2020.119384.

[96] Tan X, Li K. Membrane microreactors for catalytic reactions. Journal of Chemical Technology & Biotechnology 2013;88:1771–9. https://doi.org/10.1002/jctb.4155.

[97] Dittmeyer R, Boeltken T, Piermartini P, Selinsek M, Loewert M, Dallmann F, *et al*. Micro and micro membrane reactors for advanced applications in chemical energy conversion. Current Opinion in Chemical Engineering 2017;17:108–25. https://doi.org/10.1016/j.coche.2017.08.001.

[98] Boeltken T, Wunsch A, Gietzelt T, Pfeifer P, Dittmeyer R. Ultra-compact microstructured methane steam reformer with integrated Palladium membrane for on-site production of pure hydrogen: Experimental demonstration. International Journal of Hydrogen Energy 2014;39:18058–68. https://doi.org/10.1016/j.ijhydene.2014.06.091.

[99] Qian JX, Chen TW, Enakonda LR, Liu DB, Basset J-M, Zhou L. Methane decomposition to pure hydrogen and carbon nano materials: State-of-the-art and future perspectives. International Journal of Hydrogen Energy 2020;45:15721–43. https://doi.org/10.1016/j.ijhydene.2020.04.100.

[100] Amiri TY, Ghasemzageh K, Iulianelli A. Membrane reactors for sustainable hydrogen production through steam reforming of hydrocarbons: A review. Chemical Engineering and Processing - Process Intensification 2020;157:108148. https://doi.org/10.1016/j.cep.2020.108148.

[101] Patrascu M, Sheintuch M. Design concepts of a scaled-down autothermal membrane reformer for on board hydrogen production. Chemical Engineering Journal 2015;282:123–36. https://doi.org/10.1016/j.cej.2015.02.031.

[102] Brunetti A, Barbieri G, Drioli E. Pd-based membrane reactor for syngas upgrading. Energy & Fuels 2009;23:5073–6. https://doi.org/10.1021/ef900382u.

[103] Barbieri G, Brunetti A, Caravella A, Drioli E. Pd-based membrane reactors for one-stage process of water gas shift. RSC Advances 2011;1:651. https://doi.org/10.1039/c1ra00375e.

[104] Brunetti A, Caravella A, Drioli E, Barbieri G. Process intensification by membrane reactors: high-temperature water gas shift reaction as single stage for syngas upgrading. Chemical Engineering & Technology 2012;35:1238–48. https://doi.org/10.1002/ceat.201100641.

[105] Zhao C, Caravella A, Xu H, Brunetti A, Barbieri G, Goldbach A. Support mass transfer resistance of Pd/ceramic composite membranes in the presence of sweep gas. Journal of Membrane Science 2018;550:365–76. https://doi.org/10.1016/j.memsci.2017.12.082.

[106] Barbieri G, Brunetti A, Tricoli G, Drioli E. An innovative configuration of a Pd-based membrane reactor for the production of pure hydrogen. Journal of Power Sources 2008;182:160–7. https://doi.org/10.1016/j.jpowsour.2008.03.086.

[107] Barbieri G, Brunetti A, Granato T, Bernardo P, Drioli E. Engineering evaluations of a catalytic membrane reactor for the water gas shift reaction. Industrial & Engineering Chemistry Research 2005;44:7676–83. https://doi.org/10.1021/ie050357h.

[108] Brunetti A, Barbieri G, Drioli E, Lee K-H, Sea B, Lee D-W. WGS reaction in a membrane reactor using a porous stainless steel supported silica membrane. Chemical Engineering and Processing: Process Intensification 2007;46:119–26. https://doi.org/10.1016/j.cep.2006.05.005.

[109] Brunetti A, Barbieri G, Drioli E, Granato T, Lee K-H. A porous stainless steel supported silica membrane for WGS reaction in a catalytic membrane reactor. Chemical Engineering Science 2007;62:5621–6. https://doi.org/10.1016/j.ces.2007.01.054.

[110] Brunetti A, Caravella A, Barbieri G, Drioli E. Simulation study of water gas shift reaction in a membrane reactor. Journal of Membrane Science 2007;306:329–40. https://doi.org/10.1016/j.memsci.2007.09.009.

[111] Brunetti A, Barbieri G, Drioli E. A PEMFC and H2 membrane purification integrated plant. Chemical Engineering and Processing: Process Intensification 2008;47:1081–9. https://doi.org/10.1016/j.cep.2007.03.015.

[112] Brunetti A, Barbieri G, Drioli E. Integrated membrane system for pure hydrogen production: A Pd–Ag membrane reactor and a PEMFC. Fuel Processing Technology 2011;92:166–74. https://doi.org/10.1016/j.fuproc.2010.09.023.

[113] Brunetti A, Drioli E, Barbieri G. Medium/high temperature water gas shift reaction in a Pd–Ag membrane reactor: an experimental investigation. RSC Adv 2012;2:226–33. https://doi.org/10.1039/c1ra00569c.

[114] Wunsch A, Kant P, Mohr M, Haas-Santo K, Pfeifer P, Dittmeyer R. Recent developments in compact membrane reactors with hydrogen separation. Membranes (Basel) 2018;8:107. https://doi.org/10.3390/membranes8040107.

[115] Iulianelli A, Drioli E. Membrane engineering: Latest advancements in gas separation and pre-treatment processes, petrochemical industry and refinery, and future perspectives in emerging applications. Fuel Processing Technology 2020;206:106464. https://doi.org/10.1016/j.fuproc.2020.106464.

[116] MRT. 2022. http://www.membranereactor.com.

[117] Miller DW, Zarker KE. Process for producing hydrogen. US3965253A, 1976.

[118] Gallucci F, Antonio Medrano J, Roses L, Brunetti A, Barbieri G, Viviente J. Process intensification via membrane reactors, the DEMCAMER project. Processes 2016;4:16. https://doi.org/10.3390/pr4020016.

[119] Power+Energy – Fueling the Hydrogen Economy – Fueling the Hydrogen Economy n.d. http://www.powerandenergy.com/ (accessed April 25, 2022).

[120] Pall Corporation | Filtration, Separation, Purification n.d. https://www.pall.com/ (accessed April 25, 2022).

[121] Tokyo Gas n.d. https://www.tokyo-gas.co.jp/index.html (accessed April 25, 2022).

[122] KT - Kinetics Technology n.d. https://www.kt-met.com/it (accessed April 25, 2022).

[123] Think Hydrogen. Think Linde. | Linde Engineering n.d. https://www.linde-engineering.com/en/index.html (accessed January 20, 2024).

[124] REB Research - Home n.d. http://www.rebresearch.com/ (accessed April 25, 2022).

[125] Giorno L, Gebreyohannes AY, Drioli E, Mazzei R. Biocatalytic membranes and membrane bioreactors. Comprehensive Membrane Science and Engineering 2017;3:55–71. https://doi.org/10.1016/b978-0-12-409547-2.12234-6.

[126] Vitola G, Büning D, Schumacher J, Mazzei R, Giorno L, Ulbricht M. Development of a novel immobilization method by using microgels to keep enzyme in hydrated microenvironment in porous hydrophobic membranes. Macromolecular Bioscience 2016;17. https://doi.org/10.1002/mabi.201600381.

[127] Gebreyohannes AY, Mazzei R, Marei Abdelrahim MY, Vitola G, Porzio E, Manco G, *et al*. Phosphotriesterase-magnetic nanoparticle bioconjugates with improved enzyme activity in a biocatalytic membrane reactor. Bioconjugate Chemistry 2018;29:2001–8. https://doi.org/10.1021/acs.bioconjchem.8b00214.

[128] Vitola G, Mazzei R, Poerio T, Barbieri G, Fontananova E, Büning D, *et al*. Influence of lipase immobilization mode on ethyl acetate hydrolysis in a continuous solid–gas biocatalytic membrane reactor. Bioconjugate Chemistry 2019;30:2238–46. https://doi.org/10.1021/acs.bioconjchem.9b00463.

[129] Ranieri G, Mazzei R, Wu Z, Li K, Giorno L. Use of a ceramic membrane to improve the performance of two-separate-phase biocatalytic membrane reactor. Molecules 2016;21:345–345. https://doi.org/10.3390/molecules21030345.

[130] Mazzei R, Piacentini E, Nardi M, Poerio T, Bazzarelli F, Procopio A, *et al*. Production of plant-derived oleuropein aglycone by a combined membrane process and evaluation of its breast anticancer properties. Front Bioeng Biotechnol 2020;8:908–908. https://doi.org/10.3389/fbioe.2020.00908.

[131] Largest MBR plants worldwide. The MBR Site 2018. https://www.thembrsite.com/largest-mbr-plants/largest-membrane-bioreactor-plants-worldwide/ (accessed June 3, 2022).

[132] Henriksdal Wastewater Treatment Plant, Stockholm - Water Technology n.d. https://www.water-technology.net/projects/henriksdal-wastewater-treatment-plant-stockholm (accessed April 30, 2022).

[133] Judd SJ. The status of industrial and municipal effluent treatment with membrane bioreactor technology. Chemical Engineering Journal 2016;305:37–45. https://doi.org/10.1016/j.cej.2015.08.141.

[134] Mazzei R, Piacentini E, Gebreyohannes AY, Giorno L. Membrane bioreactors in food, pharmaceutical and biofuel applications: state of the art, progresses and perspectives. Current Organic Chemistry 2017;21. https://doi.org/10.2174/1385272821666170306113448.

[135] Xiao K, Liang S, Wang X, Chen C, Huang X. Current state and challenges of full-scale membrane bioreactor applications: A critical review. Bioresource Technology 2019;271:473–81. https://doi.org/10.1016/j.biortech.2018.09.061.

[136] Giorno L, Mazzei R, Piacentini E, Drioli E. Food applications of membrane bioreactors. Engineering Aspects of Membrane Separation and Application in Food Processing. 1st Edition, CRC Press; 2017, p. 299–360.

[137] Mazzei R, Yihdego Gebreyohannes A, Papaioannou E, Nunes SP, Vankelecom IFJ, Giorno L. Enzyme catalysis coupled with artificial membranes towards process intensification in biorefinery- a review. Bioresource Technology 2021;335:125248. https://doi.org/10.1016/j.biortech.2021.125248.

[138] Vitola G, Mazzei R, Fontananova E, Porzio E, Manco G, Gaeta SN, *et al*. Polymeric biocatalytic membranes with immobilized thermostable phosphotriesterase. Journal of Membrane Science 2016;516:144–51. https://doi.org/10.1016/j.memsci.2016.06.020.

[139] Yuan Y, Shen J, Salmon S. Developing enzyme immobilization with fibrous membranes: longevity and characterization considerations. Membranes (Basel) 2023;13:532. https://doi.org/10.3390/membranes13050532.

[140] Gebreyohannes AY, Mazzei R, Poerio T, Aimar P, Vankelecom IFJ, Giorno L. Pectinases immobilization on magnetic nanoparticles and their anti-fouling performance in a biocatalytic membrane reactor. RSC Advances 2016;6:98737–47. https://doi.org/10.1039/c6ra20455d.

[141] Acosta-Fernández R, Poerio T, Nabarlatz D, Giorno L, Mazzei R. Enzymatic hydrolysis of xylan from coffee parchment in membrane bioreactors. Industrial & Engineering Chemistry Research 2020;59:7346–54. https://doi.org/10.1021/acs.iecr.9b06429.

[142] Conidi C, Mazzei R, Cassano A, Giorno L. Integrated membrane system for the production of phytotherapics from olive mill wastewaters. Journal of Membrane Science 2014;454:322–9. https://doi.org/10.1016/j.memsci.2013.12.021.

[143] Vitola G, Mazzei R, Poerio T, Porzio E, Manco G, Perrotta I, *et al*. Biocatalytic membrane reactor development for organophosphates degradation. Journal of Hazardous Materials 2019;365:789–95. https://doi.org/10.1016/j.jhazmat.2018.11.063.

[144] Chang H-M, Chen S-S, Hsiao S-S, Chang W-S, Chien I-C, Duong CC, *et al*. Water reclamation and microbial community investigation: Treatment of tetramethylammonium hydroxide wastewater through an anaerobic osmotic membrane bioreactor hybrid system. Journal of Hazardous Materials 2022;427:128200. https://doi.org/10.1016/j.jhazmat.2021.128200.

[145] Pervez MdN, Balakrishnan M, Hasan SW, Choo K-H, Zhao Y, Cai Y, *et al*. A critical review on nanomaterials membrane bioreactor (NMs-MBR) for wastewater treatment. Npj Clean Water 2020;3. https://doi.org/10.1038/s41545-020-00090-2.

[146] Giorno L, Mazzei R, Drioli E. Biochemical membrane reactors in industrial processes. Membrane Operations 2009:397–409. https://doi.org/10.1002/9783527626779.ch17.

[147] Piacentini E, Mazzei R, Giorno L. Membrane bioreactors for pharmaceutical applications: optically pure enantiomers production. Current Pharmaceutical Design 2017;23:250–62. https://doi.org/10.2174/1381612823666161123143512.

[148] Splechtna B, Petzelbauer I, Kuhn B, Kulbe KD, Nidetzky B. Hydrolysis of lactose by β-glycosidase Celb from hyperthermophilic archaeon *Pyrococcus furiosus*. Applied Biochemistry and Biotechnology 2002;98–100:473–88. https://doi.org/10.1385/abab:98-100:1-9:473.

[149] Novalin S, Neuhaus W, Kulbe KD. A new innovative process to produce lactose-reduced skim milk. Journal of Biotechnology 2005;119:212–8. https://doi.org/10.1016/j.jbiotec.2005.03.018.

[150] Splechtna B, Nguyen T-H, Haltrich D. Comparison between discontinuous and continuous lactose conversion processes for the production of prebiotic galacto-oligosaccharides using β-galactosidase from *Lactobacillus reuteri*. Journal of Agricultural and Food Chemistry 2007;55:6772–7. https://doi.org/10.1021/jf070643z.

[151] Sen D, Sarkar A, Gosling A, Gras SL, Stevens GW, Kentish SE, *et al*. Feasibility study of enzyme immobilization on polymeric membrane: A case study with enzymatically galacto-oligosaccharides production from lactose. Journal of Membrane Science 2011;378:471–8. https://doi.org/10.1016/j.memsci.2011.05.032.

[152] Regenhardt SA, Mammarella EJ, Rubiolo AC. Hydrolysis of lactose from cheese whey using a reactor with β-galactosidase enzyme immobilised on a commercial UF membrane. Chemical and Process Engineering 2013;34:375–85. https://doi.org/10.2478/cpe-2013-0030.

[153] Patidar MK, Nighojkar S, Kumar A, Nighojkar A. Pectinolytic enzymes-solid state fermentation, assay methods and applications in fruit juice industries: a review. 3 Biotech 2018;8:199–199. https://doi.org/10.1007/s13205-018-1220-4.

[154] Bélafi-Bakó K, Eszterle M, Kiss K, Nemestóthy N, Gubicza L. Hydrolysis of pectin by Aspergillus niger polygalacturonase in a membrane bioreactor. Journal of Food Engineering 2007;78:438–42. https://doi.org/10.1016/j.jfoodeng.2005.10.012.

[155] Belafi-Bako K, Nemestothy N. The role of biocatalysis and membrane techniques in processing high-pectin content food stuffs and wastes. Food Biosynthesis 2017:277–92. https://doi.org/10.1016/b978-0-12-811372-1.00009-9.

[156] Sarbatly R, England R. Critical review of membrane bioreactor system used for continuous production of hydrolyzed starch. Chemical and Biochemical Engineering Quarterly 2004;18.

[157] Słomińska L, Szostek A, Grześkowiak A. Studies on enzymatic continuous production of cyclodextrins in an ultrafiltration membrane bioreactor. Carbohydrate Polymers 2002;50:423–8. https://doi.org/10.1016/s0144-8617(02)00060-7.

[158] Shen X, Lu L, Gao B, Xu X, Yue Q. Development of combined coagulation-hydrolysis acidification-dynamic membrane bioreactor system for treatment of oilfield polymer-flooding wastewater. Frontiers of Environmental Science & Engineering 2018;13. https://doi.org/10.1007/s11783-019-1093-8.

[159] Possebom G, Nyari NL, Zeni J, Steffens J, Rigo E, Di Luccio M. Esterification of fatty acids by Penicillium crustosum lipase in a membrane reactor. Journal of the Science of Food and Agriculture 2014;94:2905–11. https://doi.org/10.1002/jsfa.6630.

[160] Takaya M, Matsumoto N, Yanase H. Characterization of membrane bioreactor for dry wine production. Journal of Bioscience and Bioengineering 2002;93:240–4. https://doi.org/10.1016/s1389-1723(02)80021-4.

[161] Lovitt R, Jung I, Jones M. The performance of a membrane bioreactor for the malolactic fermentation of media containing ethanol. Desalination 2006;199:435–7. https://doi.org/10.1016/j.desal.2006.03.203.

[162] Gallifuoco A, Alfani F, Cantarella M, Spagna G, Pifferi PG. Immobilized β-glucosidase for the winemaking industry: study of biocatalyst operational stability in laboratory-scale continuous reactors. Process Biochemistry 1999;35:179–85. https://doi.org/10.1016/s0032-9592(99)00049-7.

[163] Gao C, Fleet GH. Cell-recycle membrane bioreactor for conducting continuous malolactic fermentation. Australian Journal of Grape and Wine Research 1995;1:32–8. https://doi.org/10.1111/j.1755-0238.1995.tb00075.x.

[164] Lipnizki F, Dupuy A. Food Industry Applications. Encyclopedia of Membrane Science and Technology 2013:1–23. https://doi.org/10.1002/9781118522318.emst126.

[165] Pastore M, Morisi F. Lactose reduction of milk by fiber-entrapped β-galactosidase. Pilot-plant experiments. Methods in Enzymology 1976:822–30. https://doi.org/10.1016/s0076-6879(76)44059-4.

[166] Yamagata H, Terasawa M, Yukawa H. A novel industrial process for l-aspartic acid production using an ultrafiltration-membrane. Catalysis Today 1994;22:621–7. https://doi.org/10.1016/0920-5861(94)80127-4.

[167] Rastall R. Novel enzyme technology for food applications 2007. https://doi.org/10.1533/9781845693718.

[168] Malandra A, Cantarella M, Kaplan O, Vejvoda V, Uhnáková B, Štěpánková B, *et al*. Continuous hydrolysis of 4-cyanopyridine by nitrilases from Fusarium solani O1 and Aspergillus niger K10. Applied Microbiology and Biotechnology 2009;85:277–84. https://doi.org/10.1007/s00253-009-2073-x.

[169] Travascio P, Zito E, De Maio A, Schroën CGPH, Durante D, De Luca P, *et al*. Advantages of using non-isothermal bioreactors for the enzymatic synthesis of antibiotics: The penicillin G acylase as enzyme model. Biotechnology and Bioengineering 2002;79:334–46. https://doi.org/10.1002/bit.10303.

[170] Přibyl M, Chmelíková R, Hasal P, Marek M. Penicillin G hydrolysis in an electro-membrane reactor with immobilized penicillin G acylase. Enzyme and Microbial Technology 2003;33:793–801. https://doi.org/10.1016/s0141-0229(03)00243-6.

[171] McConville FX, Lopez JL, Wald SA. Enzymatic resolution of ibuprofen in a multiphase membrane reactor. Biocatalysis 1990:167–77. https://doi.org/10.1007/978-94-010-9124-4_8.

[172] Liese A, Kragl U, Kierkels H, Schulze B. Membrane reactor development for the kinetic resolution of ethyl 2-hydroxy-4-phenylbutyrate. Enzyme and Microbial Technology 2002;30:673–81. https://doi.org/10.1016/s0141-0229(02)00027-3.

[173] Lyagin E, Drews A, Bhattacharya S, Kraume M. Membrane Reactor System for Parallel Continuous Screening and Characterisation of Biocatalysts. Chemical Engineering Transactions 2012;27:319–24. https://doi.org/10.3303/CET1227054.

[174] Panagopoulos A, Haralambous K-J, Loizidou M. Desalination brine disposal methods and treatment technologies - A review. Science of The Total Environment 2019;693:133545. https://doi.org/10.1016/j.scitotenv.2019.07.351.

[175] Lattemann S, Höpner T. Environmental impact and impact assessment of seawater desalination. Desalination 2008;220:1–15. https://doi.org/10.1016/j.desal.2007.03.009.

[176] Carnevale MC, Gnisci E, Hilal J, Criscuoli A. Direct contact and vacuum membrane distillation application for the olive mill wastewater treatment. Separation and Purification Technology 2016;169:121–7. https://doi.org/10.1016/j.seppur.2016.06.002.

[177] El-Abbassi A, Hafidi A, Khayet M, García-Payo MC. Integrated direct contact membrane distillation for olive mill wastewater treatment. Desalination 2013;323:31–8. https://doi.org/10.1016/j.desal.2012.06.014.

[178] Boubakri A, Bouguecha SA-T, Dhaouadi I, Hafiane A. Effect of operating parameters on boron removal from seawater using membrane distillation process. Desalination 2015;373:86–93. https://doi.org/10.1016/j.desal.2015.06.025.

[179] Tavakkoli S, Lokare O, Vidic R, Khanna V. Shale gas produced water management using membrane distillation: An optimization-based approach. Resources, Conservation and Recycling 2020;158:104803. https://doi.org/10.1016/j.resconrec.2020.104803.

[180] Criscuoli A, Bafaro P, Drioli E. Vacuum membrane distillation for purifying waters containing arsenic. Desalination 2013;323:17–21. https://doi.org/10.1016/j.desal.2012.08.004.

[181] Dao TD, Laborie S, Cabassud C. Direct As(III) removal from brackish groundwater by vacuum membrane distillation: Effect of organic matter and salts on membrane fouling. Separation and Purification Technology 2016;157:35–44. https://doi.org/10.1016/j.seppur.2015.11.018.

[182] Liu C, Martin A. Applying Membrane Distillation in High-Purity Water Production for Semiconductor Industry. Ultrapure Water: The Definitive Journal of High-Purity Water 2006;April.

[183] Woldemariam D, Kullab A, Khan EU, Martin A. Recovery of ethanol from scrubber-water by district heat-driven membrane distillation: Industrial-scale technoeconomic study. Renewable Energy 2018;128:484–94. https://doi.org/10.1016/j.renene.2017.06.009.

[184] Zarebska A, Nieto DR, Christensen KV, Norddahl B. Ammonia recovery from agricultural wastes by membrane distillation: Fouling characterization and mechanism. Water Research 2014;56:1–10. https://doi.org/10.1016/j.watres.2014.02.037.

[185] Criscuoli A, Capuano A, Andreucci M, Drioli E. Low-temperature direct contact membrane distillation for the treatment of aqueous solutions containing urea. Membranes (Basel) 2020;10:176. https://doi.org/10.3390/membranes10080176.

[186] Zhao Z-P, Xu L, Shang X, Chen K. Water regeneration from human urine by vacuum membrane distillation and analysis of membrane fouling characteristics. Separation and Purification Technology 2013;118:369–76. https://doi.org/10.1016/j.seppur.2013.07.021.

[187] Kalla S. Use of membrane distillation for oily wastewater treatment – A review. Journal of Environmental Chemical Engineering 2021;9:104641. https://doi.org/10.1016/j.jece.2020.104641.

[188] Koeman-Stein NE, Creusen RJM, Zijlstra M, Groot CK, van den Broek WBP. Membrane distillation of industrial cooling tower blowdown water. Water Resources and Industry 2016;14:11–7. https://doi.org/10.1016/j.wri.2016.03.002.

[189] Leaper S, Abdel-Karim A, Gad-Allah TA, Gorgojo P. Air-gap membrane distillation as a one-step process for textile wastewater treatment. Chemical Engineering Journal 2019;360:1330–40. https://doi.org/10.1016/j.cej.2018.10.209.

[190] Criscuoli A, Zhong J, Figoli A, Carnevale M, Huang R, Drioli E. Treatment of dye solutions by vacuum membrane distillation. Water Research 2008;42:5031–7. https://doi.org/10.1016/j.watres.2008.09.014.

[191] Liu H, Wang J. Treatment of radioactive wastewater using direct contact membrane distillation. Journal of Hazardous Materials 2013;261:307–15. https://doi.org/10.1016/j.jhazmat.2013.07.045.

[192] Woldemariam D, Kullab A, Fortkamp U, Magner J, Royen H, Martin A. Membrane distillation pilot plant trials with pharmaceutical residues and energy demand analysis. Chemical Engineering Journal 2016;306:471–83. https://doi.org/10.1016/j.cej.2016.07.082.

[193] Leuchtenberger W, Karrenbauer M, Plöcker U. Scale-up of an enzyme membrane reactor process for the manufacture of l-enantiomeric compounds. Annals of the New York Academy of Sciences 1984;434:078–86. https://doi.org/10.1111/j.1749-6632.1984.tb29803.x.

[194] Wöltinger J, Karau A, Leuchtenberger W, Drauz K. Membrane reactors at degussa. Technology Transfer in Biotechnology 2005:289–316. https://doi.org/10.1007/b98909.

[195] Bommarius AS, Schwarm M, Drauz K. Biocatalysis to amino acid-based chiral pharmaceuticals—examples and perspectives. Journal of Molecular Catalysis B: Enzymatic 1998;5:1–11. https://doi.org/10.1016/s1381-1177(98)00009-5.

[196] Tao J, McGee K. Development of a continuous enzymatic process for the preparation of (R)-3-(4-fluorophenyl)-2-hydroxy propionic acid. Organic Process Research & Development 2002;6:520–4. https://doi.org/10.1021/op010232y.

[197] Maass D, Kreutzer A, Sprenger G, Bongaerts J, Wubbolts M, Takors R, *et al*. Enhanced pilot-scale fed-batch L-phenylalanine production with recombinant Escherichia coli by fully integrated reactive extraction. Bioprocess and Biosystems Engineering 2002;25:43–52. https://doi.org/10.1007/s00449-002-0280-2.

[198] Lopez JL, Matson SL. A multiphase/extractive enzyme membrane reactor for production of diltiazem chiral intermediate. Journal of Membrane Science 1997;125:189–211. https://doi.org/10.1016/s0376-7388(96)00292-x.

[199] Lehmann SV, Breinholt J, Bury PS, Nielsen TE. Enzymatic resolution to (−)-ormeloxifene intermediates from their racemates using immobilized Candida rugosa lipase. Chirality 2000;12:568–73. https://doi.org/10.1002/1520-636x(2000)12:7<568::aid-chir4>3.3.co;2-l.

[200] Webster R, Beaumont K, Ritzau M, Stachulski AV. The synthesis of the glucuronide metabolite of UK-157,147 using immobilised uridine 5'-Diphosphoglucuronyl transferase and traditional organic chemistry techniques (imidate method). Biocatalysis and Biotransformation 2001;19:69–83. https://doi.org/10.3109/10242420109103517.

[201] Criscuoli A, Drioli E. Energetic and exergetic analysis of an integrated membrane desalination system. Desalination 1999;124:243–9. https://doi.org/10.1016/s0011-9164(99)00109-5.

[202] Mericq J-P, Laborie S, Cabassud C. Vacuum membrane distillation of seawater reverse osmosis brines. Water Research 2010;44:5260–73. https://doi.org/10.1016/j.watres.2010.06.052.

[203] Curcio E, Criscuoli A, Drioli E. Membrane crystallizers. Industrial & Engineering Chemistry Research 2001;40:2679–84. https://doi.org/10.1021/ie000906d.

[204] Macedonio F, Curcio E, Drioli E. Integrated membrane systems for seawater desalination: energetic and exergetic analysis, economic evaluation, experimental study. Desalination 2007;203:260–76. https://doi.org/10.1016/j.desal.2006.02.021.

[205] Tun CM, Fane AG, Matheickal JT, Sheikholeslami R. Membrane distillation crystallization of concentrated salts—flux and crystal formation. Journal of Membrane Science 2005;257:144–55. https://doi.org/10.1016/j.memsci.2004.09.051.

[206] Rezaei M, Warsinger DM, Lienhard V JH, Samhaber WM. Wetting prevention in membrane distillation through superhydrophobicity and recharging an air layer on the membrane surface. Journal of Membrane Science 2017;530:42–52. https://doi.org/10.1016/j.memsci.2017.02.013.

[207] Ursino C, Ounifi I, Di Nicolò E, Cheng XQ, Shao L, Zhang Y, *et al*. Development of non-woven fabric-based ECTFE membranes for direct contact membrane distillation application. Desalination 2021;500:114879. https://doi.org/10.1016/j.desal.2020.114879.

[208] Qtaishat M, Rana D, Khayet M, Matsuura T. Preparation and characterization of novel hydrophobic/hydrophilic polyetherimide composite membranes for desalination by direct contact membrane distillation. Journal of Membrane Science 2009;327:264–73. https://doi.org/10.1016/j.memsci.2008.11.040.

[209] Yalcinkaya F. A review on advanced nanofiber technology for membrane distillation. Journal of Engineered Fibers and Fabrics 2019;14:155892501882490. https://doi.org/10.1177/1558925018824901.

[210] Su C, Chang J, Tang K, Gao F, Li Y, Cao H. Novel three-dimensional superhydrophobic and strength-enhanced electrospun membranes for long-term membrane distillation. Separation and Purification Technology 2017;178:279–87. https://doi.org/10.1016/j.seppur.2017.01.050.

[211] Madalosso HB, Machado R, Hotza D, Marangoni C. Membrane surface modification by electrospinning, coating, and plasma for membrane distillation applications: a state-of-the-art review. Advanced Engineering Materials 2021;23. https://doi.org/10.1002/adem.202001456.

[212] Ahmed FE, Lalia BS, Hashaikeh R, Hilal N. Enhanced performance of direct contact membrane distillation via selected electrothermal heating of membrane surface. Journal of Membrane Science 2020;610:118224. https://doi.org/10.1016/j.memsci.2020.118224.

[213] Alsaati A, Marconnet AM. Energy efficient membrane distillation through localized heating. Desalination 2018;442:99–107. https://doi.org/10.1016/j.desal.2018.05.009.

[214] Criscuoli A. Experimental investigation of the thermal performance of new flat membrane module designs for membrane distillation. International Communications in Heat and Mass Transfer 2019;103:83–9. https://doi.org/10.1016/j.icheatmasstransfer.2019.02.015.

[215] Yang X, Wang R, Fane AG. Novel designs for improving the performance of hollow fiber membrane distillation modules. Journal of Membrane Science 2011;384:52–62. https://doi.org/10.1016/j.memsci.2011.09.007.

[216] Singh D, Li L, Obusckovic G, Chau J, Sirkar KK. Novel cylindrical cross-flow hollow fiber membrane module for direct contact membrane distillation-based desalination. Journal of Membrane Science 2018;545:312–22. https://doi.org/10.1016/j.memsci.2017.09.007.

[217] Lee H, He F, Song L, Gilron J, Sirkar KK. Desalination with a cascade of cross-flow hollow fiber membrane distillation devices integrated with a heat exchanger. AIChE Journal 2010;57:1780–95. https://doi.org/10.1002/aic.12409.

[218] Koschikowski J, Wieghaus M, Rommel M, Ortin VS, Suarez BP, Betancort Rodríguez JR. Experimental investigations on solar driven stand-alone membrane distillation systems for remote areas. Desalination 2009;248:125–31. https://doi.org/10.1016/j.desal.2008.05.047.

[219] Chafidz A, Kerme ED, Wazeer I, Khalid Y, Ajbar A, Al-Zahrani SM. Design and fabrication of a portable and hybrid solar-powered membrane distillation system. Journal of Cleaner Production 2016;133:631–47. https://doi.org/10.1016/j.jclepro.2016.05.127.

[220] Elminshawy NAS, Gadalla MA, Bassyouni M, El-Nahhas K, Elminshawy A, Elhenawy Y. A novel concentrated photovoltaic-driven membrane distillation hybrid system for the simultaneous production of electricity and potable water. Renewable Energy 2020;162:802–17. https://doi.org/10.1016/j.renene.2020.08.041.

[221] Mericq J-P, Laborie S, Cabassud C. Evaluation of systems coupling vacuum membrane distillation and solar energy for seawater desalination. Chemical Engineering Journal 2011;166:596–606. https://doi.org/10.1016/j.cej.2010.11.030.

[222] Sarbatly R, Chiam C-K. Evaluation of geothermal energy in desalination by vacuum membrane distillation. Applied Energy 2013;112:737–46. https://doi.org/10.1016/j.apenergy.2012.12.028.

[223] Criscuoli A. Thermal performance of integrated direct contact and vacuum membrane distillation units. Energies 2021;14:7405. https://doi.org/10.3390/en14217405.

[224] Criscuoli A. Improvement of the membrane distillation performance through the integration of different configurations. Chemical Engineering Research and Design 2016;111:316–22. https://doi.org/10.1016/j.cherd.2016.05.020.

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