Review

Catalytic Membrane Reactors: The Industrial Applications Perspective

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Abstract: Catalytic membrane reactors have been widely used in different production industries around the world. Applying a catalytic membrane reactor (CMR) reduces waste generation from a cleaner process perspective and reduces energy consumption in line with the process intensification strategy. A CMR combines a chemical or biochemical reaction with a membrane separation process in a single unit by improving the performance of the process in terms of conversion and selectivity. The core of the CMR is the membrane which can be polymeric or inorganic depending on the operating conditions of the catalytic process. Besides, the membrane can be inert or catalytically active. The number of studies devoted to applying CMR with higher membrane area per unit volume in multi-phase reactions remains very limited for both catalytic polymeric and inorganic membranes. The various bio-based catalytic membrane system is also used in a different commercial application. The opportunities and advantages offered by applying catalytic membrane reactors to multi-phase systems need to be further explored. In this review, the preparation and the application of inorganic membrane reactors in the different catalytic processes as water gas shift (WGS), Fisher Tropsch synthesis (FTS), selective CO oxidation (CO SeLox), and so on, have been discussed.

Keywords: catalysis; membrane reactor; process intensification; inorganic catalyst; enzyme; environmental applications

1. Inorganic Membrane Reactor

1.1. Introduction to Catalytic Inorganic Membrane Reactors

Since the conventional methodologies of chemical processes have been successfully applied to synthesize enormous numbers of sophisticated products, researchers worldwide have been searching for alternative methods, which are more efficient concerning energy consumption, space reduction, and environmental safety [1]. One of the most promising strategies to achieve these challenging goals is utilizing catalysts. Catalysts play an essential role in numerous environmental transformations with high reaction regioselectivity and stereospecificity. These peculiar characteristics allow scientists to apply them in modern chemistry and organic synthesis processes. Anyway, the rapid growth of the chemical industries for producing different chemicals requires improving manufacturing and processing by reducing the equipment size, energy consumption, and waste production to achieve sustainable and cheaper technologies (process intensification strategy) [1].

Membrane reactors, a process intensification technology, combine the membrane separation process with chemical or biochemical reactions in a single unit [2]. This combination determines higher conversion and improved selectivity and a compact and cost-effective

reactor design [3]. Considering these aspects, membrane reactors (MRs) represent a potential technology in different fields: pharmaceutical, biotechnology, petrochemical sectors, energy, and environmental applications, including phase change behaviour [4].

MRs are categorized as polymeric (or organic) and inorganic depending on the chemical process operating conditions. Polymeric membranes can operate at temperatures that do not exceed 300 °C [5,6]. Inorganic membranes can be used when polymeric ones fail considering that they can operate at higher temperatures (300–800 °C and in some case over 1000 °C) and in the aggressive chemical environment due to their high chemical resistance [7]. In addition, in polymeric membranes, there is a trade-off between permeability and selectivity. Generally, glassy polymers have high selectivity and low permeability, while rubbery polymers show high permeability and low selectivity [8]. Considering this disadvantage, inorganic membranes have elicited much attention due to their high permeability and selectivity. The limits in the inorganic membrane field are the high production cost and the brittleness [9]. Different materials have been used to fabricate inorganic membranes as carbon, silica, alumina, titania, zirconia, zeolite, palladium, silver, and alloy [10,11]. Inorganic membranes can also be classified as dense or porous. Porous membranes are categorized according to the IUPAC classification into macroporous (pore diameter (pd) > 50 nm), mesoporous (2 nm < pd < 50 nm) and microporous (0.5 nm < pd < 2 nm) [11]. These membranes are self-standing or supported, the support being used to give them mechanical strength [12].

According to the role of the membrane in the reactor, three different configurations have been identified: extractor, distributor and contactor and their; these aspects will be deeply explained in Section 2. In addition, the inorganic membranes used in MR can be inert or catalytically active. In the first case, the catalytic particles are separated from the membrane or are dispersed in its pores, and these configurations are called inert membrane reactor (IMR). In the last case, the membrane acts as both separator and catalysts, and this configuration is called catalytic membrane reactor (CMR).

In this review, the different methods used for the preparation of inorganic membranes have been presented. The application of inorganic membrane reactors in different interesting reactions has also been discussed.

1.2. Preparation of Inorganic Membrane Reactors

The materials frequently use for ceramic membrane preparation are alumina (Al_2O_3), titania (TiO_2), zirconia (ZrO), glass (SiO_2), and combinations of these metal oxides [10,11]. These membranes present an asymmetric structure with two or three layers characterized by different pore sizes [13]. The first layer acts as a support, and the second one is fragile and is responsible for the separation having a small pore size [14]. An intermediate layer is sometimes synthesized to ensure a structural fitting between the other two; the ceramic membrane layers are schematically illustrated in Figure 1 [14].
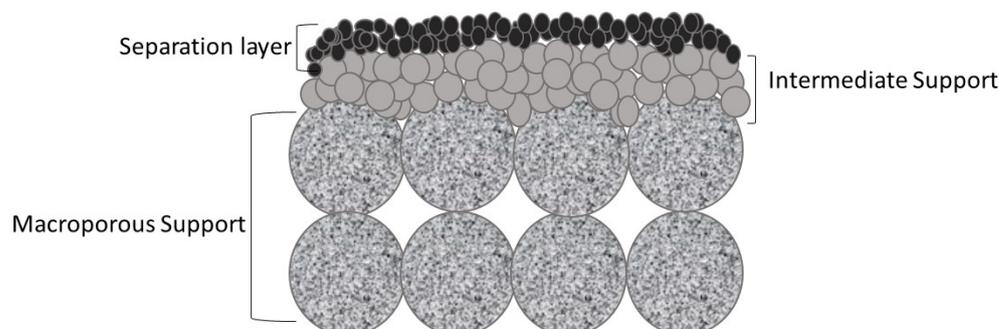
Figure 1. Scheme of ceramic membrane layers. Adapted from [15]. Reprinted with permission from ref. [15]. Copyright 2021 Elsevier.

The methods used for their synthesis are slip casting, extrusion, pressing, freeze-casting, and sol-gel [15–18]. Among them, the most used is the slip-casting that includes the following three steps: In the beginning, a paste or suspension is prepared by using a ceramic powder. The paste is deposited on a porous support. Finally, the ceramic membrane was subjected to a drying and heat treatment [19,20]. Tape casting and pressing technique permit fabricating flat sheet membranes. A ceramic paste is added to a reservoir and cast utilizing a blade adjusted at a fixed height in the tape casting. After, the membrane is dried and sintered at high temperatures [21]. In the pressing, the paste poured into a metal mould, and a force equivalent to 100 to 1000 bar was applied for producing an asymmetric membrane with a flat configuration. Finally, the sintering procedure is performed [22].

Tubular (mono and multichannel) and hollow-fibre membranes are prepared using the extrusion method. In this process, a semi-dried past passed through an orifice with a fixed cross-section and shape [22]. The freeze-casting process is used for the preparation of highly porous membranes. Initially, a solid suspension is frozen. Later, the sublimation of the frozen solvent (by operating at low pressures) allows the formation of the porous structure [23]. In the sol-gel method, the natural compound (metal alkoxide) is dissolved in a solvent, and then the hydrolysis permits the formation of a monomer [24]. The monomer polymerizes, and the formed polymer is deposited on a support surface. After drying and thermal treatment, the membrane is obtained. The high production cost hinders a broad application of the ceramic membranes; in fact, different researchers focus their activity on fabricating ceramic membranes by using waste with the urban or industrial origin [25].

Zeolites are aluminosilicate materials with pore size at the molecular scale and high thermal and chemical resistance. By changing the reaction mixture's Si/Al molar ratio the resulting zeolites can have hydrophilic or hydrophobic character [26]. Considering these peculiar characteristics, zeolite membranes can continuously separate a mixture of liquid and gas species with similar sizes and shapes and different adsorption properties [27]. They can be used as membrane reactors [28]. Zeolite membranes are prepared on supports (usually in alumina or stainless steel) to ensure their mechanical stability [29]. Two main methods are used for their synthesis: the traditional method (called too one-step or in-situ) [30] and the secondary growth [31]. In the first one, the support is added in an autoclave in contact with a synthesis solution. In this case, nucleation and crystal formation occurs in the same chemical environment [31]. Considering this last aspect, this method is not reproducible, and the membranes are very thick. The second one is reproducible and permits fabricating membranes fragile because the nucleation is separated from the crystal growth [32]. In particular, it presents the seeding and growth steps. During the first step, pre-synthesized nuclei of zeolites are seeded on the support. The zeolite layer is held on the support through weak chemical interaction [33]. Then, the support is put in contact with a precursor solution of the zeolite in an autoclave (under hydrothermal treatment) to ensure the growth of crystals present on the support and stabilize the zeolite layer by forming a chemical bond. A schema of the secondary growth method is illustrated in Figure 2.

The critical step is seeding, and the procedures used for performing it are different, and the most used are dip-coating [34,35], rubbing [36,37], electrostatic and covalent chemical deposition [38,39], and filtration [33,40–42]. During the dip-coating, the zeolite crystals dribble in the suspension owing to the gravitational force. For this reason, it is performed several times, and it is less reproducible [43]. The rubbing procedure is also less reproducible considering that it is achieved with small brushes using a zeolite paste and has limitations during the coverage [44]. More reproducible are the procedures where a filtration process is involved because, being a well-known membrane process, it is possible to obtain a uniform and thin layer by choosing appropriate operating conditions [40–42]. After the synthesis, the zeolite membranes are thermally treated (calcination process) for the template removal, an organic chemical species used for orienting the zeolite formation [45]. During this process, defects are formed owing to the different thermal expansion coefficients of support and zeolite. Anyway, the preparation of thin, defect-free, and high-

reproducible, and low –cost membranes represent still challenges. Indeed, today, at an industrial level, a few zeolite-membrane topologies are used in the dehydration of various organic solvents [46].
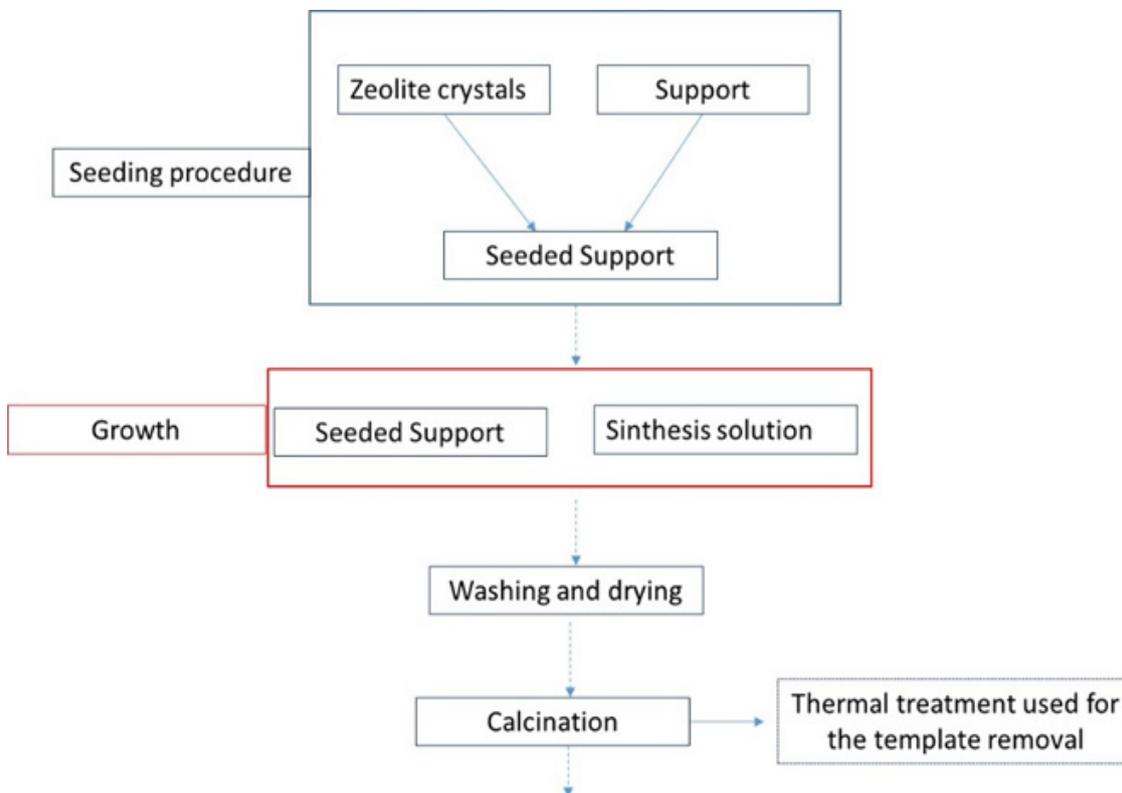

Figure 2. Scheme of the secondary growth method.

The metal materials mainly used for the membrane preparation are palladium and alloys due to the high solubility and permeability of hydrogen [47]. These membranes have a dense structure and are applied in the gas separation process and as membrane reactors when H_2 is a reactant or a product of the process [48–50].

Different methods are available for synthesizing Pd-based membranes, and the most used are electroless plating (ELP) [51], chemical vapour deposition (CVD) [52], physical vapour deposition (PVD) [53] and the electroplating deposition (EPD) [54]. In this review, the ELP method has been discussed as being mainly exploited for membrane fabrication [55]. This method includes four steps: the cleaning/smoothing of the support surface [56]. In the second and third ones, the activation of the support and the deposition of the palladium is carried out, respectively. The membrane is dried and annealed for performing the Pd activation [57]. The precursor of the metal species, dissolved in an aqueous solution, is stabilized by using ligand (as ammonium hydroxide and ethylene-diamine-tetra acetic acid (EDTA)) that can form a metal complex [58]. Then, the palladium ions are reduced by an appropriate chemical reaction [59].

1.3. Inorganic Membrane Reactor Applications

Different MR configurations, classified into three groups, can be identified by varying the membrane role in the process [60]: extractor, distributor and contactor membrane [61]. In the extractor, the membrane is used to remove a reaction product and improve the conversion (reaction equilibrium shift according to Le Chatelier's principle) [62]. The role of the membrane in the extractor configuration is illustrated in Figure 3. In distributor one, the reactant passes through the membrane and reaches the reaction environment in a

controlled way by limiting side reactions (see Figure 3) [63]. In these two configurations, the membrane is catalytically inert, and it is coupled with a conventional catalytic process. In the contactor, the membrane is catalytically active, and it is used for improving the contact between reactants and catalytic sites [64]. This last configuration is shown in Figure 3.
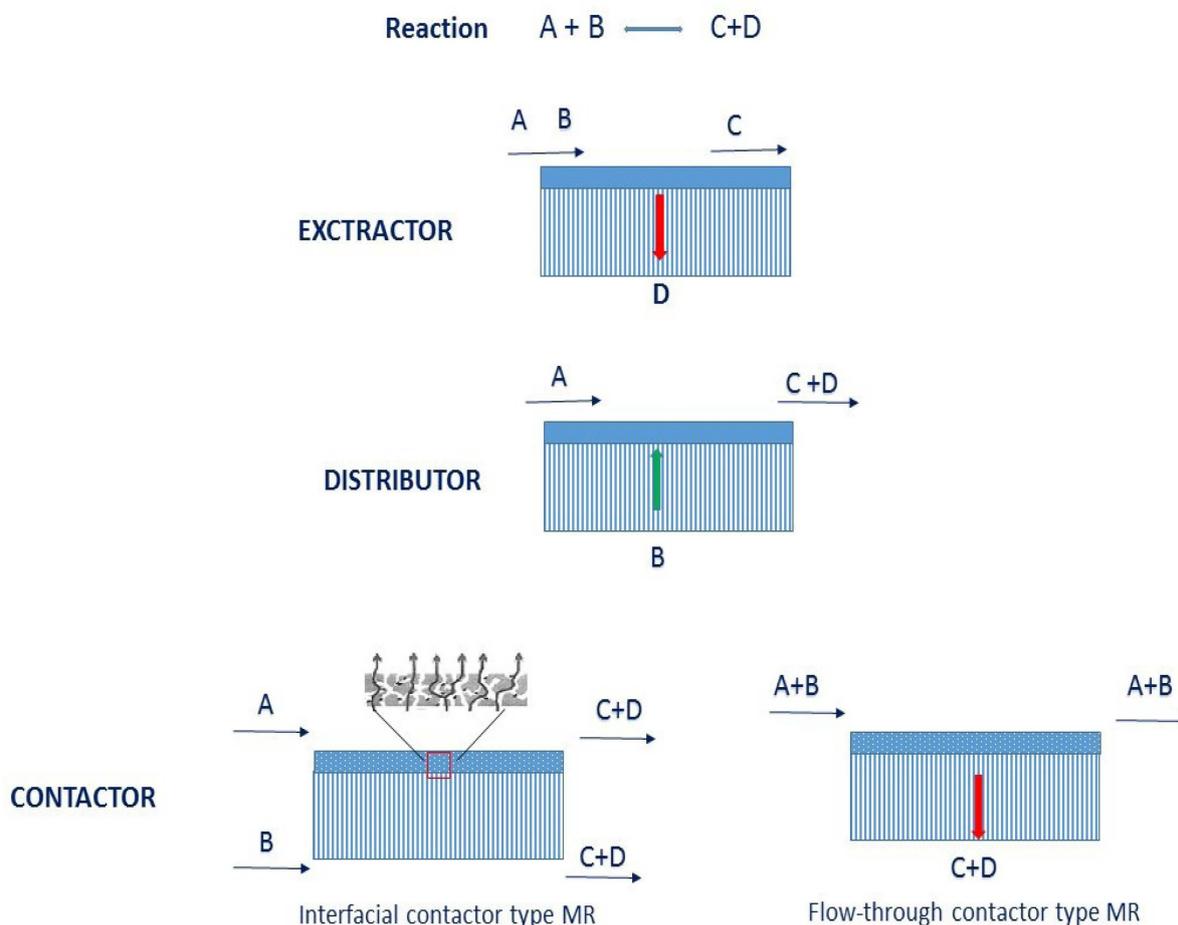
Figure 3. Membrane role in a membrane reactor.

The applications of inorganic membrane reactors in various chemical reactions have been reported and discussed. Today, steam methane reforming (SMR) is the primary process for hydrogen production [65]. A gaseous mixture, called syngas, is produced containing hydrogen, carbon monoxide, and a low amount of carbon dioxide [64]. For increasing the hydrogen produced by SMR, the water-gas shift (WGS) produces H_2 and CO_2 from carbon monoxide and steam. The WGS is limited by the thermodynamic equilibrium at elevated temperatures [65]. A possible way to improve the CO_2 conversion is to remove a reaction product to overcome the chemical equilibrium limitation [66]. Kim et al. used MFI zeolite membranes as membrane reactors for performing a WGS reaction at high temperatures [67], and the catalyst used was Fe/Ce nanoparticles. The membranes showed a reasonable hydrogen selectivity (H_2/CO_2 = 31 and H_2/CO = 25) at 500 °C. In this work, the CO conversion enhanced (98.5%), overcoming the equilibrium limit by using the silicalite membranes and operating at high temperature (>500 °C) and pressure (6 bar). In addition, Simulation studies indicated that the zeolite MRs could achieve a very high CO conversion ($\geq$99%) with these operating conditions: T > 500 °C, P = 30 atm and $RH_2O/CO\sim3.5$ [67].

Arvanitis et al. have also obtained exciting results by using MFI zeolite membrane reactors [68]. A complete conversion of the carbon monoxide (>99.9%) was achieved and with a hydrogen recovery of 99.9%, operating at 500 °C and 20 bar. The catalyst remained

stable for about 50 h of WGS reaction at 20 bar. However, carbon deposition on the surface appeared, causing a CO conversion decline from 99.9% to ~96% within two days. In addition, a low purity of hydrogen was due to the moderate H_2 selectivity of the zeolite membrane. Table 1 reports other results on H_2 production by WGS by using the zeolite membrane reactors.

Table 1. Performance of zeolite membrane reactors in the WGS process.

Zeolite Topology	Temperature (°C)	CO Conversion%	H_2 Recovery (%)	References
MFI *	350	73.6	>98.2	[69]
MFI	300	95.4	-	[70]
MFI	550	81.7	18	[71]
MFI	-	>99	>60	[72]

* MFI = Mobil-Type Five.

Lee and coworkers produced H_2 from WGS and using a Pd-Cu membrane reactor coupled with a pressure swing adsorption (PSA) [73]. A commercial catalyst (composed of aluminium oxide, chromium oxide, chromium trioxide and copper oxide) has been used for carrying out the catalytic process. The experimental results evidenced raising the steam/CO ratio from 1 to 5 the CO conversion increased from 85.4% to 94.8% and the H_2 recovery from 53.4% to 56.1% (as illustrated in Figure 4). When the CMR has been integrated with a PSA unit (using activated carbon and zeolite), the H_2 recovery has improved by about 31.2–35.7%. The combination of a CMR with PSA could be used to produce hydrogen rich-stream to use in a proton-exchange membrane fuel cell; in fact, this system permitted to enhance CO conversion (almost complete CO conversion) and H_2 recovery (R = 99.9991%).
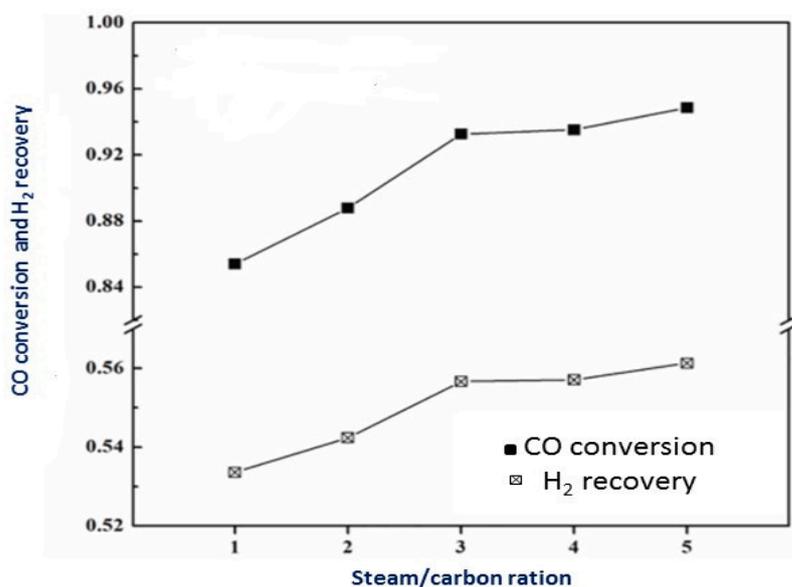
Figure 4. CO conversion and H_2 recovery (at the steady-state) as a function of the steam/carbon ratio [73].Tsotsis and coworkers prepared an ultra-permeable palladium membrane via ELP method, and it was used for hydrogen production using the WGS process [74]. A commercial Cu/Zn has been used as a catalyst. The authors found that increasing the feed pressure decreased the purity of the hydrogen owing to an increased driving force through the membrane for all the gas species. In addition, the membrane exhibited good stability for one month, and the change in H_2 permeance was equal to 6%. A complete CO conversion and an H_2 recovery of 90% have been obtained at 300 °C and 4.6 bar. Other results present in the open literature with metal membrane reactors in WGS are presented in Table 2.

Table 2. Metal membrane reactors are applied in WGS process.

Membrane	Temperature (°C)	CO Conversion%	H$_2$ Recovery (%)	References
Pd	410	85	-	[75]
Pd-Ag	200	96.6	92	[76]
Pd-Ag	300	99.1	98	[76]
Pd	400	92	<80	[77]
Pd-Ag	400	99.5	<89	[77]
Pd-Ag	330	85	80	[78]
Pd-Cu	900	65	85–90	[79]

Fisher Tropsch synthesis (FTS) converts the syngas, obtained from natural gas or biomass, into liquid hydrocarbons (see Equation (1)) and on an industrial scale, iron and cobalt-based catalysts are used [80].

$$(2n + 1)H_2 + nCO \rightarrow CnH_{2n+2} + nH_2O \tag{1}$$
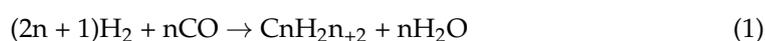
The membrane combined with the FTS can improve the performance of the catalytic process, exerting a function of extractor or distributor. In the first case, the membrane is used to remove water, a reaction product, to reduce the catalyst deactivation, increase conversion and displacing the water gas-shift equilibrium, and enhance the hydrocarbon production [81]. When it is used as a distributor, the membrane must be selective towards the H$_2$ or CO. In this case, it is possible to maintain the reactants' ratio and avoid side reactions [82]. Different research groups studied the possibility of using hydrophilic zeolite membranes for water removal from hydrogen and carbon monoxide using the operating conditions typical of the FT process. In 2005, Zhou et al. [83] studied the separation of H$_2$O/CO, H$_2$O/H$_2$, and H$_2$O/CH$_4$ versus the temperature using NaA membranes. The selectivities of H$_2$O/CO, H$_2$O/H$_2$, and H$_2$O/CH$_4$ were 30, 72, and 323 at 100 °C. The water quickly passes through the membrane for the high affinity with the zeolite NaA strongly hydrophilic. Kapteijn and coworkers prepared sodalite membrane on alumina support that exhibited very high H$_2$O/H$_2$ selectivity up to 200 °C and so it is very promising for the water removal in FTS [84].

Recently, palladium membranes have been used to control hydrogen in a fixed-bed catalytic reactor for the FTS [85]. In particular, three different systems have been considered: (i) traditional fixed-bed reactor (FBR) using as catalyst CoRu/Al$_2$O$_3$, (ii) traditional FBR and CoRu/Al$_2$O$_3$-zeolite as a catalyst and the CMR (catalyst: CoRu/Al$_2$O$_3$). The selectivity of different hydrocarbon (HC) fractions versus the product distribution for the other experiments is shown in Figure 5. The results evidenced as the CMR permits to have better results due to the possibility to add in a controlled way the H$_2$ avoiding the formation of methane (side reaction). The carbon monoxide conversion was about 45% after 15 h of catalytic test for the three experiments. FBR (catalyst: CoRu/Al$_2$O$_3$), FBR (catalyst: CoRu/Al$_2$O$_3$-zeolite); CMR (catalyst: CoRu/Al$_2$O$_3$).

The distributor configuration is usually used in different reactions such as the oxidation or oxy-dehydrogenation of hydrocarbons and oxidative coupling of methane. The oxygen, a reactant of the responses, is provided in a controlled manner [86,87]. The oxidative dehydrogenation of alkanes allows olefin production conveniently than dehydrogenation and steam cracking [87]. This process shows no chemical equilibrium limitations as the dehydrogenation and required mild temperatures than the steam cracking [88]. In 1999, Santamaria and coworkers studied the oxidative dehydrogenation of propane by using a macroporous alumina membrane coated with the catalyst [89]. In particular, the researchers found that the membrane used as a distributor improved the reaction conversion [89]. The membrane application as the distributor has also been studied by Kartell et al., employing a theoretical study [90]. They proposed, using numerical simulations, a new membrane reactor for the direct synthesis of propylene oxide (PO) in the liquid phase. The reactor combines two consecutive catalytic reactor units: the hydrogen peroxide synthesis and the reaction of H$_2$O$_2$ with the propylene for synthesizing PO. Pd/SiO$_2$ is the top layer

of the membrane (used and for H_2O_2 synthesis), and titanium silicalite-1 is the bottom layer (used for promoting the reaction between H_2O_2 and propylene). The theoretical results indicated as a thickness of 250 μm for Pd/SiO_2 layer and 100 μm for the other catalytic layer are required to achieve attractive conversion and selectivity [90]. Recently, by Ermilova et al. performed the ethane oxidative dehydrogenation to ethylene by using a catalytic membrane reactor (as a distributor) [91]. In particular, the external surface of the asymmetric alumina membrane has been coated with a catalyst (Mo-V-Te-Nb-Ox) and used as a distributor. Figure 6 shows how the co-current mode of the supply of the reactant to the catalytic surface of the membrane enables a significant increase in the ethane conversion compared to the counter-current mode. This is owing to due to the different distribution of ethane and oxygen fluxes along the membrane. In particular, when the reactants are fed in co-current mode arrive on the catalyst surface with a maximum concentration, ensuring an almost complete conversion.
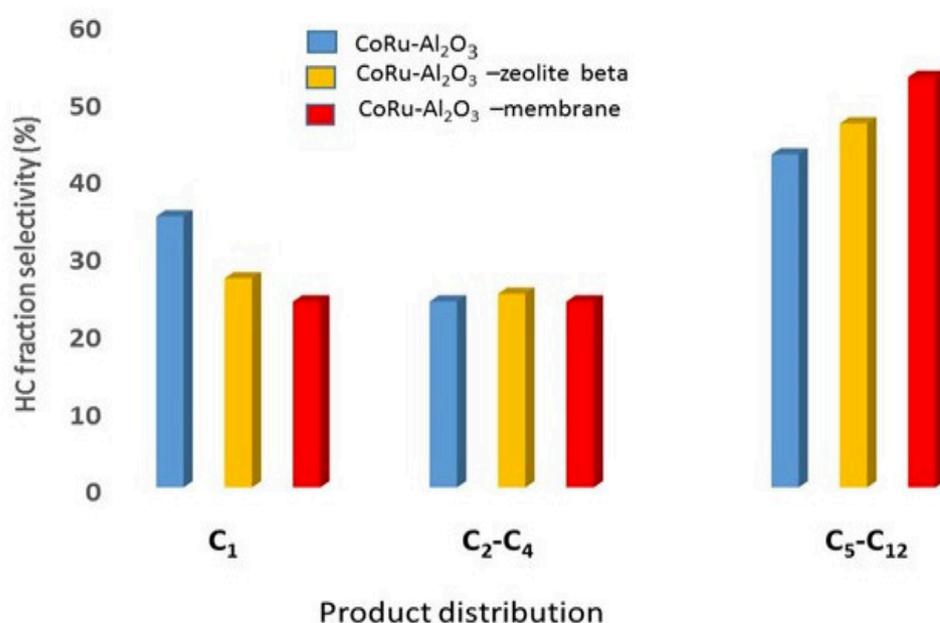
Figure 5. Hydrocarbons (H.C.) fraction selectivity versus the product distribution for three experiments after 15 h on stream (XCO ≈ 45%).

Anyway, the researcher obtained better results (ethane conversion of 70% and an ethylene selectivity of 95–98%) with a layer of titanium oxide deposited on the Al_2O_3 membrane.

The deep purification of hydrogen, produced for steam reforming, is a critical technology for producing energy by proton exchange membrane fuel cells (PEM-FCs) [92]. However, the carbon monoxide present in hydrogen-rich streams, produced by steam reforming, poisons the anode of the PEM-FCs. Furthermore, it is necessary to reduce the CO amount (down to 10 ppm) [93] The CO selective oxidation (SelOx) is a promising and economical approach [93]. During the process, not only the CO oxidation but also the H_2 oxidation happens; the reactions involved are:

$$2CO + O_2 \rightarrow 2CO_2 \tag{2}$$

$$2H_2 + O_2 \rightarrow 2H_2O \tag{3}$$

A selective catalyst must be used to consider this aspect, and a good compromise between cost and functionality is represented by the platinum (Pt) [93]. Bernardo et al. used NaY zeolite membrane loaded with Pt for performing the CO SelOx [28]. The catalytic membrane reactor acts as a catalytic contactor and permits to achieve exciting results in C. conversion and CO_2 selectivity than the traditional fixed bed reactors. A comparison

between the results obtained with the Pt-NaY membrane reactor and the traditional ones for the CO SelOx is illustrated in Figure 7.
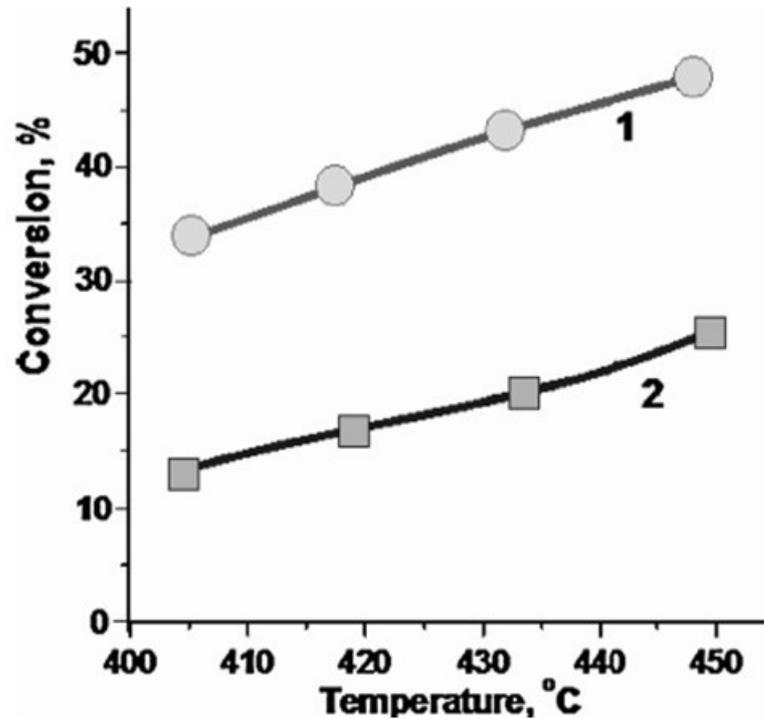
Figure 6. Ethane conversion in the membrane reactor (alumina support coated with the Mo-V-Te-Nb-Ox active phase at different stream modes: (1) co-current; (2) counter-current; operating conditions: initial flow rates in the membrane reactor are: 558 cm^3/h for O_2 and 1672 cm^3/h for C_2H_4 (O_2:C_2H_6 = 1:3).
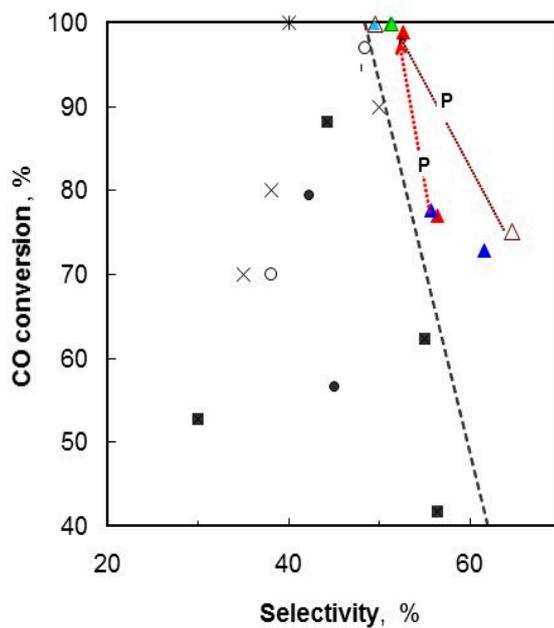
Catalytic System	Symbol	References
Pt-NaY membrane	triangle	[94]
Pt/NaY crystals	Square	[95]
Pt/Al$_2$O$_3$	Star	[96]
Pt/Al$_2$O$_3$	Black circle	[97]
Pt-Ni/γ-Al$_2$O$_3$	circle	[98]
Pt/Al$_2$O$_3$	cross	[98]

Figure 7. Comparison between Pt-NaY zeolite CMR and traditional reactors for the CO SelOx [94–98].

The better results obtained with the zeolite membrane reactor are due to the excellent dispersion of the catalytic particles in the zeolite layer. Good contact between reactants and catalytic sites is ensured [94,99]. Besides, considering that the zeolite layer is fragile a reduced by-pass and low-pressure drop are attained [94,99]. In an actual SelOx process, the gas stream, after the WGS, contains CO_2 (20–25%) and Medrano et al. [99] demonstrated as the CO_2 causes a decrease of the conversion and the selectivity due to the presence of the reverse water gas shift that limited the CO oxidation at elevated temperature.

Their use at an industrial scale is missing among the different works focused on applying membrane reactors in various industrial processes. The main drawbacks are the lack of scientific evidence about the long-term stability of the membrane reactors applied in actual operating conditions of the processes and the very high cost for the fabrication.

2. Organic Membrane Reactors

2.1. Introduction of Organic Membrane Reactors

Industrial-scale membrane units are often based on polymers, either natural (cellulose, rubbers and wool) or synthetic (Teflon, polyamide, polystyrene). Essentially, any kind of polymer can suit membrane casting, but, taking into account the wide range of physical and chemical features that they can exhibit, just a restricted part can be utilized. Choosing a polymer for a specific membrane is centred on precise features that regard the structural organization of the polymers themselves.

Porous or dense polymeric membranes are usually employed in processes with low reaction temperatures or in the presence of biocatalysts. Sorption–diffusion principles can couple catalytic reactions so that membranes such as the dense polymeric ones can act well to separate gases and liquids from mixtures in processes where separation and reaction act in the same step. Polymeric membranes need to be highly selective and exhibit high permeability to convey a satisfactory separation. Also, polymeric membranes may be well employed in catalytic reactions (liquid phase) [100].

2.2. Enzymatic Membrane Reactors: Preparation and Applications

A catalytic membrane reactor (E-MBR) offers advantages concerning conventional reactors because of the membrane's ability to operate simultaneously as catalyst support and selective barrier, combining a reaction with a particular mass transfer through the membrane.

Simultaneous removal of products from the reaction site allows effective conversion, even inhibiting or thermodynamically unfavourable reactions [101]. Researchers have developed enzyme-catalyzed response at room temperature to reduce energy consumption and minimize thermal degradation of the products. One of the essential characteristics of the catalyst is activation by organic/aqueous biphasic interface (interface activation). The membrane allows them to independently control the catalyst and substrate concentrations, residence time and permeate flow; this, in turn, increases CMR productivity over a batch reactor.

Membrane reactors can be categorized into two types: inert and catalytic reactors. The membrane is next to the reaction bulk in the inert type, which contains the catalyst, either suspended or packed. In contrast, in the catalytic reactors, the membrane is fixed on the catalysts or has its catalytic activity. Often the inert types encounter inadequate compound transport due to the locking effect of particles, even by the enzymes/NPs, on the pores. At the same time, catalytic membrane reactors don't suffer from these issues because of their fixed embedding of the catalysts on the membrane itself. Metal nanoparticles seem to be often chosen as catalysts, especially in environmental remediation scopes. They can have very high catalytic performances; as an example Au and Pt nanoparticles are widely used. In this context, Huang et al., as a solution for reducing 4-nitrophenol, developed a catalytic membrane reactor embedding a film by alloy nanoparticle-loaded β-lactoglobulin fibrils. They observed Cu nanoclusters' formation, which stimulated the Ag^0 synthesis as a reducing agent for the 4-nitrophenol [101].

Biofilms have widely been applied to civil water treatment before activated sludge processes were available. In addition, biofilm reactors are used primarily in industrial fields for their reliability and ease of use. Biofilm growth begins by molecules (e.g., lipids, proteins) adsorption on a surface. These molecules can modify the physicochemical features of the surface, being a nutrient source for microbes, alter the release of metal ions, and cause the adsorption of inhibitory matters. As a general rule, biofilm reactors are consisted of: inlet and outlet sections, a biofilm carrier, an aeration unit in case of aerobic processes or a mixing device in case of anoxic processes. Lai et al. demonstrated how perchlorate, mainly known as a groundwater contaminant, can undergo microbial reduction to form chloride. The process was driven by C_2H_6 or C_3H_8 with oxygen as a limiting compound. The research applied two membrane biofilm reactors in parallel resulting in novel applications for groundwater remediation [102].

Anaerobic membrane bioreactor (AnMBR) is a valid technology for domestic, civil, and wastewater treatment. This because of the high separation between hydraulic and solid retention times (HRT and SRT), thus consenting to the growth of anaerobic bacteria; in addition, they appear to have a low footprint and high treatment capacity while producing high-quality effluents. AnMBR, in contrast with aerobic MRs have low energy consumption (no aeration needed), exhibit lower solid yield and lower carbon dioxide emissions. The main downside of AnMBRs being the fast decay of permeate flux caused by membrane fouling. Berkessa et al. studied two formulations of AnMBRs applied on wastewater treatment with long hydraulic retention times (47 days) and a $22 \, g \cdot L^{-1}$ sludge concentration. The long HRT leadss to biofilm reduction by *Chloroflexi* (heterotrophic bacteria), resulting in large fluxes. Either the membrane resistances and the fouling rates values resulted as low so that the study resulted in AnMBRs with excellent membrane fouling control [103].

Immobilized catalysts in Figure 8 have widespread organic synthesis, pollution control and diagnostic purposes. It is well understood that the enzyme has some specific advantages over inorganic, metal-derived or chemical catalysts. Products with high purity and high added value can be obtained with enzymes immobilized on porous supports. Moreover, enzymes decrease the side reactions and simplify post-reaction separation problems. Due to the considerably unstable nature of enzymes, there has been constant endeavour to develop different efficient immobilization techniques, which can protect enzymes from various physical and chemical stresses, such as pH, temperature, salts, solvents, inhibitors, and poisons. Immobilization is achieved by fixing catalyst to or within solid supports, resulting from which heterogeneous immobilized catalytic systems are obtained [102]. The physical methods are simple and based on weak chemical interactions (van der Waal forces, electrostatic force and hydrogen bonds) between the enzyme and the membrane [103]. Chemical immobilization is based on the formation of covalent bonds. In this case, the enzyme is not released in the reaction environment [104]. At the same time, this problem is usually found with the physical methods. Usually, immobilization strategy improves the stability and also permits its re-use. However, it reduces the catalytic activity because the catalytic sites are less accessible to the reactants.

Although the enzymes can be quite expensive, recycling the used enzyme makes the process more economically viable. When the enzyme has been immobilized, it makes the process simpler in terms of design and easier to control the different reaction parameters. To reuse the enzyme, it must be active after use, and it has to be stable in the reaction media. It is only possible when the catalyst is in immobilized conditions in porous support. Table 3 the advantages and disadvantages of different immobilization of biocatalysts, which are mainly used in the chemical and biochemical processes industry.
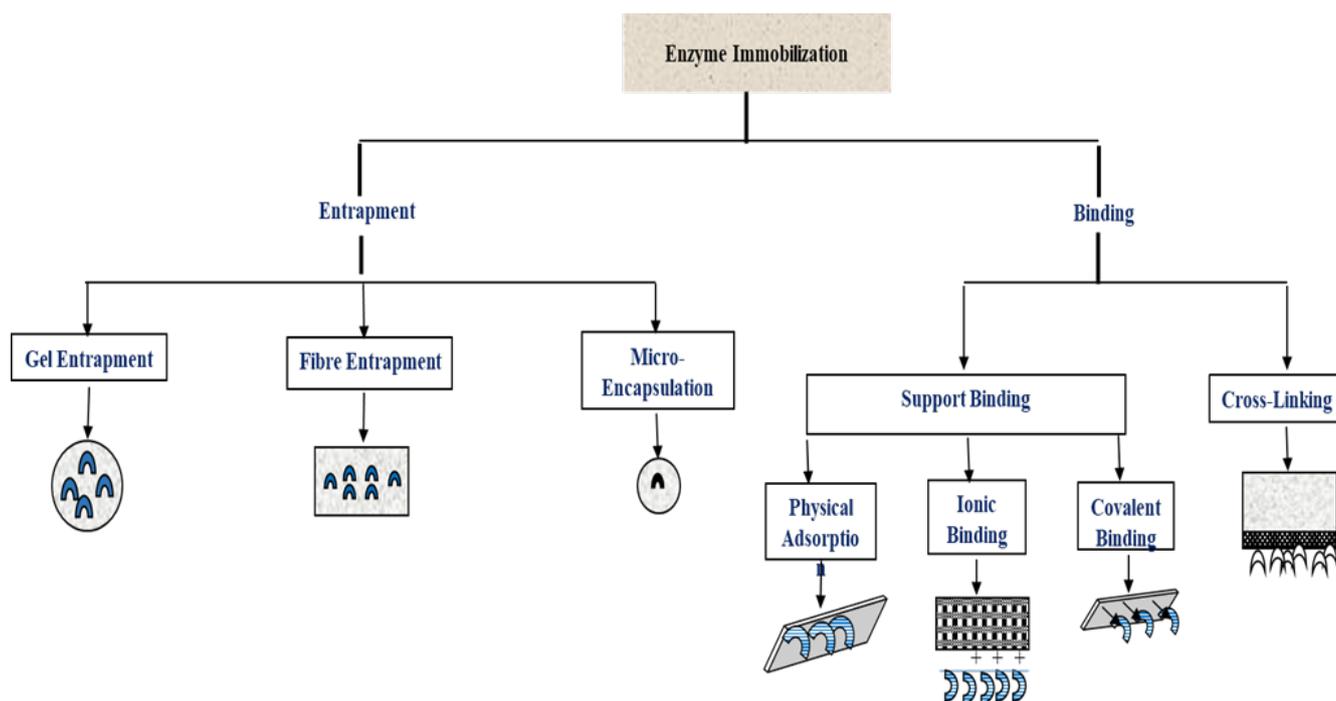
Figure 8. Different biocatalyst immobilization mechanism.

Table 3. Advantages and disadvantages of biocatalysts immobilized on porous supports.

Binding Method	Binding Nature	Advantages	Disadvantages
Adsorption	Weak bonds	Simple and easy to use	Desorption
		Limited loss of enzyme activity	Non-specific adsorption
Covalent Binding	Chemical binding between functional groups of the enzyme and those on the support	No diffusion barrier	Matrix not regenerable
-	-	Stable & Short response time	Coupling with toxic product
Entrapment	Incorporation of the enzyme within a gel or a polymer	No chemical reaction between the monomer and the enzyme that could affect the activity of enzyme	Enzyme leakage and Diffusion barrier
-	-	Several types of enzymes can be immobilized within the same polymer	High concentrations of monomer and enzyme for electropolymerization
Cross-linking	Bond between enzyme/cross-linker (e.g., glutaraldehyde)/inert molecule	Simple	High enzyme activity and activity loss
Affinity	Affinity bonds between a functional group on a support and affinity tag on a protein sequence	Controlled and oriented immobilization	Need of the presence of specific groups on enzyme

Membrane bioreactors (MBR) are part of an established -developed technology found throughout the years' many industrial applications worldwide. To mention one of the leading applications, many municipal and industrial wastewater is treated through MBR systems. Still, substantial research and progress are needed in this field as technical difficulties are still encountered, such as membrane fouling and not so low energy needs, thus slowing down the spread of MBR plants.

Nonetheless, as membrane costs of production have been reduced in recent years, MBR technology has gained increasing attention, mainly for constructing medium-size

wastewater plants, corresponding to a water feed of an equivalent of up to 100,000 people. Moreover, in the same years, a focus on process optimization led to a substantial reduction of capital and operating expenses of new MBR plants.

Summing up all the features, it can be stated that the excellent quality of purified water mainly drives MBR technology in water treatment applications interest, the increasing water scarcity issues, the growing strictness of quality and discharge legislations worldwide, the lower costs of investment, the fact that MBR technology is becoming more accepted as a valid option over time, and the possibility to be applied as an upgrade to existing water treatment plants [101,105,106].

MBR devices can be organized in two main configurations, in which the positioning of the two main elements, the membrane and the reactor, varies. The first one can be seen as a side-stream method with a membrane situated outside the reactor, as in Figure 9a. The second one has the membrane collocated in the bulk of the reactor, so it acts while submerged in the feed stream (Figure 9b).
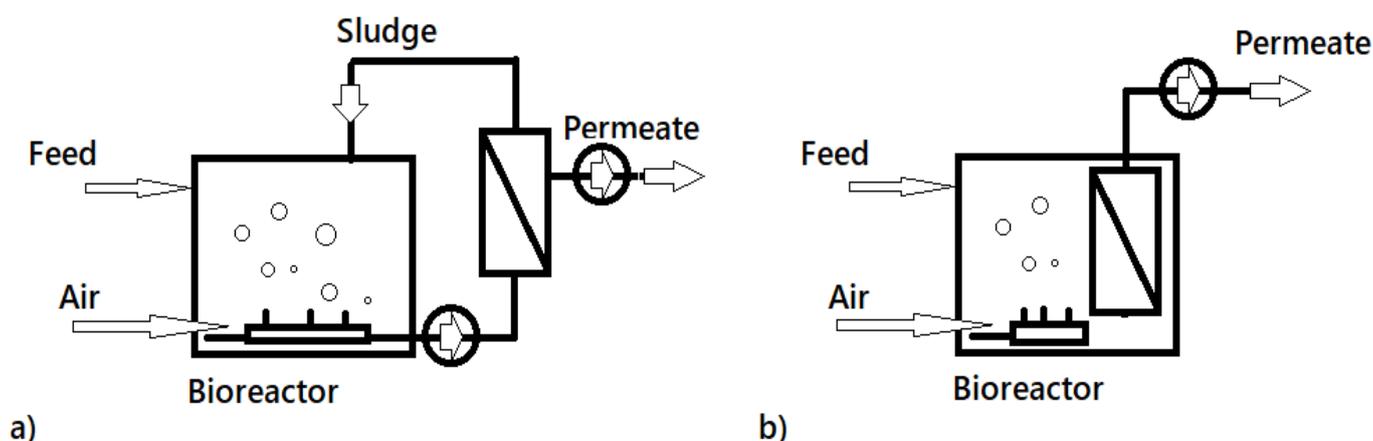

Figure 9. MBR configurations: (**a**) Side-stream and (**b**) submerged.

In Table 4, the two configurations are compared in terms of applications and operational features [107].

Table 4. Comparison between the two MBR configurations. Adapted from [107].

	Submerged MBR	**Sidestream MBR**
Application	Municipal-scale systems Solids in activated sludge	Industrial systems Feed with high temperature
Shear by	Aeration	Pump
Operation Mode	Dead-end filtration	Cross-flow filtration
Pressure	Low	High
Energy Consumption	Significantly low	High
Fouling	Low	High

The membrane in an MBR system works by three main principles: size exclusion, adsorption, electrostatic repulsion [107]. In size-exclusion, any compound larger than the membrane's pores' dimension is rejected or adsorptions of chemical species are governed by hydrophobicity and electrostatic repulsion [108]. The optimal circumstance occurs when the two constituents have either opposite charge or just a reduced charge; besides, a low pH usually enhances adsorption. When the membrane and the chemical species have an identical account, the molecules are rejected [108]. This determines the biomass growth in the reactor bulk, with the development of a phase with suspended solids and a (cake) layer directly attached to the surface of the membrane [109]. As an addition to that, the

cake layer growth offers additional adsorption points, this because they are composed of microbial products and polymers that can virtually act as an adsorbent for the chemical species, which must be rejected [110,111].

MBR technology can improve water recycling thanks to its high pathogen elimination performance. The typically accepted limit of total suspended solids of 10 mg/L is not reachable by standard activated sludge technology but can be easily reached by MBR devices in deeper detail. Furthermore, MBR technology applies physical disinfection to the treated water, so the succeeding disinfection unit reaches a higher degree of effectiveness, thus reaching compliance with the imposed microbiological values. We can affirm that water recycling is significant to locate water scarcity and environmental remediation concurrently. In addition, MBRs can efficiently eliminate an extensive range of organic pollutants, even some types that are immune to activated sludge [110].

Pharmaceutically-active compounds (PhACs) characterize an essential fraction of organic pollutants traced in urban water environments. PhACs reach wastewater treatment plants (WWTPs) after human utilization either as metabolized or unmetabolized components. Even in PhACs remediation, MBR technology can deliver an efficient biological action on pollutants and a physical filtration without the limits that activated sludge (CAS) can bring. In fact, in MBR processes, biomass growth is not limited to flocculation microorganisms, however, bacteria can mature as dispersed. More than one study reported the successful usage of MBR technology for PhACs in urban wastewaters [112,113].

Urban and industrial wastewater streams may even contain an assortment of enteric viruses, which take advantage of the faecal-oral routes of transmission to spread and cause numerous severe diseases like hepatitis and gastroenteritis [114]. In municipal sewage, the primary source of infection by enteric viruses starts with detachment from infected people. The norovirus's detaching (or shedding) rate surpasses 10^{10} particles per gram of faeces [115]. Furthermore, waterborne viruses result in more resistance to either environmental variables and treatments when compared to other pathogens (e.g., bacteria), this thanks to some of their peculiar features, either physical and biological.

It is easy to state that MBR applications can expand in many other wastewater streams, an example of greywater. Greywater is domestic sourcing wastewater (e.g., from kitchens, laundries and hand basins). These streams contain a wide range of pollutants like preservatives, emulsifiers, surfactants, softeners and solvents, and some heavy metals (Cd, Hg, Ni, Pb) lower concentrations than in urban wastewaters.

In the most recent years, the problem of energy recovery has mostly narrowed to methane generation by anaerobic digestion (A.D.). The steps involved in the process are hydrolysis, acidogenesis, then acetogenesis, followed by methanogenesis. The latter is the main critical phase because it results in the slowest of all four A.D. steps. So A.D. methane production improvement has been studied with lots of efforts to achieve higher energy efficiencies [116].

Anaerobic membrane bioreactors (AnMBRs) can harvest energy sourcing from wastewater feeds by degradation the organic waste content. Generally speaking, anaerobic methods are preferred because of the high energy recovery rates, thus producing biogas with some important methane content, so they resemble a well promising application route so long. In Figure 10, a scheme of a pilot-scale AnSMBR unit for municipal wastewater treatment is shown [117].
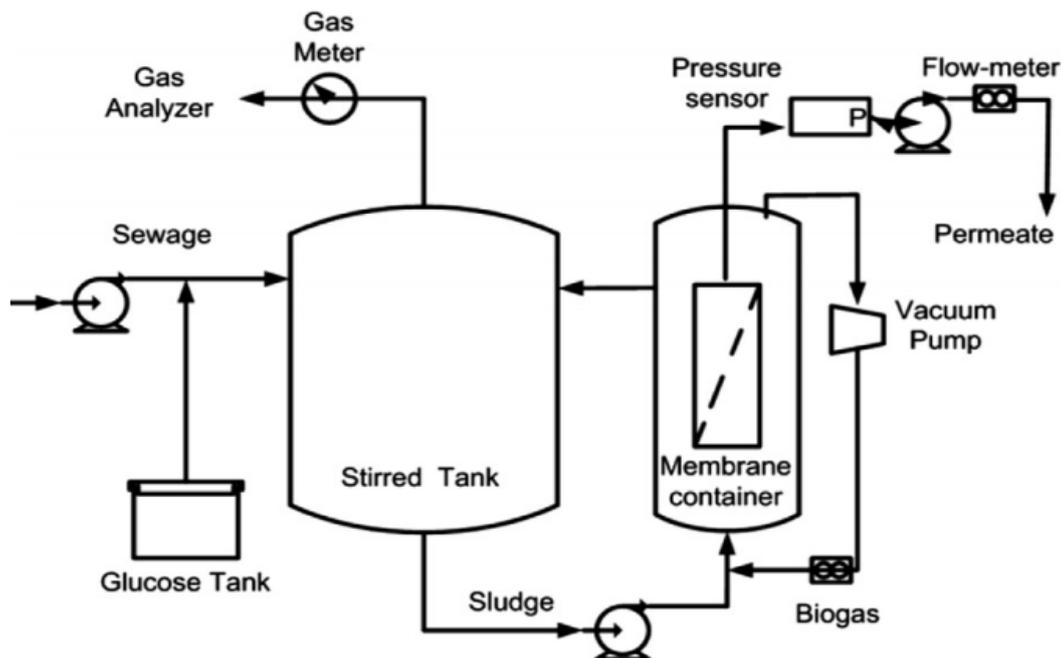
Figure 10. Pilot scale AnSMBR unit for municipal wastewater treatment, as presented by D. Martinez-Sosa et al. [117].

With improved process variables optimization, AnMBR technology for methane production is now a fully developed technology. It has been found that under thermophilic circumstances (ranging from 50 to 0 °C), the growth rates of methanogenic bacteria are better compared to mesophilic conditions. Besides, coadjutants as nanoparticles (N.P.s) (Co, Ni, Fe oxides etc.) and modification methods as high-pressure treatments, alkaline pre-treatments, ammonia soaking can substantially increase the production yields [118].

As a valid application worth mentioning, biohydrogen production by anaerobic processes is in some ways preferred over methane for more than several reasons, such as the more comprehensive flammability limits, higher energy density, and the lower environmental impact during combustion which make hydrogen a preferable energy source. AnMBRs for biohydrogen production have a lesser environmental effect because of the absence of dissolved methane. Simultaneously, addressing both shows (hydrogen and methane) can increase efficiency in an AnMBR process.

Anyway, the more significant issue in biohydrogen production resides in the storage and transportation structure design. Storages with little densities, product losses (because of the hydrogen boiling-off), and methane chemical embrittlement (due to the penetration of hydrogen) are the main concerns in this field.

Nevertheless, energy production by AnMBRs still has engineering, financial, and ecological fields issues. It has been already said that methanogenesis is the slowest of the A.D. stages, resulting in really overall slow processes. Some treatments (either pre-or post) can be combined to quicken the initial steps of hydrolysis and acidogenesis, but in an case those might not increase the overall methane yield. Methane content is one of the critical features in biogases. For AnMBR processes, the product's composition is directly linked to bacterial activity and substrate, starting with the feeds and process variables [119]. In an addition to that, the main challenge in the implementation of AnMBR applications on an industrial scale is the need for invariability of the feed composition to avoid consequent alteration of the methane fraction in the biogas during the time.

The efficiency of AnMBR systems is furthermore affected by the effect of inhibition on the methanogenesis step. This is due to some of the chemical compounds produced during the intermediary stages of the A.D. In some instances, AnMBR goes through fast hydrolysis, leading to better rates of volatile fatty acids (VFAs) generation. The VFAs can

gather in the reactor because they are transformed by methanogens in a extended manner, causing a severe reduction of pH and causing a level of instability in the process.

2.3. Cell Bioreactors

Microbial membrane bioreactors incorporate either a bioreactor in which biomass is suspended and a microfiltration (or even ultrafiltration) unit. Microbial cells are continuously recycled in the reactor through the retentate. Consequently, the biomass concentration is enhanced in the reactor, resulting in efficiency and lower hydraulic residence times.

As membrane fouling is a significant disadvantage in MBR processes, alternative MBR technologies can lead to better results. For instance, the incorporation of a posttreatment with micro-fuel cells (MFCs) in wastewater processing leads, at the same time, to high-quality effluents and modest bioelectricity harvesting, thus empowering the sustainability of wastewater treatments. The whole system is referred to as a microbial fuel cell–membrane bioreactor (MFC-MBR) system.

Two main types of MFCs can be distinguished: dual chamber and single chamber type. The dual-chamber MFC is subdivided in anode and cathode chambers through a membrane, either an ion or proton exchange membrane or even reverse osmosis or UF type. In the anode chamber, microorganisms electrochemically degrade organic and inorganic compounds, thus generating electrons and protons. Bacteria enable electron transfer to the anode by a peripheral circuit, while the protons cross the membrane towards the cathode, reacting with electrons in the cathode chamber. This process generates a current while the contaminants are oxidized [1]. In the following Figure 11 the single chamber and the dual-chamber MFC-MBR layouts are presented.
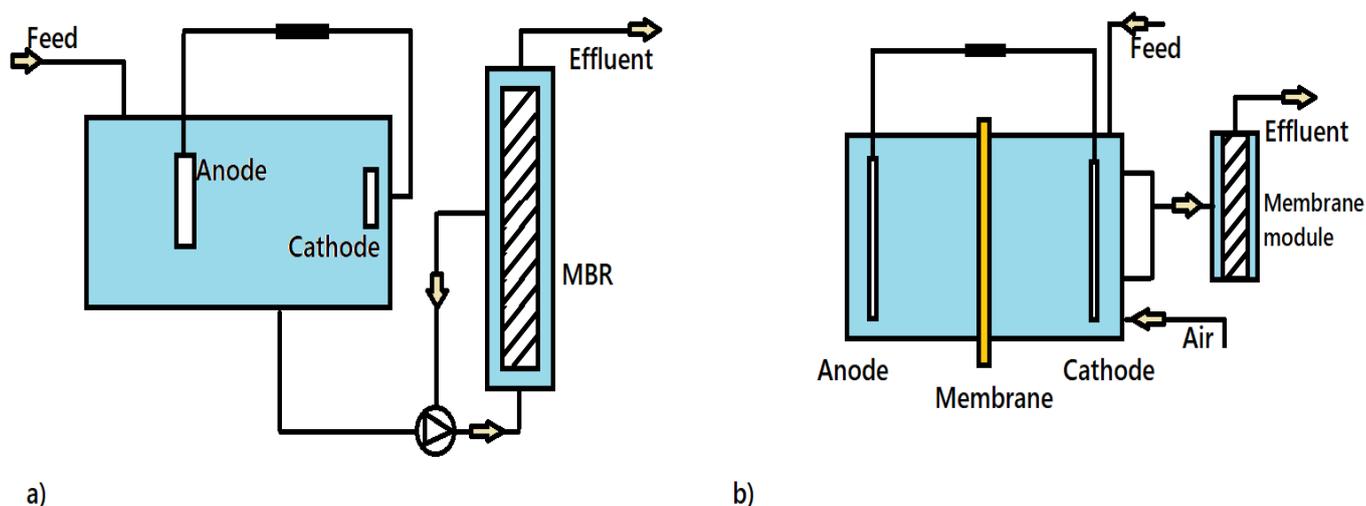
Figure 11. MFC-MBR layouts: (**a**) single chamber, (**b**) dual chamber.

The high contaminant removal of MFC-MBR units has been the focus of many studies. To cite one, Li et al. coupled MBR and MFC and for sewage water treatment. As a result, the COD removal was nearly 94%, near the standard MBR systems [2]. In the Table 5 below, the application of MFC-MBR systems on sewage treatment is reported and the corresponding studies, summing the most recent trends in this research area [3].

Table 5. MFC-MBR coupling systems for wastewater treatment.

Membrane Type	Brand-Model	COD Removal Rate	NH3-N Removal Rate	References
HOLLOW-FIBER MEMBRANE	Self-preparation	95.6%	92.4%	[117]
HOLLOW-FIBER MEMBRANE	Self-preparation	89.6 ± 3.7%	-	[118]
HOLLOW-FIBER MEMBRANE	Motian, China	>90%	90 ± 3%	[119]
HOLLOW-FIBER MEMBRANE	Self-preparation	95 ± 5%	70%	[120]
-	-	>90%	-	[121]
-	-	97%	97%	[122]
HOLLOW-FIBER MEMBRANE	Self-preparation	>95%	-	[123]
-	-	92.5%	70.6%	[124]
HOLLOW-FIBER MEMBRANE	Self-preparation	95 ± 2.5%	85 ± 2.5%	[125]
PVDF	RuiBang, China	90%	80%	[126]
TUBULAR MEMBRANE	Motian, China	86.21%	-	[127]
HOLLOW-FIBER MEMBRANE	Self-preparation	77 ± 7%	-	[128]
PVDF	Koion, South Korea	89 ± 3%	-	[129]
PVDF	Self-preparation	90%	80%	[130]
PVDF	Self-preparation	73.87%	-	[131]

3. Conclusions and Future Perspective

Catalytic membrane reactors (CMRs) represent a process intensification-based technology that combines chemical or biochemical reactions with a membrane separation process in a single unit. CMR promotes an increase in process efficiency and a decrease in capital cost and energy consumption. The membranes used can be polymeric and inorganic, depending on the operating conditions of the process. The membranes can also be inert or catalytically active. Different catalytic processes are performed in very harsh conditions and elevated temperatures, and so the use of the inorganic membranes is favored. The first part is devoted to preparing and applying inorganic membrane in catalytic membrane reactors in this review. Besides, the membrane roles in CMR have also been discussed. They can function as an extractor, distributor, and contractor. As an extractor, removing a reaction product is achieved with better conversion due to the possibility of overcoming chemical equilibrium limitations when the membrane function as a distributor as a reactant is added to the reaction environment in a controlled way by limiting the side reactions. The membrane as a contactor ensures better interaction between reactants and catalytic particles by determining a conversion increase. Afterwards, MR application in various catalytic processes has also been reported and discussed. However, among the different works focused on the CMR application on various industrial processes, their use at an industrial scale is missing. The main disadvantages that block their application on a large scale are the lack of scientific evidence about the CMRs' long-term stability (when used under actual operating conditions) and the high capital costs for their fabrication. Biocatalyst-based processes are currently running in different parts of the world, but the application of inorganic catalysts still needs lots more research before being applied industrially.

Author Contributions: Conceptualization by S.C. (Sudip Chakraborty) and C.A.; data investigation by G.C., data curation, C.A. and D.M.; writing—original draft preparation, S.C. (Sudip Chakraborty), C.A., G.C., D.M.; writing—review S.C. (Sudip Chakraborty) Sudip Chakraborty and C.A., M.I.S., editing, S.C. (Stefano Curcio), V.C.; supervision, S.C. (Sudip Chakraborty). All authors have read and agreed to the published version of the manuscript.

Data Availability Statement: Not applicable.

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