

Membrane Reactors for *in Situ* Water Removal: A Review of Applications

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ABSTRACT: This paper reviews the investigated applications of membrane reactors for *in situ* water removal during catalytic reactions in the food, pharmaceutical, cosmetics, and petrochemical sectors. The global target in the works reported herein was the design of a compact and more efficient catalytic reactor (process intensification). By applying *in situ* water removal, two objectives have been pursued: i) overcoming the thermodynamic limitations of the reaction and ii) avoiding catalyst poisoning. Different solution strategies proposed to overcome the difficulties in operating a membrane reactor in extreme acidic or temperature conditions are addressed covering various aspects ranging from membrane materials to reactor configuration design using pervaporation or vapor permeation techniques. As a general remark, membrane materials (polymeric and inorganic) still lack the required characteristics or reproducibility necessary for industrial application in the sectors under study. Further investigation is required to accomplish this task.

1. SCOPE

Water removal is important in several industrial applications, such as the drying of natural gas and compressed air,¹ the dehydration of solvents^{2–7} or monomers for polymeric reactions,⁸ and the separation of azeotropic mixtures.^{9,10} Moreover, water is a byproduct in several chemical reactions, such as in the formation of esters^{11–13} or alternative fuels (e.g., methanol,¹⁴ dimethyl ether,¹⁵ and linear paraffins (C₁–C₁₂₀)¹⁶). These reactions typically have thermodynamic limitations. According to the Le Chatelier principle, the yield and selectivity of the targeted compound are boosted by the removal of the byproducts of the reaction, which in the present study is water. These are also catalytic reactions in which the presence of water inhibits activity, so water removal is desired.

Different technologies have been suggested to remove water from reaction mediums, including heteroazeotropic distillation,¹⁷ sparging of dry inert gas through the reaction medium,¹⁸ or the application of salt hydrates.^{19,20} The most popular technologies involve reactive distillation,^{21–23} sorption,^{23–25} and membrane reactors (MRs)²³ (pervaporation (PV)²⁶ or vapor permeation (VP)¹⁶).

Reactive distillation requires high-energy consumption and is limited because certain water/alcohol mixtures lead to azeotrope formation. Adsorption drawbacks are i) the large dimensions of the fixed-bed reactor required, with the corresponding pressure drop and design problems, and ii) if the adsorbent cannot be regenerated, it creates additional waste with the added complication of selective separation when the reaction is heterogeneously catalyzed. Additionally, certain adsorbents may react with the acid catalyst in the case of homogeneous reactions.¹⁷

The quest for cost-reduction and competitiveness in production has driven the idea of process intensification.²⁷ One of the objectives sought under this idea is the integration of reaction and separation processes in the same unit.^{28–30} The MR in particular is one of the most promising reactor

configurations, as it combines reaction and product separation to reduce capital costs and enhance reactor performance.²⁹

Extensive reviews on MRs dealing with the types of membranes,^{31–33} reactor configurations and modeling,^{28,32,34–40} and specific applications^{26,41–43} have been published previously. A detailed description of MR configurations is beyond the scope of the present work, but a brief summary with the most commonly employed MR configurations will be presented to help the reader follow the discussion.

In the processes where the feed phase is liquid (PV or biological processes), the reactor and the membrane separation layouts might be either two physically distinct units (External Separation Unit, ESU) or integrated into a single unit (*In situ* Separation Unit, ISU).⁴⁴ The most common configurations are diagrammed in Figure 1. When the separation is carried out in an external unit, the stream leaving the catalytic reactor containing both the nonconverted reactants and the products enters the unit for selective product or byproduct removal and the retentate is recirculated to the catalytic reactor. The ISU approach has been very popular in biotechnology and bioprocesses. In this type of process, product accumulation limits the productivity and may degrade into undesirable compounds. In these systems, downstream separations are expensive and technically challenging.³⁴ When the feed phase is formed from gas or vapor components, the separation unit is usually embedded into the reaction system in an ISU configuration.

MRs can be classified as a) inert membrane reactors (IMRs), in which the membrane is adjacent to the catalytic reaction

Special Issue: Enrico Drioli Festschrift

Received: October 29, 2012

Revised: January 21, 2013

Accepted: January 24, 2013

Published: January 24, 2013

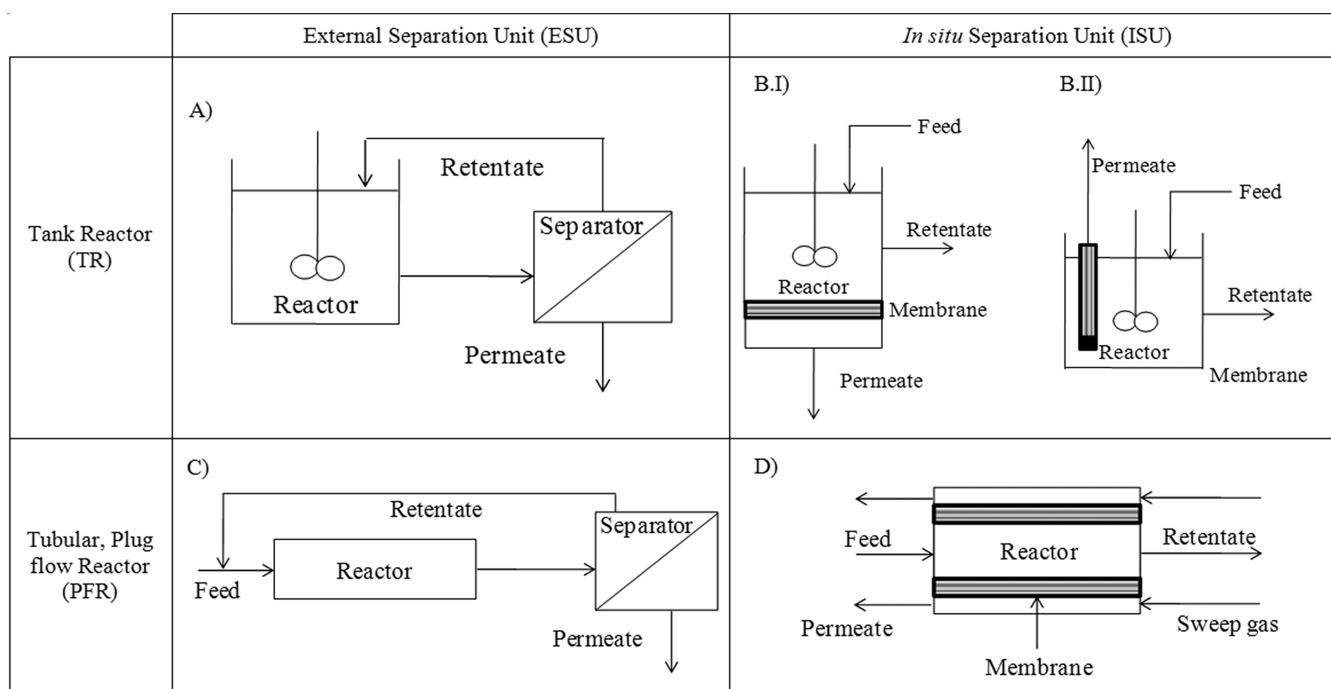


Figure 1. General reactor-membrane separator configurations: A) TR with ESU or semibatch reactor (SBR), B) continuously stirred tank reactor, CSTR, with Flat ISU (B.I) or with Tubular ISU (B.II), C) PFR with ESU, and D) PFR with ISU.

zone located on the feed side, or b) catalytic membrane reactors (CMRs), in which the membrane has the catalyst embedded or the membrane itself possesses catalytic activity to combine the reaction and separation zones within the membrane.⁴⁰ Examples of the possible MR configurations in terms of catalyst configuration²⁹ are shown in Figure 2.

The present work reviews the most important applications for which MRs are employed for *in situ* water removal in catalytic reactions.

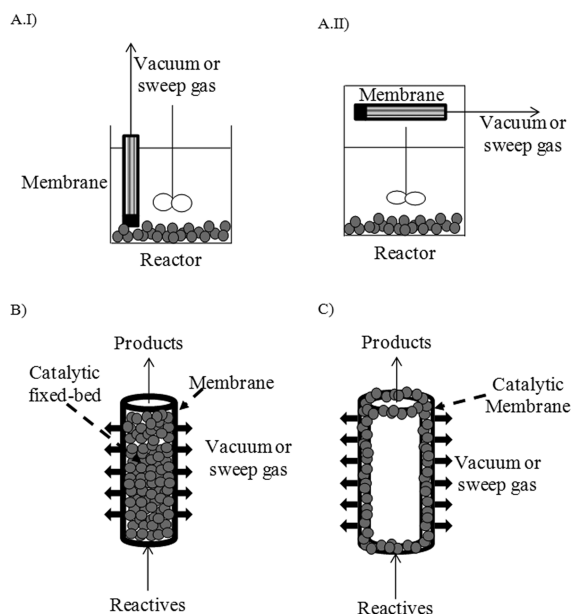


Figure 2. Possible catalyst configurations in the MRs: A.I) suspended catalyst (in PV configuration); A.II) suspended catalyst (in VP configuration); B) catalytic packed-bed MR; and C) CMR (catalyst embedded in the membrane or a membrane with catalytic properties).

2. APPLICATIONS OF MEMBRANE REACTORS FOR *IN SITU* WATER REMOVAL

Water is a byproduct in many catalytic reactions. The presence of this water may inhibit the catalytic reaction because it limits the thermodynamic equilibrium and/or poisons the catalyst. The *in situ* removal of water using MRs has therefore attracted interest for use with many reactions. Some of the most important applications will be presented below.

2.1. Bioapplications: Food, Pharmaceutical, and Cosmetics Industries. Condensation and Dehydration Reactions. Some of the most important components employed in the food, pharmaceutical, and cosmetic industries are synthesized by means of catalytic condensation and dehydration reactions that produce water as a byproduct.

2.1.1. Esterification Reactions. Esters are obtained by reacting alcohols and carboxylic acids in the presence of a homogeneous catalyst that traditionally consists of a mineral acid. Esters are very important components for the manufacture of medicines and solvents.⁴⁵ Moreover, biodiesel consists mainly of fatty acid methyl esters (FAME) (see details in section 2.2.1) that may be obtained by esterification. Therefore, the interest in esterification reactions has gained importance in the last few decades. A list of some commercialized esters, their component precursors, and main applications are collected in Table 1.

During ester synthesis, water is produced as byproduct. In this case, water not only causes the inhibition mentioned previously (thermodynamic equilibrium limitation and catalyst deactivation) but may also hydrolyze the esters, thus hampering reaction efficiency.⁴⁵ Since the 1990s, there has been a steadily growing interest in the application of MRs for selective removal of the products from esterification reactors. Recent studies⁵² comparing hydrophilic and hydrophobic membranes for the selective removal of either the water or the ester confirmed that with the currently available membranes, water removal rather

Table 1. Main Esters Studied in the Literature: Compound Precursors and Industrial Applications

ester	carboxylic acid	alcohol	applications	reference
butyl acetate	acetic acid	butanol	solvent (e.g., for lacquers and coatings manufacture)	Tian et al. ⁴⁶
ethyl acetate	acetic acid	ethanol	solvent (e.g., for lacquers and coatings manufacture)	Tian et al. ⁴⁶
ethyl lactate	lactic acid	ethanol	food and perfumery additive, flavor chemical, and solvent	Delgado et al. ⁴⁷
ethyl oleate	free fatty acid oleic	ethanol	biodiesel	Yin et al.; ⁴⁸ Figueiredo et al. ⁴⁹
geranyl acetate	acetic acid	geraniol	flavor and fragrance compound	Kang et al. ⁵⁰
i-amyl acetate	acetic acid	i-amylol	flavor ester for foods and cosmetics essence	Ping et al. ⁵¹
i-butyl acetate	acetic acid	i-butanol	cosmetics, aroma, and paint industries	Korkmaz et al. ⁵²
i-propyl acetate	acetic acid	i-propanol	solvent for synthetic resins, adhesives, flavoring agents and perfumes; component of printing inks	Qi et al. ⁵³
propyl propanoate	propionic acid	n-propanol	solvent in coatings and printing inks; it is also used in perfumes and fragrances and as a flavoring in food industry	Cruz-Díaz et al. ²²
sugar (glucose) fatty acid esters	fatty acids	carbohydrates (sugar)	nonionic surfactants in pharmaceutical, cosmetics, and food industry	Ganske and Bornscheuer ⁵⁴

than ester removal led to higher esterification conversions. The use of MRs for this purpose is attractive, as they allow enhancement of the process efficiency while reducing process costs due to the smaller amounts of reactants required and the higher conversions obtained.^{13,55} Table 2 chronologically presents the system configurations and main working conditions employed over the last 10 years on MRs for water separation in esterification reactions. Interestingly, the first work reporting a MR to improve esterification was a patent dating back to 1960.⁸⁵

Lim et al.⁵⁶ and Parulekar²⁶ evaluated different alternative configurations of pervaporation membrane reactors (PVMR) for water removal in esterification reactions by means of modeling. Both tubular and tank reactors were assessed, with continuous feeding or batch-wise operations with the reaction and separation taking place at the same time or in two different steps. In the latter case, the stream leaving the membrane unit was recirculated to the reactor unit to increase efficiency.⁷⁴ Although *in situ* membrane separation presented superior conversion results relative to external membrane separation (in both stirred tank and tubular flow reactors),²⁶ the latter type of configuration is convenient when the membrane durability is limited under the acidic conditions typical of esterification reactions. This was also a reason for the authors to use VP technology instead of PV for this application.^{12,58,59,80}

In VP, the membrane is not in direct contact with the reaction environment but, in fact, is in the headspace of the reactor. The components present in the reactor vaporize, and ideally water is selectively separated by the membrane. The components retained by the membrane (reactants) are then condensed back to the reaction media to continue the esterification. Another important advantage of VP is that the membrane lifetime is expected to be longer because it is not in direct contact with the feed.¹ Comparison of the performance of VP and PV configurations depends strongly on the type of membrane employed; therefore, each case must be evaluated independently.

As observed in Table 2, the most typical membrane material employed in PV-aided esterification reactions is poly(vinyl alcohol) (PVA), and they are commonly commercial membranes. For instance, in particular esterification reactions in which lipase-catalyzed reactions occur (glucose fatty acid esters),⁵⁹ a PVA-based membrane working in a VP configuration was advantageous for removing water from the ternary azeotropic mixture formed between the solvents of the system

(ethyl methyl ketone and hexane) and the water produced during the reaction at the mild conditions required for the enzyme to be active (<60 °C).

In general, PVA membranes applied to PV-aided esterification processes must be cross-linked to avoid the esterification of the alcoholic groups of the membrane and its consequent loss of separative properties.⁸⁶ This polymeric material presents high hydrophilicity and stability under acidic conditions upon undergoing the cross-linking treatment. Nonetheless, the limited resistance of the nonpretreated polymeric membranes under low pH conditions hinders their application in these acid systems. Therefore, some authors propose the use of inorganic membranes such as zeolitic membranes, including MFI (i.e., ZSM5),^{66,87} T-type zeolites,⁸⁸ mordenite (MOR) zeolites,⁸⁷ and merlonite (MER), phillipsite (PHI), or chabacite (CHA) zeolites^{76,82} that have high stability at extreme pH conditions. In particular, MER and CHA zeolite membranes present high water fluxes and separation factors greater than 500 in both PV-⁷⁶ and VP-assisted⁸² esterification. It must be noted that certain LTA-type zeolites have acid sensitivity. For instance, de la Iglesia et al.⁷⁵ observed that MOR membranes showed better resistance working under acidic conditions relative to zeolite A membranes. Several works also reported poor resistance of NaA zeolite membranes under acidic conditions^{12,80} and applied VP technology to avoid membrane damage. For example, NaA membranes working in VP mode presented higher acid conversions than PVA commercial polymeric membranes (PERVAP 2201) during VP-aided esterification of i-propyl propionate⁸⁰ due to a higher water affinity and higher fluxes. Nevertheless, the comparison between the performance of PV and VP of a zeolite T membrane working with a 10/90 wt % water/ethanol liquid mixture presented higher total fluxes and selectivities for the PV configuration than for the VP configuration.⁵⁸ The membrane Hydroxy Sodalite (H-SOD) was presented¹³ as a membrane with long-term stability under mild pH conditions (pH > 2.9). However, at lower pH or in the initial stages of an esterification reaction in which the concentration of carboxylic acid is near 50 mol %, the ability of the catalyst to quickly boost the reaction conversion becomes crucial for maintaining the structural integrity of the H-SOD membrane.

Systems with homogeneous catalysts have some important drawbacks, including equipment corrosion and final separation of the neutralized catalyst from the products stream. The replacement of liquid mineral acids by ion exchange resins with

Table 2. Literature Review of MRs Employed for Water Removal in Esterification Reactions

esterification product	membrane	membrane configuration	membrane technology	T ^a (°C)	catalyst	reactor/separator configuration	reference
ethyl acetate	H-ZSM5	tubular	PV	60–90	catalytically active membrane	PPR+ISU	Bernal et al. ⁵⁵
ethyl lactate	zeolite NaA	tubular	VP	25–70	no catalyst and <i>p</i> -toluene sulfonic acid	CSTR+ISU	Jafar et al. ¹²
ethyl acetate	PVA ^d	tubular	PV	nd ^h	sulfuric acid	PPR or CSTR+ISU	Lim et al. ⁵⁶
butyl acetate	PVA-ceramic composite	flat	PV	70–90	Zr(SO ₄) ₂ ·4H ₂ O	CSTR+ISU	Liu and Chen ⁵⁷
ethyl acetate	zeolite T	tubular	VP	87–120	Amberlyst 15	CSTR+ISU	Tanaka et al. ⁵⁸
glucose fatty-acid esters	Pervap2200 (cross-linked PVA)	flat	VP	59	lipase (Chirazyme L-2)	CSTR+ISU	Yan et al. ⁵⁹
ethyl lactate	GFT-1005 (PVA)	flat	PV	75–95	Amberlyst XN-1010	SBR	Benedict et al. ⁶⁰
propyl propanoate	cross-linked blend PVA/PSSH ^b 33/67	flat	PV	50	catalytically active membrane	CSTR+ISU	Nguyen et al. ⁶¹
biolubricant	CMC-VP-43, Celfa-CM	flat	PV	60	immobilized lipase enzyme (Novozym 435)	SBR	Dórmó et al. ⁶²
ethyl acetate	PERVAP 1000 and 1001 (PVA/PAN ^c support)	nd ^h	PV	60	Amberlyst 15	PPR+ESU or SBR	dos Reis Gonçalves et al. ⁶³
i-amyl oleate (biolubricant)	PERVAP-1005 (PVA)	flat	PV	40	immobilized lipase enzyme (Novozym 435)	CSTR+ISU	Koszorz et al. ⁶⁴
ethyl acetate	PEI ^d /γ-alumina composite	tubular	PV(+adsorption)	30–70	sulfuric acid	PPR+ISU (enclosed in a tank)	Park and Tsotsis ³⁰
nd ^h	Ceramic composite	hollow fibers	PV	75	catalytically active membrane	PPR+ISU	Peters et al. ⁶⁵
propyl propanoate	MFI ^e zeolite (Si/Al = 96)	nd ^h	PV	70	nd ^h	nd ^h	Caro et al. ⁶⁶
geranyl acetate	CA/ceramic composite	flat	PV	30	Novozym 435	CSTR+ISU	Kang et al. ⁵⁰
butyl acetate	PERVAP 2201 (cross-linked PVA)	flat	PV	30–90	no real esterification reaction	CSTR+ISU	Kasaini et al. ⁶⁷
diethyl tartrate	Pervatech silica	hollow fibers	PV	85	Amberlyst 15	PPR+ESU (parallel, series) and PPR+ISU	Nemec and van Gemert ⁶⁸
butyl acetate	H-USY zeolite+ amorphous silica layer	hollow fibers	PV	75	catalytically active membrane	PPR+ISU	Peters et al. ⁶⁹
butyl acetate	H-USY zeolite+ amorphous silica layer	hollow fibers	PV	75	catalytically active membrane	PPR+ISU	Peters et al. ⁷⁰
ethyl lactate and ethyl succinate	GFT-1005 and T1-b (PVA-based)	flat	PV	80–95	Amberlyst XN-1010 and Nafion NRS50	SBR	Benedict et al. ⁷¹
i-amyl acetate	PVA cross-linked with sulfonic acid groups	flat	PV	80	catalytically active membrane (sulfonic acid groups)	SBR	Castanheiro et al. ⁷²
ethyl acetate	two layered H-ZSM5-MOR/α-alumina composite	tubular	PV	60–90	catalytically active membrane	PPR+ISU	de la Iglesia et al. ⁷³
i-propyl acetate	PERVAP 2201	flat	PV	50–70	Amberlyst 15	SBR	Sanz and Giméling ⁷⁴
ethyl acetate	MOR and zeolite A	tubular	PV	85	Amberlyst 15	PPR+ISU	de la Iglesia et al. ⁷⁵
methyl acetate	MER, PHI, and CHA	tubular	PV	40	Amberlyst 15(H) and scandium trifluoromethanesulfonate	CSTR+ISU	Inoue et al. ⁷⁶
ethyl lactate	GFT-1005	flat and tubular	PV	95	Amberlyst XN-1010	CSTR or PPR+ISU	Parulekar ²⁶
ethyl acetate	PERVAP 1000 and PVA + Amberlyst 35 particles	flat	PV	80	catalytically active membrane	CSTR+ISU ⁶⁸	Figureiredo et al. ⁷⁷
propyl propanoate	PERVAP 2201D	flat	PV	~60–70	Amberlyst 46	PPR+ESU	Mitkowski et al. ⁷⁸
ethyl lactate	nd ^h	nd ^h	PV	50–95	nd ^h	CSTR+ISU	Wasewar et al. ⁷⁹
i-propyl propanoate	NaA zeolite and PERVAP 2201	tubular and flat	VP	nd ^h	<i>p</i> -toluene sulfonic acid	SBR	Ameri et al. ⁸⁰
ethyl lactate	PERVAP 2201	flat	PV	65–85	Amberlyst 15	SBR	Delgado et al. ⁸¹
ethyl oleate (biodiesel)	PERVAP 1000	flat	PV	60	Amberlyst 15	SBR	Figureiredo et al. ⁴⁹
di- <i>i</i> -propyl adipate	CHA	tubular	VP	92	sulfuric acid	CSTR+ISU	Hasegawa et al. ⁸²
ethyl/butyl acetate	H-SOD	tubular	PV	70–90	Amberlyst 15	SBR	Khajavi et al. ¹³

Table 2. continued

esterification product	membrane	membrane configuration	membrane technology	T ^a (°C)	membrane technology	membrane configuration	membrane technology	membrane configuration	membrane technology	membrane configuration	membrane technology	reference
methyl oleate (biodiesel)	PVA/PES substrate and CM-Celfa	flat	PV	65	PV	flat	PV	flat	PV	flat	PV	Sarkar et al. ⁸³
propyl propanoate	PERVAP 2201D	flat stack module	PV	85–95	PV	flat stack module	PV	flat	PV	flat	PV	Roth et al. ⁸⁴
i-butyl acetate	PVA, PERVAP 1201, PERVAP 2216, and Nafion 117	flat	PV	60–70	PV	flat	PV	flat	PV	flat	PV	Korkmaz et al. ⁵²
butyl acetate	PVA and PVA-TEOS	flat	VP	100	VP	flat	VP	flat	VP	flat	VP	Uragami et al. ⁴⁵

^aPVA: poly(vinyl alcohol). ^bPSSH: poly(styrenesulfonic acid). ^cPAN: polyacrylonitrile. ^dPEI: polyetherimide. ^eMFI: MOR framework inverted. ^fCA: cellulose acetate. ^gThe CSTR+ISU configuration was modified: the feed was continuously fed into a flat membrane PV unit where a catalytically active membrane was placed. The retentate was continuously recirculated into the feed tank. ^hnd: not defined.

strong acid sites is one of the most popular alternatives employed in the literature to avoid the problems listed above (e.g., Parulekar,²⁶ Tanaka et al.,⁵⁸ Benedict et al.,^{60,71} Nemeč and van Gemert,⁶⁸ Sanz and Gmehling,⁷⁴ de la Iglesia et al.,⁷⁵ Mitkowski et al.,⁷⁸ and others; Table 2). Some researchers applied bifunctional membranes, which are membranes combining the catalytic and separatory functions. The material for these membranes can be very different, ranging from zeolitic membranes without further modification (the acid groups from the zeolite material acting as catalyst)^{55,65,69,70,73} to polymeric membranes modified by cross-linking with acid groups, such as PVA membranes cross-linked with sulfonic acid groups,⁷² or blended and cross-linked with ionic polymers, such as poly(styrene sulfonic acid) (PSSH).⁶¹ In addition, a suspension of Amberlyst 35 particles was cast in a layer and cross-linked to the polymeric material of the membrane—in this case, PVA.⁷⁷ The mass of catalyst incorporated in the PVA membrane was lower than that in experiments using a conventional MR configuration with an independent catalyst and thus had a lower ester yield.⁷⁷ However, higher water permeance in the catalytically modified membrane was observed when compared to the PVA membrane without a catalyst. This effect was attributed to the fact that in the catalytically active membrane water was produced in the membrane, and thus a high water driving force was generated. This membrane therefore has the ability to shift the equilibrium of esterification reactions toward ester production.

Novel configurations of the PVMR have been tested in the literature. For example, Park and Tsotsis³⁰ employed an adsorbent in the permeate side of the PV membrane to reduce the partial pressure of water in the permeate side and showed a 10% improvement in conversion over a conventional tubular PV system. An automated system to maintain the water activity constant in the reaction media was developed by Kang et al.⁵⁰ and consisted of a validated method for determining the water activity from the values of water fluxes and permeate partial pressures. These last two values were measured and monitored online during the reaction and were related to water activity. To control the water activity, the vacuum pressure in the permeate was regulated. The online measurement and control of the water activity at a constant optimum value provided an important enhancement in the initial rate of esterification. A very novel approach was introduced by Uragami and co-workers⁴⁵ that employed a combination of several modifications to accelerate the esterification conversion of butyl acetate, including i) the addition of ionic liquid (1-allyl-3-butylimidazolium bis(trifluoromethanesulfonyl)imide ([ABIM]TFSI)) to the reaction media as an insoluble catalyst, causing water phase separation; ii) the use of a hybrid membrane made of poly(vinyl alcohol)/tetraethoxysilane (PVA-TEOS), which has higher water selectivity than a PVA membrane, working in VP conditions and generating higher rates of ester conversion; and iii) the acceleration of the reaction rate efficiency by microwave heating.

Many efforts have focused on model development^{67,78} and process variable assessment.⁷⁹ The design of the system configuration has also been evaluated theoretically through modeling assumptions. For instance, a comparison of the performance of an esterification reaction (diethyl tartrate) in different configurations was performed⁶⁸ by considering a process of two separated units or a coupled separation-reaction unit in a multifunctional module. The coupled separation-reaction configuration presented low viability for slow reactions

and had the drawbacks of low flexibility in the design and operation and difficult maintenance. However, the application of this configuration would be interesting when fast reactions take place and/or when high selectivity is a major concern for removing the product *in situ*. Moreover, regarding the configuration of the two separated units (reaction and separation), a comparison between operating the system in parallel (catalytic esterification reaction and PV in two different loops) or in series (both stages belonging to the same loop) showed that the in-series configuration presented a slightly better performance. However, the parallel configuration allowed the system to work without PV in the initial reaction time where the medium is highly acidic and may significantly damage membranes. Moreover, despite the fact that PV was only applied after reaching maximum water production, the ethanol conversion with a parallel esterification and PV system was practically equal after 18 h of PV-assisted reaction.

2.1.2. Knoevenagel Reactions. The Knoevenagel reaction was named after the German organic chemist Emil Knoevenagel, who first established the mechanism in 1896.⁸⁹ It is a condensation reaction between a carbonilic compound (aldehyde or ketone) and a compound with an active methylene group in the presence of a basic catalyst, traditionally alkali metal hydroxides like NaOH and KOH, or pyridine and piperidine. Important key products are nitriles used in anionic polymerization and α,β -unsaturated esters employed as intermediates in the synthesis of therapeutic drugs and pharmacological products.⁹⁰ Knoevenagel reactions are, like esterification reactions, equilibrium limited. According to the condensation reaction mechanism, a molecule of water is also formed.

Very few works dealing with *in situ* water removal from Knoevenagel reactions by MRs have been published so far. Efforts in this field are relatively recent and were mainly triggered by the study of the substitution of traditional homogeneous catalysts with heterogeneous basic-zeolite catalysts (e.g., Cs-exchanged NaX and mesoporous silicas) that were sensitive to water poisoning.⁹¹ This catalyst substitution led to cleaner production, avoided neutralization and separation steps, and allowed heterogeneous catalyst recovery and regeneration.

The main motivation for research on Knoevenagel reactions, all of which are driven by the Yeung research group,^{90–94} was the development of microreactors. Fine chemicals and pharmaceuticals are high added value products produced in low quantities in batch processes that generate large amounts of waste and demand high catalyst consumption and extensive product purification. Process intensification and miniaturization are keys to clean and efficient fine chemicals production. Indeed, a comparison of the productivity between a multi-channel membrane microreactor and a classical packed-bed MR in terms of product yield and reactant conversion showed a much better performance for the membrane microreactor.⁹¹ This fact was attributed to the higher mass transport rate characteristic of the microchannels that also caused a better performance of the membrane in the microsystem.

Zeolitic membranes have been applied for water removal in Knoevenagel reactions in membrane microreactors. The selection of this type of membranes was based on the reaction temperatures, which are typically between 363 and 413 K, and on the reactants and products of the Knoevenagel reaction (with the exception of water), which are very hydrophobic in character, so high water selectivity was expected. Moreover, it

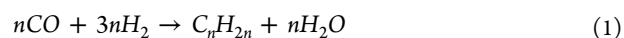
has been proven that zeolite and molecular sieve materials can be incorporated as membranes in miniature chemical devices (microreactors and microseparators).⁹⁵ From the different zeolite membrane types available, only ZSM5⁹¹ and NaA zeolite^{90,93,94} were studied. A comparison between ZSM5 and NaA membranes⁹² showed that to produce a defect-free ZSM5 zeolite membrane, higher membrane thickness was required ($\sim 30 \mu\text{m}$) versus the $6 \mu\text{m}$ thickness for a NaA membrane. Therefore, NaA membranes achieved water fluxes 1 order of magnitude higher than ZSM5 membranes, while the separation factor was maintained at $\alpha_{(\text{H}_2\text{O}/\text{organics})} = 150,000$.

2.1.3. Other Dehydration Reactions. The dehydration of butanediol to form tetrahydrofuran (THF),⁹⁶ an important organic solvent and intermediate for fine chemicals widely used in pharmacy, chemical engineering, and organic synthesis, was previously catalyzed heterogeneously by $\text{H}_3\text{PW}_{12}\text{O}_{40}$. This catalyst was immobilized on a porous ceramic support, and then a cross-linked PVA layer was deposited on top of the support. The catalytically active membrane presented a slightly reduced catalytic activity than the free catalyst. The PVA membrane allowed a very high water/THF permselectivity, between 250 and 425, and water permeation fluxes ranged from 325 up to $500 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, depending on the water partial concentration difference during the reaction.

2.2. Petrochemical Applications: Production of Alternative Fuels and Fuel Additives. The energy sector is one of the most important industries in developed and developing countries. The majority of the energy supplied in these countries comes from fossil fuels.⁹⁷ Constant reduction in petroleum feedstocks leads to the necessity of revising the energetic model to an alternative fuel-based energy model to maintain economic, political, and environmental stability.⁹⁸ Moreover, the quality of gasoline and diesel is ensured by the presence of certain additives that increase the octane number to the standards required by the market.⁹⁹ These additives are oxygenates—primarily ethers and alcohols. It must be noted that both the alternative fuels and gasoline additives (mainly ethers and acetals) herein are considered to have the characteristic that they are produced by means of catalyzed condensation reactions where a molecule of water is produced, hence the current interest in their production.

An alternative fuel is defined as an energy carrier that is not from crude oil origin, has a high heating value, and has combustion that causes lower pollution levels in comparison with conventional fuels.¹⁰⁰ In the present work, we refer to alternative fuels as either those compounds that may be a complete or partial substitute for gasoline or diesel as an energy source (e.g., methanol (MeOH) and dimethyl ether (DME), also oxygenates or fuel additives, or biodiesel) and those synthetic hydrocarbons obtained by means of Fischer–Tropsch (FT) synthesis. These compounds are usually produced from coal, natural gas, or biomass and are therefore sometimes considered renewable fuels when their raw material sources are plants or biological wastes.

2.2.1. Synthetic Hydrocarbon. The typical production of synthetic hydrocarbons from C_1 to C_{120+} constitutes the FT process. In this reaction, synthesis gas, a mixture of CO and H_2 , produced by coal, natural gas, or biomass oxygen/steam gasification or partial oxidation reactions is converted into a complex mixture of hydrocarbons employing a metallic catalyst based on either cobalt (Co) or iron (Fe):



In this reaction, large amounts of water are obtained causing catalyst deactivation and high partial pressures of water that decrease the reaction rate (inhibitory effect).¹⁰¹ Apart from the classical interest in water removal, some research has tackled a more ambitious challenge: the incorporation of CO₂ (CO₂ capture and valorization) into the process as a reactant.^{102,103} The direct hydrogenation of CO₂ to hydrocarbons is not significant, but an indirect hydrogenation via CO as an intermediate is dominant (eq 2). At the usual CO₂ concentrations present in the synthesis gas stream, the Water-Gas Shift (WGS) reaction (eq 2) proceeds to the right. The promotion of the reverse WGS reaction was theoretically proven to occur¹⁰² by removing H₂O from the reaction media according to Le Chatelier's principle:



The first mention of a MR for the *in situ* water removal in a FT synthesis was found in 1999 in a patent by Espinoza et al.¹⁰⁴ applied to MRs with a reactor zone provided by a slurry or fluidized bed. In this patent, the performance of several tubular zeolite-based membranes was tested experimentally, e.g., MOR, ZSMS, zeolite A, chabazite, and silicalite, under typical FT reactive conditions (T between 200 and 250 °C for low temperature FT reactions (gas–liquid–solid reaction) that lead to wax or 300–360 °C for high temperature FT reactions (gas–solid reaction) that lead to short chain alkenes and gasoline¹⁰⁵ with pressures between 2 and 4.5 MPa) using N₂ as inert sweep gas. Different porous membrane supports (stainless steel or ceramic, such as α -alumina) were employed in the fabrication of the membranes, although stainless steel was preferred. The successful deposition of zeolite membranes on stainless steel supports is very important for the viability of its industrial applications.¹⁰⁶

Other membranes proposed in the literature for a fixed-bed reactor configuration were amorphous silica membranes on a ceramic support (Si(OH)_xO_y/ α -Al₂O₃),^{102,103,107,108} 4A-zeolite,^{103,109} and ceramic-supported polymer (CSP) membranes.¹⁰⁷ Amorphous silica membranes presented low hydrothermal stability, whereas CSP membranes suffered from wax deposition blocking the membrane pores¹⁶ and low temperature resistance (CSP membranes resisting 290 °C have not been reproduced). Although the H-SOD membrane was considered a promising candidate for this application due to its high H₂O/H₂ permselectivity,^{16,101} it was never tested above 190 °C, and recent works have noted the thermal and hydrothermal instability of this material.¹¹⁰ From the results, both experimental and theoretical, it was concluded that zeolite membranes were the most suitable materials for FT applications due to their adequate water permeance and permselectivity and their hydrothermal and mechanical stability under the reaction conditions.

Comparison of conversions and yields between conventional PBR and a MR employing different sweep gases showed that when the membrane selectivity was low, i.e., with amorphous silica membranes, using Ar as inert sweep gas caused reactant loss through the membrane and a reduction in reaction performance. This effect could be overcome by using H₂ or feed gas (synthesis gas).¹⁰³ When the membrane selectivity was high, such as with the CSP membrane, the application of a MR for *in situ* water removal always led to higher reaction performance independent of the sweep gas employed.¹⁰⁷

Recently, theoretical approaches to enhance the design of MRs for *in situ* water removal in FT synthesis have been

published.^{111–113} One of the proposed configurations to increase the gasoline production rate consisted of a packed-bed MR with *in situ* water removal, considering an ideal H-SOD membrane, followed by a fluidized bed MR with *in situ* H₂ removal by means of a Pd–Ag membrane in a coupled system.¹¹¹ This system achieved a 37% improvement in gasoline production compared to conventional packed-bed reactors. Another configuration was a thermally coupled membrane dual-type reactor where the dehydrogenation of decalin (endothermic reaction) was coupled to the FT synthesis (exothermic reaction).¹¹² The coupling of exothermic and endothermic reactions in the same reactor increased the heat exchange efficiency. With this configuration, enhanced hydrogen and gasoline production rates and reduced CO₂ and methane yields were found. The optimization of the operating conditions of a thermally coupled MR was addressed by Rahimpour et al.¹¹³

2.2.2. Biodiesel and Biolubricants. Biodiesel consists mainly of fatty acid methyl esters (FAME) that are employed in diesel engines mostly in blends ranging between 5 and 20 vol% with petrodiesel.¹¹⁴ There are two main fabrication methods of FAME: i) the trans-esterification of trialkyl glycerides (TAG) with basic catalysis (eq 3) and ii) the acid-catalyzed esterification of free fatty acids (FFA) with alcohols (eq 4) such as methanol.²³ The trans-esterification of TAGs produces glycerol as a byproduct, whereas esterification leads to water (section 2.1.1). It is in this second route, or when both routes are combined in the same reaction, that we are interested in the present work.



Biolubricants are fatty acid esters also produced by esterification of FFA from plant oils, such as oleic acid, with long chain alcohols, such as those present in fusel oil (e.g., ethanol, propanol, i-propyl alcohol, i-butyl alcohol, and i-amyl alcohol) (eq 5).^{62,64}



While biodiesel and biolubricants herein are produced by means of an esterification reaction, they have been treated in this separate section due to their specific applications. A literature review was therefore collected in Table 2.

Similarly to other ester syntheses, different types of catalysts have been tested to improve FAME esterification yield. As previously mentioned in section 2.1.1, in homogeneously catalyzed systems the membrane stability is very important. For example, a hollow fiber module made of an aromatic polyimide membrane tested by Okamoto et al.¹¹⁵ in the PV configuration using p-toluenesulfonic acid as catalyst presented plastification (they attributed this phenomena to the presence of ethyl oleate and oleic acid in the feed solution). When they worked in VP,¹¹⁶ however, the membrane was stable. The strategy followed by Sarkar et al.⁸³ to avoid damage to the composite PVA/PES-supported membrane by acids was to reduce the sulfuric acid concentration to 0.3 wt %. Even at this low catalyst concentration, the application of a PV-assisted technique at 65 °C allowed for a 99.9% conversion. The MER and CHA membranes developed by Inoue et al.⁷⁶ were very acid-tolerant and water permselective, even in the presence of methanol. These characteristics made these membranes promising

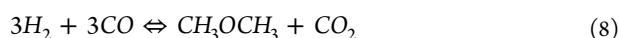
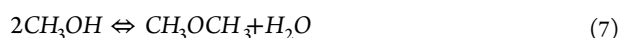
candidates for biodiesel synthesis by PV-assisted esterification with homogeneous catalysts.

The application of heterogeneous catalysts in the esterification of fatty acids is still rare.⁴⁹ Similarly to the majority of heterogeneous esterification literature analyzed in section 2.1.1, in this case⁴⁹ also a PVA-based membrane was employed. The application of the PVA membrane for water removal caused a 2-fold increase in the FAME conversion (above the equilibrium limit). In addition, water/ethanol selectivities near 120 at 25 °C were observed.

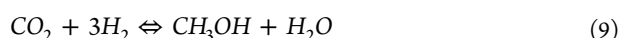
Esterification to produce biolubricants can be catalyzed by lipase enzymes. The effect of *in situ* water removal in different immobilized lipase-catalyzed systems has therefore been investigated.^{62,64} The activity of these enzymes was very sensitive to water and alcohol content.⁶⁴ High alcohol caused nonreversible inactivation of the enzyme, and a minimum amount of water was required for the enzyme to show activity. As a consequence, the rate of reaction was slow at the beginning of the reaction, and when water was formed, the activity of the enzyme increased until the water content began to inhibit the reaction. The membrane applied in these systems should therefore maintain the optimum water content required by the enzyme catalyst.

2.2.3. Methanol and Dimethyl Ether. Nowadays, MeOH and derived DME are primary raw materials for the chemical industry as intermediates to produce light olefins⁹⁷ or gasolines,^{117,118} among other materials. These compounds present excellent combustion characteristics and high octane numbers and are therefore excellent fuels in internal combustion engines and in new generation direct methanol fuel cells (DMFC). They can also be employed as fuel additives to increase octane number.^{100,119,120}

MeOH and DME are currently synthesized by the catalytic hydrogenation of syngas (CO + H₂), which is produced by the gasification of fossil fuels or biomass. Eq 6 presents the conventional reaction for MeOH production. To obtain DME, a subsequent dehydration reaction (eq 7) is required. The WGS equilibrium reaction (eq 2) is always present in this route. The net reaction for the synthesis of DME is presented in eq 8:



Eq 6 and eq 8 show that no net water content is formed during MeOH and DME production. However, the drive to find techniques for CO₂ capture and recycle it into fuels and other products has evolved into the assessment of the feasibility of synthesizing MeOH and DME with CO₂ present in the reactant mixture (eq 9):¹²¹



The types of membranes studied in the literature for *in situ* water removal (MRs) in MeOH and DME production are mainly silica–alumina composite membranes^{15,121} and zeolite membranes, such as A-type,¹⁴ FAU-type,¹²² and MOR.¹²³ Water permeances ($Q_{\text{H}_2\text{O}}$) and water/hydrogen ($S_{\text{H}_2\text{O}/\text{H}_2}$) and water/MeOH ($S_{\text{H}_2\text{O}/\text{MeOH}}$) permselectivities in zeolite membranes were usually higher than in the silica–alumina membranes (e.g., $Q_{\text{H}_2\text{O}} = 2.8 \times 10^{-7} \text{ mol m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ and $S_{\text{H}_2\text{O}/\text{H}_2} = 49\text{--}159$ and $S_{\text{H}_2\text{O}/\text{MeOH}} = 73\text{--}101$ for MOR^{123,124} vs

$Q_{\text{H}_2\text{O}} = 0.76 \times 10^{-7} \text{ mol m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ ¹⁰⁸ and $S_{\text{H}_2\text{O}/\text{H}_2} = 1.5\text{--}2.5$ and $S_{\text{H}_2\text{O}/\text{MeOH}} = 8.4$ for silica–alumina composite¹⁵). Moreover, silica–alumina membranes were found to be unstable at high temperatures.^{15,16} The comparison of CO₂ conversion into MeOH between a conventional reactor and a MR with a zeolite-A membrane¹⁴ showed that the vapor components (H₂O and MeOH) preferentially permeated the membrane instead of the gas components (H₂, CO, and CO₂). A theoretical evaluation of the influence of the zeolite-A membrane permselectivity ($S_{\text{H}_2\text{O}/\text{MeOH}}$) in the MR performance¹²⁵ demonstrated that this parameter had negligible influence in terms of CO₂ conversion and MeOH selectivity, but this work did not consider catalyst deactivation caused by water and further MeOH purification.

Additional research dedicated to the evaluation of membrane characteristics also reported the fabrication and application of ZSM5 and composite MOR/ZSM5/CHA membranes for ternary water/alcohol (methanol, ethanol, or i-propanol)/O₂ mixture dehydration¹²⁴ and for binary water/light hydrocarbon (methane, propane, n-butane) mixtures.¹²⁶ The composite MOR/ZSM5/CHA membrane presented higher $S_{\text{H}_2\text{O}/\text{MeOH}}$ (4.4 at 25 °C) and water/propane ($S_{\text{H}_2\text{O}/\text{C}_3\text{H}_8} = 6.6$) selectivities than ZSM5 membranes ($S_{\text{H}_2\text{O}/\text{MeOH}} = 2.3$ and $S_{\text{H}_2\text{O}/\text{C}_3\text{H}_8} = 1.7$, respectively). The water permeance of composite membranes in the temperature range 25–250 °C for water/alcohol/O₂ mixtures was maintained practically constant at $2.7 \times 10^{-7} \text{ mol m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$. The temperature impact was higher in MeOH and O₂ permeance, therefore reducing the water permselectivity of the membrane to $S_{\text{H}_2\text{O}/\text{MeOH}} = 2.5$ at 250 °C. This was consistent with the results of Bernal et al.,¹²⁶ who found a water permeance in water/propane mixtures at 31 °C of $2.7 \times 10^{-7} \text{ mol m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$.

FAU-type zeolite membranes¹²² presented preferential permeation of polar molecules, showing water/MeOH selectivities of $S_{\text{H}_2\text{O}/\text{MeOH}} = 1.9\text{--}9.0$, while water/hydrogen selectivities were much higher, $S_{\text{H}_2\text{O}/\text{H}_2} = 10\text{--}830$ at temperatures between 130 and 180 °C. This effect was caused by a mechanism of preferential adsorption in the hydrophilic material rather than a size exclusion mechanism. Therefore, the presence of water and MeOH in systems with FAU membranes limited the permeation of H₂. This behavior was also observed in other zeolitic materials. For example, the effect of the presence of water vapor at high temperatures (>300 °C) on the gas component permeance of a ZSM5 membrane was assessed by Wang and Lin.¹²⁷ The comparison between the component permeance of a H₂/CO₂ binary mixture and a H₂/CO₂/H₂O ternary mixture between 300 and 550 °C showed a suppression effect on H₂ and CO₂ permeances in the presence of water due to preferential water vapor adsorption in the membrane. This result on MFI zeolite membranes has also been shown in other works at lower temperatures (<300 °C).¹⁰⁹ This effect results in a promising characteristic of these zeolite membranes for the present application. As a general remark, it must be noted that industrial implementation of zeolitic membranes is still limited by their poor synthetic reproducibility.¹²⁸

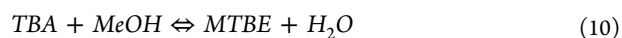
The most popular MR configuration presented in the literature for MeOH and DME production is a tubular MR containing the catalyst in a packed-bed. Under this configuration, theoretical studies were performed on the synergy

present during single-step DME production, that is, the production of MeOH and its further transformation into DME in a single reactor by means of a bifunctional catalyst.¹²⁹ While this synergy was evident when CO-rich feed gases were employed, if CO₂ was incorporated in the feed this synergy disappeared. In this latter case, the application of a membrane for *in situ* water removal significantly improved the theoretical DME selectivity.

Some alternative reactor configurations including an *in situ* water removal stage have been proposed. For example, Bayat and Rahimpour¹³⁰ proposed a thermally coupled multitubular two-bed MR. The exothermic side of the reactor consisted of catalytic MeOH production with an internal hydrophilic H-SOD membrane (ideal hypothesis) and an external endothermic side consisting of the dehydrogenation of cyclohexane to produce H₂ that was selectively separated by a Pd–Ag membrane located outside the fixed-bed. This configuration presented the following advantages: the reaction was displaced to the formation of both high-added value products (MeOH and H₂) by applying specific permselective membranes and the performance was enhanced by coupling the energy balance of the endothermic and exothermic reactions. Another thermally coupled two-bed multitubular reactor configuration proposed consisted of the synthesis of DME from biosyngas coming from an integrated aqueous-phase glycerol reforming process.¹³¹ While this system did not display favorable behavior without *in situ* H₂O removal, when a membrane was integrated into the process the amount of waste byproducts was minimized and it became an energetically efficient alternative for producing DME.

2.2.4. Other Fuel Additives. A fuel additive is any substance added to fuel for any desired quality, e.g., anti-icing, anticorrosive, and higher octane number. Oxygenates have been considered fuel additives since the 1970s to increase the antidetonating power of the gasoline and to reach the minimum oxygen content required by regulations to reduce emissions.^{99,132} The most popular oxygenated additive families are alcohols (methanol, ethanol, and tert-butyl alcohol, TBA) and ethers (methyl tert-butyl ether, MTBE; ethyl tert-butyl ether, ETBE; and tert-amyl methyl ether, TAME). Acetals are considered important biobased diesel additives.²¹

MTBE was one of the first compounds added to gasoline to replace lead to boost octane number and is also used to reduce monoxide emissions.⁹⁹ Although it is currently rarely employed due to environmental issues, Salomon et al.¹³³ evaluated an alternative route of production to the original Hüls process¹³⁴ by applying a MR for *in situ* water removal. The reaction path is presented in eq 10, which is divided into two secondary reactions (eq 11 and eq 12) and is heterogeneously catalyzed by an acid resin or polymer



with IB standing for i-butene.

Composite MOR/ZSM5/CHA and NaA zeolite membranes were tested in the application of MTBE syntheses.¹³³ Water fluxes varied between 0.06 and 0.76 kg·m⁻²·h⁻¹, and the water permselectivities decreased in the order of polarity of the components ($S_{H_2O/IB} > S_{H_2O/MTBE} > S_{H_2O/TBA} > S_{H_2O/MeOH}$). The water/MeOH selectivity, the lowest in all the sets of

experiments, was found to be between 1.4 and 6.7, respectively. By applying the MR configuration, the MTBE yield was 6.7% higher than the equilibrium predictions.

The application of NaA zeolite membranes to the general synthesis of ethers was evaluated using the liquid-phase etherification reaction of n-pentanol to di-n-pentyl ether (DNPE) catalyzed by ion exchange sulfonated resins as a model.¹³⁵ Under nonreactive PV conditions, high water membrane permselectivity and sufficient fluxes were found. It must be noted, however, that the NaA membrane is restricted to heterogeneously catalyzed reactions due to dealumination of the membrane under acidic conditions. A theoretical technico-economical comparison between a MR and a reactive distillation showed a reduction of up to 60% of the operating costs in the former case.

In the synthesis of ETBE from TBA and ethanol using immobilized β -zeolite as catalyst at 70 °C, a PVA membrane in the PV configuration for *in situ* water removal proved to have higher yields than conventional reactors.¹³⁶ Theoretical comparison of the reactor configuration efficiency between SBR, CSTR+ISU, and PFR+ISU demonstrated higher reaction yields for PFR under the working conditions employed in the studied system.

Acetals are produced by an equilibrium reaction between an alcohol and an aldehyde with water as a byproduct. Aguirre et al.²¹ performed a feasibility assessment of the application of a commercial hybrid silica membrane, HybSi, developed by the Energy research Center of The Netherlands (ECN) in 1,1-diethoxybutane production from bioethanol and butanal. Previous research on the application of reactive distillation in the present system proved that equilibrium limitations were overcome, but the small differences in volatilities resulted in a small increase in the final conversions.¹³⁷ The integration of the chemical reaction and the MR in a single unit increased the conversion from 40% to 70% at 70 °C. HybSi membranes presented high water permselectivity and long time working stability (4 month test period). From these promising results, further conceptual design and techno-economic evaluation of the MR was performed specifically for industrial production of 1,1-dimethoxybutane.^{137,138}

3. OUTLOOK

A comprehensive review of the main applications of MRs for *in situ* water removal is presented, extending it from the food, pharmaceutical, and cosmetic sectors to petrochemical applications. As a common feature of the reported applications the main product was obtained through a thermodynamically limited catalytic reaction where water was produced as a byproduct and could act as a catalyst inhibitor. As a general conclusion, all the presented studies found evidence for higher performance when MRs were employed for *in situ* water removal compared to conventional reactors independently of the reactor configuration.

The most comprehensive studies on water removal with MRs have been performed in esterification reactions. In low temperature reactions, typical in food, pharmaceutical, and cosmetic applications, the most popular membrane employed in the collected references was PVA-based. The principal membrane technology applied was pervaporation. Innovative strategies were developed and directed at avoiding membrane damage by the acidic environment present in the liquid system by i) using two different chemical and separation units and ii) applying vapor permeation instead of pervaporation, iii)

looking for higher acid-resistant membranes, like zeolites, iv) employing a heterogeneous catalyst, such as an acid resin, and v) using catalytically active membranes. Flat sheet membranes were mainly employed in these esterification systems. The search for intensified batch processes for high added-value pharmaceutical products (the Knoevenagel reaction) that generate an excessive amount of waste from the neutralization of unreacted chemicals was an important motivation for the development of micro-MRs.

Studies on *in situ* water removal with MRs in petrochemical applications are scarce. The principal drawback of the application of MRs in this field is the requirement of hydrothermally stable membranes at high pressures (1–4 MPa), high temperatures (200–300 °C), and in the presence of water vapor. Zeolite membranes are the most adequate materials to withstand these restrictive working conditions, but the lack of reproducibility in the fabrication of these materials has been so far a limiting factor to their commercialization. The production of the fuel additive 1,1-dimethoxybutane employing the commercial hybrid silica membrane HybSi at a mild temperature (70 °C) is the only example with a promising industrial application.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support of a postdoctoral grant from the Spanish Ministry of Science and Innovation through the JDC-MICINN program and by projects CTQ2008-00690, CTQ2010-19188, and ENE2010-15585 is kindly acknowledged.

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