Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.855675

53 (2015) 1196–1203
February

Taylor & Francis
Taylor & Francis Group

Progress in membrane liquid–liquid reactor—a review

Zhiqian Jia*

Lab for Membrane Science and Technology, College of Chemistry, Beijing Normal University, Beijing 100875, P.R. China
Tel. +86 010 58802945; email: zhqjia@bnu.edu.cn

Received 26 June 2013; Accepted 3 October 2013

ABSTRACT

Liquid–liquid reactions are crucial in chemical synthesis and industries, such as hydrolysis, oxidation, reduction, nitration, and sulfonation of organic compounds. In recent years, membrane liquid–liquid reactors have drawn great attentions due to the elevated conversion, selectivity, yield, and efficiency. Membrane liquid–liquid reactors can be divided into membrane dispersive reactor and membrane non-dispersive reactor. The membrane dispersive reactor has been employed in the preparation of polymer microspheres and microcapsules. The non-dispersive membrane reactors are widely used in chemical reactions (e.g. consecutive, reversible, and irreversible reactions) and biochemical reactions (e.g. resolution of racemic compounds, and reaction of non-chiral substrate). The feature, applications, advantages, and limits of the membrane liquid–liquid reactors are briefly reviewed.

Keywords: Membrane liquid–liquid reactor; Membrane dispersive reactor; Membrane non-dispersive reactor; Liquid–liquid reaction

1. Introduction

Liquid–liquid (L–L) reactions, occurring between two immiscible liquids, are crucial in chemical synthesis and industries, such as ester hydrolysis, oxidation, reduction, aromatic nitration, sulfonation, Friedel-Crafts alkylation, etc. The L–L reaction rate is determined by mass transfer of chemical species between the two liquid phases and chemical reaction kinetics.

In traditional L–L reactors, e.g. stirred tank, spray reactor, rotor-stator spinning disk reactor [1], one liquid is dispersed into another one, and the interfacial area is limited and varies with operation conditions, resulting in low apparent reaction rate, difficulty in process design, control, and scale-up. For parallel or consecutive L–L reactions, mass transfer may affect the reaction selectivity. Although ultrasound is able to enhance the apparent L–L reaction rate by cavitation, reducing droplets size and intensifying mixing [2], the commercial application of ultrasound reactors is seldom reported. Micro-reactors can increase the interfacial area and then the overall reaction rate [3]. Nevertheless, currently the micro-reactors are still very expensive. Moreover, the conversion of reversible reactions in the above-mentioned reactors is limited by chemical equilibrium.

In recent years, membrane L–L reactors have drawn great attentions due to elevated reaction rate, conversion, selectivity, yield, and efficiency, along with relatively low price, easily in scale-up. As shown in Table 1, membrane L–L reactors can be generally divided into two categories: (1) Membrane dispersive

*Corresponding author.

Table 1
Membrane liquid-liquid reactors

Category	Feature	Applications	Advantages
Membrane dispersive reactor	One liquid is dispersed into another one through membrane pores to obtain tiny droplets	(1) Preparation of polymer microspheres (2) Preparation of polymer microcapsules	Generation of uniform tiny droplets with high efficiency
Membrane non-dispersive reactor	The membranes separate the two liquid phases. The reactant or product is extracted from one phase to another one through membranes	(1) Chemical reactions (i) Consecutive reactions (partial oxidation, chlorination of benzene, etc.) (ii) Reversible reactions (esterification, transesterification, hydrolysis, alcoholysis, etc.) (iii) Irreversible reactions (e.g. phase-transfer catalytic reaction)	Large and defined interfacial area; elevated conversion for reversible reactions, improved selectivity for consecutive reactions, or enhanced mass transfer rate for irreversible reactions; easily in scale-up
		(2) Biochemical reactions (i) Resolution of racemic compounds (drugs, organic acids, amino acids and ester) (ii) Non-chiral reactions (hydrolysis, wastewater treatment, preparation of organic acid, etc.)	High productivity and conversion, minimized loss of activity, stable quality of products, resistance towards organic solvents or substrate

L–L reactor. In this reactor, a liquid phase is dispersed into another one through porous membranes to obtain tiny droplets, which can subsequently conduct polymerization to form polymer microspheres or microcapsules (Fig. 1(a)). (2) Membrane non-dispersive L–L reactor. In this reactor, the two liquid phases are separated by microporous or non-porous membranes (Fig. 1(b)). The reactant or product is extracted from one liquid phase into another one through membranes to enhance the selectivity or conversion. This paper briefly reviewed the progress in membrane L–L reactors, including feature, applications, advantages, and limits.

2. Membrane dispersive L–L reactor

2.1. Preparation of polymer microspheres

Polymer microspheres with mean diameter of 1–40 μm can be used as packing materials for column chromatography techniques, carriers of enzymes, drug delivery systems, dry and liquid toners for electrophotography, spacers for liquid crystal displays [4], etc.

Uniform polymer microspheres can be produced using membrane emulsification-polymerization or membrane emulsification-swelling-polymerization techniques. In membrane emulsification, the disperse phase is forced through the membrane pores into the continuous phase, and fine droplets are formed *in situ* at the membrane/continuous phase interface. To allow continuous and optimal production of mono-dispersed emulsions, affinities between the membrane surface, disperse, and continuous phase should considered. In the preparation of O/W emulsions, hydrophilic membrane (e.g. Shirasu-porous-glass membrane, stainless steel membrane) is used to disperse the oil phase into aqueous phase so that the wetting and spreading of the oil phase on the membrane surface can be avoided [4]. Analogously, in the preparation of W/O emulsions with narrow size distribution, hydrophobic membrane is employed to disperse the aqueous phase into the oil phase.

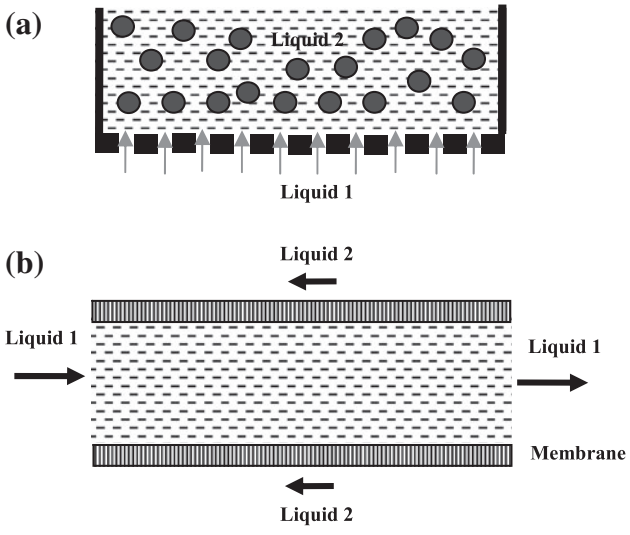

Fig. 1. Schematic diagram of membrane liquid-liquid reactors. (a) Membrane-dispersive reactor. (b) Membrane non-disperse reactor.

2.1.1. Membrane emulsification-polymerization

In membrane emulsification-polymerization, membrane emulsification is firstly employed to prepare O/W, W/O, or W/O/W emulsions. Then, polymerization is carried out to obtain polymer microspheres. For example, Dowding et al. [5] used hydrophilic SPG membrane to disperse an oil phase containing a monomer or a mixture of monomer, initiator, and other potential additives (solvents, diluents, cross-linking agents, etc.) into an aqueous solution of emulsifiers and stabilizers to form uniform O/W emulsion. Then polymerization is conducted by transferring the emulsion into a reactor and heating it above the decomposition temperature of the initiator under mild agitation and nitrogen bubbling conditions. Polymer microspheres with relative standard deviation (RSD) in diameter of about 10% are produced, and classification is needed to obtain particles of RSD 4%, which is a minimum requirement for liquid crystal displays spacers.

For the preparation of W/O emulsion, Nagashima et al. [6] dispersed an aqueous mixture of acrylamide (AAm) and acrylic acid into the oil phase using a hydrophobic SPG membrane (modified with octadecyltrichlorosilane and trimethyl chlorosilane). The W/O emulsion was then subjected to polymerization at 70˚C to form poly(acrylamide-*co*-acrylic acid) hydrogel particles, which can be used in swelling-controlled drug delivery systems.

In the preparation of W/O/W emulsions, Ma et al. [7] dispersed acrylamide aqueous solution into styrene (St) using an ultrasonic homogenizer. Then, the W/O emulsions were forced through a hydrophilic SPG membrane into the external aqueous phase. After polymerization, the PSt-PAAm composite particles were obtained. As amides can be easily hydrolyzed to carboxylic acids or degraded to amines, the PSt-PAAm particles can serve as immobilization media for biologically active substances such as proteins and cells.

To prepare porous polymer microspheres, an inert diluent can be included in the monomer phase. After polymerization, the diluent is removed by extraction and porous microspheres are obtained. Dowding et al.

[5] used a stainless steel plate membrane (laser-drilled pores, 100 or 150 μm in diameter) in emulsion. The continuous phase comprised aqueous solution of poly(vinyl alcohol) (PVA) and sodium chloride (5.66% w/w), while the dispersed organic phase comprised styrene (monomer), divinyl benzene (cross-linking monomer), 4-methyl-2-pentanol (diluent), and polystyrene (0.93% w/w). The addition of polystyrene can increase the viscosity of the dispersed phase and the rigidity of the droplet/water interface.

2.1.2. Membrane emulsification-swelling-polymerization

The hydrophilic nature of SPG membranes favors the formation of uniform microspheres from hydrophobic monomers, while hydrophilic monomers tend to yield a wider droplet size distribution due to the wetting of SPG surface. To overcome this problem, Omi et al. [8] prepared the primary emulsion of hydrophobic monomers by SPG membrane and the secondary emulsion of hydrophilic monomers by conventional rotor-stator homogenization. Mixing these two emulsions causes absorption of the hydrophilic monomers from the secondary emulsion in the primary emulsion droplets. Despite the polydispersity of the secondary emulsion, the swollen droplets retain the uniformity of the primary emulsion.

2.2. Preparation of polymer microcapsules

Microcapsules have wide applications in controlled release, storage, phase change materials, etc. Layer-by-layer, cross-linking, emulsification, solvent evaporation, and spray drying are often employed in the preparation of microcapsules. However, the microcapsules size is difficult to control and the size distribution is usually broad for most of these techniques.

Charcosset and Fessi [9] prepared nanocapsules by membrane emulsification-interfacial polymerization method. The oil phase (containing acetone, Span 80, hexyl laurate, and sebacoyl chloride) is dispersed into the aqueous phase (containing Tween 20 and diethylene triamine) by the membranes, and interfacial polymerization occurs on the droplets interface. It was found that, the size of nanocapsules increased with the average membrane pore size (1,000 Da, 150,000 Da, 0.1 μm), and nanocapsules of 260 nm in size was obtained for membranes cut-off of 1,000 Da.

3. Membrane non-dispersive L–L reactor

In membrane non-dispersive L–L reactor, microporous or non-porous membranes are used to separate the two phases and extract the component from one phase into another one. Microporous membranes provide large and defined interfacial area, which is beneficial for mass transfer, process design, and scale-up. However, microporous membranes may run into difficulties in maintaining an aqueous-organic interface because some species (e.g. biomedium) presenting in the reactions system can act as surfactants, resulting in considerable reduction in membrane breakthrough pressure, and mixing of the two phases. Thus, membrane structure, surface property, and transmembrane pressure should be carefully chosen, which may be difficult to achieve in actual membrane reactors [10]. Non-porous membranes such as silicone rubber membranes exhibit high permeability and selectivity to small hydrophobic molecules. High permeability is mainly due to extensive swelling of the membranes in the presence of organic solvents. However, excessive swelling may cause deterioration of membranes mechanical properties. The membrane non-dispersive L–L reactor has been widely employed in chemical and biochemical reactions.

The application in chemical reactions can be divided into three categories: (1) Consecutive reaction. Consecutive reactions include partial oxidation, chlorination of benzene, etc. In order to improve the selectivity, the intermediate products are extracted from the reaction zone by membranes to avoid further reaction. (2) Reversible reaction. Most chemical reactions are reversible, such as esterification, transesterification, hydrolysis, alcoholysis, etc. To overcome the limitation of chemical equilibrium, the product is continuously extracted from the reaction system through membranes. (3) Non-reversible reaction. In non-reversible reactions such as phase-transfer catalysis (PTC), the membranes can provide large and fixed interfacial area to improve mass transfer, process control, and design.

Biochemical reactions play increasingly important role in chemical, biological, and environmental fields. In biochemical reactions, most biocatalysts (enzyme, microorganisms, animals, or plant cells) have optimal biological performance in water. However, lots of substrates or products of biochemical reactions are poorly soluble in water, and some of them inhibit biocatalytic activity above critical concentrations. Moreover, the direct mixing of biomedium and organic phases also cause emulsions that make downstream separation a practical constraint. In membrane non-dispersive reactor, biocatalysts are immobilized on the membrane surface by adsorption or chemical binding, or freely circulated on the retentate side. The membrane separates the aqueous and organic phases to avoid emulsion formation and toxicity of the organic solvent

or substrate, while enable the transportation of substrate and/or removal of product, resulting in high productivity and conversion, minimized loss of activity, stable quality of products, resistance towards organic solvents, or substrate, etc. [11]. The applications of the membrane reactor include: (1) Resolution of racemic compounds and (2) Non-chiral reactions. For instances, hydrolysis, wastewater treatment, preparation of organic acid, etc.

3.1. Chemical reaction

3.1.1. Consecutive reaction

Partial oxidation of primary alcohols to aldehydes is important in organic synthesis because aldehydes are important intermediates and high-value products in perfume and dyestuff industries [12]. In the selective oxidation of benzyl alcohol (BzOH) to benzaldehyde (BzH), Julbe et al. [13] and Buonomenna and Drioli [14] employed a PVDF microporous flat membrane reactor (Fig. 2), in which the organic phase containing BzOH contacts the aqueous solution of hydrogen peroxide (as oxidizing agent) and ammonium molybdate (as catalyst). The reaction showed high selectivity (> 98%) to BzH because the generated BzH is extracted back to the organic phase and over-oxidation is prevented.

In organic electrochemical synthesis, Ce^{4+} and Co^{3+} are often used as oxidizers. Due to the low solubility of organic substrate in the aqueous electrolyte, electron fouling frequently occurs and the regeneration efficiency of oxidizers is generally low. To solve the problems, Scott [15] extracted the organic substrate methylanisole from the organic phase into the electrolyte solution with a membrane, and the product methylbenzaldehyde was extracted back to the organic phase. Deep oxidation and electrode passivation were effectively inhibited by this means.

3.1.2. Reversible reactions

Fatty acid methyl ester (FAME), which is also known as biodiesel, is a mixture of monoalkyl esters of long-chain fatty acids derived from renewable lipid feedstocks, such as vegetable oil and animal fats. FAME has similar physical properties to diesel fuels. To prepare FAME, transesterification is usually used, which consists of three consecutive reversible reaction steps: conversion of triglycerides to diglycerides, monoglycerides, and lastly glycerol. Each reaction step produces an alkyl ester. In conventional process, large quantities of alcohol are needed to shift the reaction equilibrium to the product side. However, high consumption of alcohol is associated with high production cost. In membrane L–L reactor [16,17], glycerol and methanol are continuously removed from the reaction system through the catalytic PVA membranes, while the unreacted lipids and the produced biodiesel are retained within the reactor. The conversion is greatly enhanced by the integration of reaction and separation.

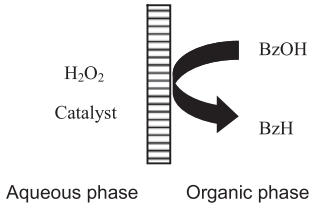

Fig. 2. Partial oxidation of BzOH to BzH by a membrane non-dispersive L–L reactor.

3.1.3. Non-reversible reactions

PTC is an effective tool for liquid–liquid reactions such as nucleophilic substitution, oxidation, reduction, hydrolysis, etc. The most important phase-transfer catalysts are quaternary ammonium, phosphonium salts, crown ethers, and cryptands. Stanley and Quinn [18] firstly employed porous polytetrafluoroethylene membranes to separate the aqueous and organic phases, stabilize the L–L interface, and transfer the phase transfer catalyst (tetra-n-butyl ammonium bromide). The membrane reactor obviates the emulsification/coalescence problems frequently encountered in conventional dispersed reactors. Later, Grigoropoulou et al. [19] reported the selective oxidation of BzOHs using a porous PTFE membrane with tetrabutylammonium hydrogen sulfate as the homogeneous catalyst. However, in these membrane configurations, the catalysts are not immobilized on membranes. After reaction, the catalyst must be separated from the reaction mixture. Okahata and Ariga [20] used capsule membranes with pendant quaternary ammonium groups and poly(ethylene glycol) groups for the reaction of sodium azide with benzyl bromide. Yadav and Mehta [21] presented theoretical and experimental analyses of catalytic capsule membrane in alkaline hydrolysis of benzyl chloride to BzOH. Nevertheless, the capsule membrane is not suitable for industrial production due to the inconvenience of working with capsules. Wu and Wu [22,23] prepared plate anion exchange membrane by coating chloromethylstyrene-co-divinylbenzene on polypropylene nonwoven fabric and then quaternization with trimethyl or tributyl amine. The catalytic membrane was used in the allylation of phenol, in which the membrane kept the organic

solution and alkali aqueous solutions apart. Increasing the lipophilicity of the quaternary amine group in the membrane accelerates the reaction. However, the membrane surface area is limited and pre-swelling is needed prior to reaction.

Recently, Jia et al. [24] grafted 4-vinyl pyridine on polyethelene hollow fiber microfiltration membranes by γ-ray irradiation and then quaternized with octyl iodide. The catalytic membranes were employed in the nucleophilic substitution reaction between bromooctane and KI aqueous solution. The bromooctane phase flowing in the fiber lumen contacts with the KI solution in the shell side, and the quaternary amine groups carry I^- ions from the aqueous phase to the organic phase where the reaction occurs. The generated Br^- ions are transported to the aqueous phase. The membranes provide substantially large and fixed interfacial area. Every grafted chain has multiple catalytic sites, resulting in elevated catalytic activity. The problems such as emulsion and foaming, frequently occurring in dispersive reactors, can be eliminated.

3.2. Biochemical reactions

3.2.1. Resolution of racemic compounds

Resolution of racemic drugs [25,26], organic acids [27], amino acids [28], and ester [29,30] by hydrolysis or esterification reactions in the membrane reactor has been reported. The substrate usually has high solubility in the organic solvent while the product dissolves easily in the aqueous phase. As lots of enzymes have a molecular weight between 10 and 80 kDa, ultrafiltration membranes with a molecular cut-off between 1 kDa and 100 kDa are usually employed [31].

For examples, Lopez and Matson [32] synthesized the optically active (2R, 3S)-3-(4-methoxyphenyl)-glycidic acid methyl ester (−MPGM), an important calcium channel blocker used for hypertension and angina treatment, by lipase-catalytically asymmetric hydrolysis of the racemic compound (±MPGM). The by-product of methoxyphenylacetaldehyde, an enzyme inhibitor, was continuously extracted and eliminated by an adduct formation with bisulfite in the aqueous phase. The process gave 42.6% conversion and product enantiomeric excess of 84.4%. In the resolution of racemic sulfomethyl ibuprofen [33], the racemate was dissolved in sodium phosphate buffer (pH 7) and fed to the shell-side of a cellulose membrane module, while hexane flowed in the lumen-side to recover the ibuprofen acid. Protease (Prozyme 6) was dissolved in the aqueous phase and the hydrolytic reaction took place at room temperature. The conversion of the racemic ester attained 50% at 6.3 h.

3.2.2. Reactions of non-chiral substrates

3.2.2.1. Hydrolysis. The substrates in hydrolysis include fat, starch, protein, ester, etc. The conventional technique for fat hydrolysis is the Colgate Emery process [34], which conversion is high (97–98%). However, the process operates at elevated temperature (150–260°C) and high pressure (~5 MPa), and is of high energy consumption. In membrane reactor, the two phases is separated by membranes, and the product is continuously removed by the membranes to increase the conversion. Therefore, hydrolysis can be carried out at mild conditions [35]. Olive oil [36], palm oil [37], corn oil [38], butter oil, and babassu oil were successfully converted to fatty acids in the biphasic reactor. For examples, Shukla and Kumar [39] used chemically modified zeolite-clay composite membranes for immobilization of porcine lipase in the hydrolysis of olive oil. Hydrolysis occurs at enzyme located at the mouth of membrane pores. The extraction of fatty acid into aqueous phase is facilitated by instantaneous reaction of the acid with the alkaline aqueous solution. Darnoko et al. [40] used membrane reactor in starch hydrolysis. To inhibit membrane fouling, pre-hydrolysis was conducted to reduce the viscosity of the initial solution.

3.2.2.2. Wastewater treatment. In wastewater treatment, toxic organic pollutants in wastewater are transferred through membranes to bio-medium for subsequent degradation. Bodzek et al. [41] immobilized an enzymatic fraction, isolated from a bacterial strain of Pseudomonas, on ultrafiltration membranes. In the biodegradation of real wastewater, at the contact time of 4 h, the degradation rates of phenols and cyanides were 25% and 50%, respectively. Jolivalt et al. [42] reported the decomposition of phenyl urea pesticide in wastewater. It was found that the immobilized laccase on PVDF microfiltration membrane showed high activity, which was comparable to that of free enzyme.

3.2.2.3. Preparation of organic acid. Lactic acid has wide applications in food and nonfood industries such as leather, textile, pharmaceutical, and rubber industries. The advantages of microbial fermentation over chemical synthesis of lactic acid are utilization of renewable carbon sources (e.g. corn) and exclusive production of the L or D-isomer of lactic acid, which is critical in polylactic acid production. To separate lactic acid from fermentation broth, conventional liquid–liquid extraction is usually employed. It consists of two steps: extracting lactic acid from fermentation broth (aqueous phase) into organic phase

(organic solvent with carrier); stripping the extracted lactic acid into another aqueous phase. In an emulsion liquid-membrane extraction system [43], an emulsion phase is obtained by emulsification of stripping solution in organic solvent containing carrier and surfactant. Then, a hydrophobic membrane is employed as barrier between fermentation broth and the emulsion phase so that extraction and stripping are performed simultaneously.

3.2.3. Preservation of biocatalysts activity

In biochemical applications, biocatalysts activity decay may occur. In order to preserve the biocatalysts activity, Bullon et al. [44] immobilized enzyme according to the following protocols: zirconia/α-alumina membranes (20 nm in pores size) are coated with an ultrathin gel layer by filtrating an inert protein solution such as gelatin; after activated with a cross-linking agent (glutaraldhehyde), the gelatin layer contacts with α-chymotrypsin to immobilize the enzyme by covalent bonds. The hydrophilic nature of the gelatin layer provides a good environment to preserve enzyme towards deactivation by the organic solvent. Another hydrophilic coating agent polyethyleneimine (PEI), which has a high content of free primary amino group, can increase the number of potential centers for enzymatic attachment. The best result is obtained at equal part mixture of gelatin and PEI [45].

4. Conclusions

Membrane L–L reactor can be divided into membrane dispersive L–L reactor and membrane non-dispersive L–L reactor. The membrane dispersive L–L reactor provides an efficient tool for the preparation of mono-dispersed polymer microspheres and microcapsules by using membrane emulsification-polymerization or membrane emulsification-swelling-polymerization techniques. Microporous or non-porous membranes cab be employed in membrane non-dispersive L–L reactor to separate the two phases and extract component from one phase into another phase. The membrane non-dispersive L–L reactor exhibits elevated conversion and selectivity in consecutive and reversible chemical reactions, or enhanced mass transfer and reaction rates in irreversible chemical reactions. In biological reactions, the membrane non-dispersive L–L reactor shows high productivity and conversion, minimized loss of biocatalysts activity, and stable quality of products. Membrane L–L reactor is compact, energy efficient, simple in design, operation, and scale-up. As a competitive and prospect technology for L–L reactions, membranes fouling, stability to organic solvent, modules sealing, cost, and lifetime are challenges in the process development and industrial application. These problems should be paid more attention in the future investigation.

Acknowledgments

The authors gratefully acknowledge the supports from the National Natural Science Foundation of China (No. 20676016, 21076024), State Key Laboratory of Fine Chemicals, and State Key Laboratory of Chemical Resource Engineering.

References

[1] F. Visscher, J. van der Schaaf, M. de Croon, Liquid-liquid mass transfer in a rotor-stator spinning disc reactor, Chem. Eng. J. 185–186 (2012) 267–273.
[2] A.M. Wilhelm, F. Laugier, R. Kidak, B. Ratsimba, H. Delmas, Ultrasound to enhance a liquid-liquid reaction, J. Chem. Eng. Japan 43 (2010) 751–756.
[3] E. Sinkovec, M. Krajnc, Phase transfer catalyzed Wittig reaction in the microtube reactor under liquid-liquid slug-flow pattern, Org. Process. Res. Dev. 15 (2011) 817–823.
[4] G.T. Vladisavljevic, R.A. Williams, Recent developments in manufacturing emulsions and particulate products using membranes, Adv. Colloid. Interf. Sci. 113 (2005) 1–20.
[5] P.J. Dowding, J.W. Goodwin, B. Vincent, Production of porous suspension polymer beads with a narrow size distribution using a cross-flow membrane and a continuous tubular reactor, Colloid. Surf. A 180 (2001) 301–309.
[6] S. Nagashima, M. Koide, S. Ando, K. Makino, T. Tsukamoto, H. Ohshima, Surface properties of monodisperse poly(acrylamide-co-acrylic acid) hydrogel microspheres prepared by a membrane emulsification technique, Colloids Surf. A 153 (1999) 221–227.
[7] G.H. Ma, H. Sone, S. Omi, Preparation of uniform-sized polystyrene-polyacrylamide composite microspheres from a W/O/W emulsion by membrane emulsification technique and subsequent suspension polymerization, Macromolecules 37 (2004) 2954–2964.
[8] S. Omi, T. Taguchi, M. Nagai, G.H. Ma, Synthesis of 100 μm uniform porous spheres by SPG emulsification with subsequent swelling of the droplets, J. Appl. Polym. Sci. 63 (1997) 931–942.
[9] C. Charcosset, H. Fessi, Preparation of nanoparticles with a membrane contactor, J. Membr. Sci. 266 (2005) 115–120.
[10] A.M. Vaidya, P.J. Halling, G. Bell, Surfactant-induced breakthrough effects during the operation of 2-phase biocatalytic membrane reactors, Biotech. Bioeng. 44 (1994) 765–771.
[11] L. Giorno, J.C. Zhang, E. Drioli, Study of mass transfer performance of naproxen acid and ester through a multiphase enzyme-loaded membrane system, J. Membr. Sci. 276 (2006) 59–67.

[12] M.G. Buonomenna, E. Drioli, Solvent free selective oxidation of benzyl alcohol to benzaldehyde using a membrane contactor unit, Appl. Catal. B: Environ. 79 (2008) 35–42.
[13] A. Julbe, D. Farrusseng, C. Guizard, Porous ceramic membranes for catalytic reactors—Overview and new ideas, J. Membr. Sci. 181 (2001) 3–20.
[14] M.G. Buonomenna, E. Drioli, Benzyl alcohol oxidation to benzaldehyde in multiphase membrane reactor, Org. Process. Res. Develop. 12 (2008) 982–988.
[15.] K. Scott, Membrane reactors for electrical synthesis processes, J. Membr. Sci. 90 (1994) 161–172.
[16] J. Saleh, A.Y. Tremblay, M.A. Dubé, Glycerol removal from biodiesel using membrane separation technology, Fuel. 89 (2010) 2260–2266.
[17] M.C.S. Gomes, P.A. Arroyo, N.C. Pereira, Biodiesel production from degummed soybean oil and glycerol removal using ceramic membrane, J. Membr. Sci. 378 (2011) 453–461.
[18] T.J. Stanley, J.A. Quinn, Phase transfer catalysis in a membrane reactor, Chem. Eng. Sci. 42 (1987) 2313–2324.
[19] G. Grigoropoulou, J.H. Clark, D.W. Hall, K. Scott, The selective oxidation of benzyl alcohols in a membrane reactor, Chem. Comm. (2001) 547–548.
[20] Y. Okahata, K. Ariga, A new type of phase-transfer catalysts (PTC) reaction of substrates in the inner organic phase with the outer aqueous anions catalyzed by PTC grafted on the capsule membrane, J. Org. Chem. 51 (1986) 5064.
[21] G.D. Yadav, P.H. Mehta, Theoretical and experimental analysis of capsule membrane phase transfer catalysis: Selective alkaline hydrolysis of benzyl chloride to benzyl alcohol, Catal. Lett. 121 (1993) 39.
[22] H.S. Wu, Y.K. Wu, Kinetics of allylation of phenol using quaternary ammonium membranes in a membrane reactor, J. Chin. Institute Chem. Eng. 39 (2008) 29–35.
[23] H.S. Wu, Y.K. Wu, Preliminary study on the characterization and preparation of quaternary ammonium membrane, Ind. Eng. Chem. Res. 44 (2005) 1757–1763.
[24] Z.Q. Jia, T.L. Zhen, X.Q. Zhang, Q.Y. Gu, Preparation of phase-transfer catalytic porous membrane by γ-ray irradiation grafting and its application in nucleophilic substitution reaction, J. Membr. Sci. 448 (2013) 74–80.
[25] W.S. Long, A.H. Kamaruddin, S. Bhatia, Chiral resolution of racemic ibuprofen ester in an enzymatic membrane reactor, J. Membr. Sci. 247 (2005) 185–200.
[26] L. Giorno, E. D'Amore, R. Mazzei, E. Piacentini, J. Zhang, E. Drioli, An innovative approach to improve the performance of two separate phase enzyme membrane reactor by immobilizing lipase in presence of emulsion, J. Membr. Sci. 95 (2007) 95–101.
[27] K. Sakaki, S. Hara, N. Itoh, Optical resolution of racemic 2-hydroxy octanoic acid using biphasic enzyme membrane reactor, Desalination 149 (2002) 247–252.
[28.] S.L. Matson, Method for resolution of stereoisomers in multiphase and extractive membrane reactors, US Patent 4800162 (1989).
[29.] J. Ceynowa, I. Koter, Methyl-β-cyclodextrin assisted enantioselective ester hydrolysis catalyzed by lipase immobilized in a polymer membrane, Sep. Sci. Technol. 36 (2001) 2885–2898.
[30] J.L. Lopez, S.A. Wald, L. Matson, J.A. Quinn, Multiphase membrane reactors for separating isomers, Annals New York Acad. Sci. 613 (1990) 155–166.
[31] G.M. Rios, M.P. Belleville, D. Paolucci, J. Sanchez, Progress in enzymatic membrane reactors-a review, J. Membr. Sci. 242 (2004) 189–196.
[32] J.L. Lopez, S.L. Matson, A multiphase/extractive enzyme membrane reactor for production of diltiazem chiral intermediate, J. Membr. Sci. 125 (1997) 189–211.
[33] S.L. Matson, S.A. Wald, C.M. Zepp, D.R. Dodds, Method for membrane reactor resolution of stereoisomers, US Patent 5077217 (1991).
[34] C. Brady, L. Metcalfe, D. Slaboszewski, D. Frank, Lipase immobilized on a hydrophobic, microporous support for the hydrolysis of fats, J. Am. Oil. Chem. Soc. 65 (1988) 917–921.
[35] M.M. Hoq, T. Yamane, S. Shimizu, T. Funada, S. Ishida, Continuous hydrolysis of olive oil by lipase in microporous hydrophobic membrane bioreactor, J. Am. Oil. Chem. Soc. 62 (1985) 1016–1021.
[36] H.T. Deng, Z.K. Xua, Z.W. Dai, J. Wu, P. Seta, Immobilization of Candida rugosa lipase on polypropylene microfiltration membrane modified by glycopolymer: Hydrolysis of olive oil in biphasic bioreactor, Enzyme Microb. Technol. 36 (2005) 996–1002.
[37] L. Giorno, E. Drioli, Catalytic behavior of lipase free and immobilized in biphasic membrane reactor with different low water-soluble substrates, J. Chem. Technol. Biotechnol. 69 (1997) 11–14.
[38] Y. Wang, Y.L. Hsieh, Immobilization of lipase enzyme in polyvinyl alcohol (PVA) nanofibrous membranes, J. Membr. Sci. 309 (2008) 73–81.
[39] A. Shukla, A. Kumar, Experimental studies and mass-transfer analysis of the hydrolysis of olive oil in a biphasic zeolite-membrane reactor using chemically immobilized lipase, Ind. Eng. Chem. Res. 43 (2004) 2017–2029.
[40] D. Darnoko, M. Cheryan, W.E. Artz, Saccharification of cassava starch in an ultrafiltration reactor, Enzyme Microb. Technol. 11 (1989) 154–159.
[41] M. Bodzek, J. Bohdziewicz, M. Kowalska, Immobilized enzyme membranes for phenol and cyanide decomposition, J. Membr. Sci. 113 (1996) 373–384.
[42] C. Jolivalt, S. Brenon, S.E. Caminade, C. Mougin, M. Pontié, Immobilization of laccase from Trametes versicolor on a modified PVDF muicrofiltration membrane: characterization of the grafted support and application in removing a phenylurea pesticide in wastewater, J. Membr. Sci. 180 (2000) 103–113.
[43] A. Demirci, J.C. Cotton, L.P. Anthony, R.H. Kristi, N.H. Paul, Resistance of *lactobacillus casei* in plastic-composite-support biofilm reactors during liquid membrane extraction and optimization of the lactic acid extraction system, Biotechnol. Bioeng. 83 (2003) 749–759.
[44] J. Bullon, M.P. Belleville, G.M. Rios, Preparation of gelatin formed-in place membranes: Effect of working conditions and substrates, J. Membr. Sci. 168 (2000) 159–165.
[45] P. Lozano, A.B. Pérez Marın, T. Diego, D. Gómez, D. Paolucci-Jeanjean, M.P. Belleville, G.M. Rios, J.L. Iborra, Active membranes coated with Candida antartica lipase B: Preparation and application for continuous butyl butirate synthesis in organic media, J. Membr. Sci. 201 (2002) 5–64.