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Perspective

# Gas–liquid separation processes based on physical solvents: opportunities for membranes

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ABSTRACT

Membrane contactors have received increased attention since the 1980s and are already used for different industrial applications. A very large number of studies have been reported, more specifically to achieve intensified gas–liquid mass transfer, almost exclusively in water or aqueous solutions. In contrast, the potentialities of membrane contactors for gas–liquid processes based on non-aqueous physical solvents are essentially unexplored. This study intends to discuss the difficulties associated with the specific physical solvent context and explore the potentialities of membrane contactors for both absorption and regeneration steps. Theoretical arguments show that dense membranes based on superpermeable and mechanically resistant polymers could offer promising performances, owing to their capacity to simultaneously prevent wetting effects, sustain a high transmembrane pressure and offer process intensification possibilities. Moreover, a significant improvement in terms of energy efficiency is theoretically achievable for the regeneration step. A preliminary proof of concept study, which supports these potentialities, is presented and the research needs for this new approach in order to possibly achieve applications at industrial scale are discussed.

## 1. Introduction

Maximizing the mass transfer performances of separation processes or reactors has been one of the major targets of chemical engineering research for decades [1,2]. Membrane contactors, which make use of a thin permeable membrane in order to increase the overall mass transfer between two fluid phases (e.g. gas–liquid, liquid–liquid), are intensively investigated in order to achieve that purpose (Fig. 1). The attainment of an increased interfacial area based on this type of system indeed offers unique opportunities for enhanced mass transfer performances compared to traditional processes. Membrane contactors are considered as one of the most promising process intensification strategies, the devices being possibly between 5 and 20 times smaller than conventional separation processes [2–5]. Their interest has been shown and validated at an industrial scale for several applications such as degassing of water [6], carbonation of beverages [7], blood oxygenation [8], or solute recovery by liquid–liquid extraction, including proteins [9,10]. The generic concept of a membrane contactor is also currently investigated for other operations such as emulsification, crystallization, distillation, osmotic distillation and liquid membrane applications [11–13].

This study intends to provide, in a first step, a short historical overview of membrane contactor researches and applications, especially through membrane materials and process engineering developments. In a second step, an important industrial area of gas–liquid processes, which makes use of physical (non-aqueous) solvents, will be described and analyzed. The challenges and issues associated with this surprisingly almost unexplored field for membrane contactors applications will be detailed. The potentialities for both the absorption and solvent regeneration steps are then approached through a preliminary experimental work of proof of concept type. It is concluded that membrane contactors could offer attractive opportunities in terms of intensification and improved energy efficiency for gas–liquid absorption processes based on physical solvents. The research efforts which are required to make these theoretical possibilities an industrial reality are finally discussed.

## 2. Membrane contactors & gas liquid processes: a short historical perspective

A simplified overview of the evolution of researches in the field of membrane contactors, including landmarks, membrane

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materials developments and target applications, is proposed in Fig. 2. The general concept of inserting a membrane material between a gas and a liquid phase for mass transfer purposes can be dated back to more than 50 years. Schaffer indeed proposed in 1960 in a pioneering study of using dense polymeric films in order to achieve bubbleless oxygen dissolution for wastewater treatment applications [14]. The same concept was further suggested for other applications such as gas absorption [15] or artificial gills [16]. Nevertheless, the high mass transfer resistance of a tenth of millimeter thick dense membrane was a major limitation of these early approaches.

In 1972, Yasuda and Lamaze pointed out the interest in using hydrophobic porous membranes in place of dense polymeric materials, for gas dissolution applications [17]. This study opened the way to the development and use of hydrophobic microporous membrane materials, most often of hollow fiber type, with enhanced mass transfer performances. Provided that non-wetting conditions prevail (due to the hydrophobic properties of the material), the mass transfer resistance of the gas filled porous matrix is effectively much lower than the corresponding dense material. Historically, the hollow fiber membrane based blood oxygenator is often considered as the first effective application of this porous membrane contactor concept [18]. Numerous developments, mostly based on polypropylene or Teflon microporous materials, followed and thereof industrial applications, particularly for gas absorption or degassing of aqueous solutions in the food (carbonated beverages), pharmaceutical and microelectronics (oxygen removal for ultrapure water production) sectors [19]. The latter is currently considered as the largest application of membrane contactors [20].

The interest in the membrane contactor concept for gas absorption processes based on chemically reactive aqueous systems (and not only the aqueous physical applications listed above) was later on addressed in seminal papers by Cussler [21]. This new field of application is of major importance for large-scale industrial operations such as acid gas removal (natural gas purification, coal gasification) [22], bubbleless aeration of bioreactors and wastewater treatment plants [23–25] or gaseous effluents treatment, such as ammonia removal in acidic solutions [26]. Nevertheless, new challenges emerged:

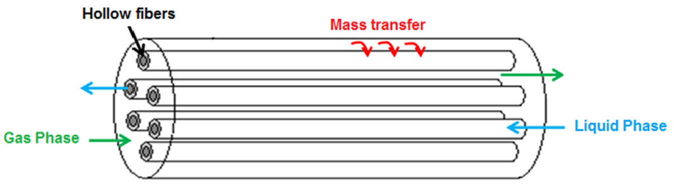

**Fig. 1.** Schematic representation of a hollow fiber membrane contactor for gas–liquid absorption.

(i) First, the much higher mass transfer coefficient in the liquid phase, due to the beneficial effect of the chemical reaction (usually expressed through an enhancement factor), imposed the development of highly permeable materials, in order to limit the membrane mass transfer resistance. More specifically, membrane wetting phenomena, even of limited extent, can drastically affect in that case the overall mass transfer performances [27–29,37,38].

(ii) Second, the chemically reactive, if not aggressive, environment in the liquid addresses new materials compatibility issues [39].

The challenges and the corresponding appealing industrial applications have stimulated research efforts in this area and an impressive and continuously increasing number of publications have been reported [37]. More specifically, the capture of carbon dioxide from flue gases by selective absorption in chemical solvents can be considered as the currently most investigated target of membrane contactors [40]. This application, initiated by Kvaerner company in the late 1980s [41], clearly aims to use membrane contactors in a harsh environment (dust, SOx and NOx in the flue gases, heat-stable salt formation in the solvent…) which is very different from the clean, water based applications developed up to now in the food and pharmaceutical sectors. From the membrane point of view, the sensitivity to wetting and the challenges of material stability in chemically aggressive solutions are considered as major potential bottlenecks [33–37,40]. In that context, the interest in dense skin asymmetric or composite materials has been investigated in order to prevent wetting and/or material degradation. The idea of using a dense skin layer for membrane contactors was initiated in the 1990s [42–44]. It was further extended for VOC recovery applications [45] and recently showed increased interest for $CO_2$ recovery by absorption in chemically reactive aqueous solutions [46–49].

Recent trends in membrane contactor development include new application areas such as crystallization and distillation [12,19]. For the gas–liquid processes, an increasing number of studies recently addressed the solvent regeneration step [28–32], which is classically achieved by steam stripping for chemical solvents. These specific operating conditions again impose challenges because temperature resistance and non-wetting phenomena have to be ensured. Inorganic membrane materials have been proposed in order to possibly fulfill these specifications [32].

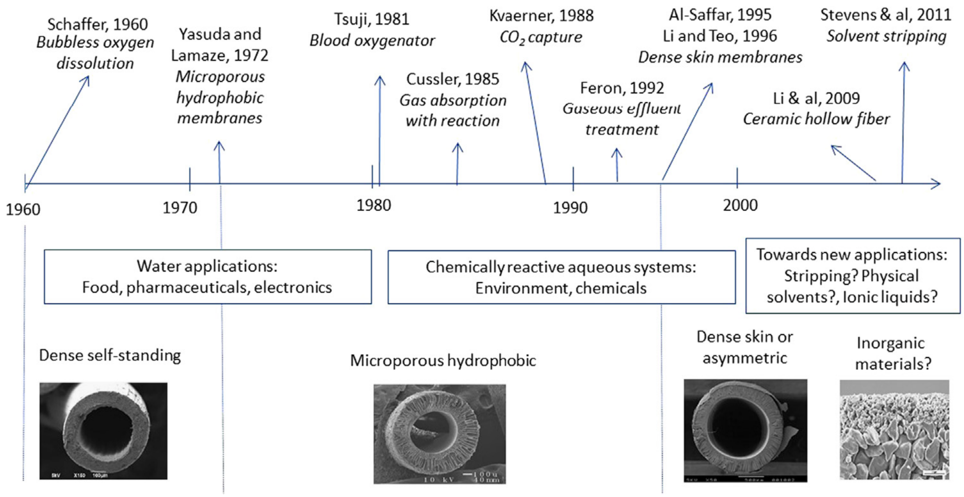

**Fig. 2.** Tentative historical perspective of membrane contactors developments for gas–liquid separation processes.