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Process intensification by coupling the Joule effect with pervaporation and sweeping gas membrane distillation

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ABSTRACT

This work concerns the intensification of membrane processes by coupling the Joule effect with two membrane processes: pervaporation and sweeping gas membrane distillation. For this purpose, conducting metallic hollow fibers impregnated or coated with polydimethyl siloxane were simultaneously used as membrane and heating electric resistance. The application of an electrical potential resulted in an enhancement of 40% of the water vapor permeate flux in sweep gas membrane distillation. However, the flux enhancement is the result not only of the heating on the membrane vicinity but also on the enhancement of the feed temperature. In the case of pervaporation of aqueous ethanol solutions (20%), the direct heating of fibers allowed improving by 100% the ethanol permeate flux while increasing the process selectivity.

1. Introduction

The sweeping gas membrane distillation process (SGMD) is a hybrid evaporation-concentration or distillation process carried out in membrane contactors with hydrophobic macroporous membranes. In this process, the membrane is not selective but it is only the support of a liquid-vapor interface located at the pore inlet between an aqueous solution on the membrane feed side and a flow of dry air on the membrane permeate side. SGMD involves evaporation of water from the hot feed solution, and transfer of the vapor molecules through the non-wetting pores of the hydrophobic membrane. This transport is driven by the water vapor partial pressure difference between feed and permeate sides of the membrane. Subsequently, the permeated molecules are carried by an inert cold sweeping gas and finally collected outside the membrane module. In the case that SGMD is used as distillation process, the permeate flow is then cooled down in order to condense the evaporated water. The SGMD [1–3] process is less often studied compared to other membrane distillation configurations, like direct contact membrane distillation (DCMD), due to the small volume of permeate vapors generated and the need of external condensers. However, SGMD presents lower internal heat losses by conduction compared to DCMD and higher permeate fluxes in comparison to air gap membrane distillation (AGMD) due to the non-stationary sweeping gas. This makes SGMD a technology with promising future perspectives.

In pervaporation, a liquid feed mixture contacts one side of a membrane while the permeate is removed as a vapor from the other side. The membrane can be hydrophobic or hydrophilic, depending on the targeted application. Transport through the membrane is induced by the difference in vapor partial pressure between the feed solution and the permeate vapor. This vapor pressure difference can be maintained in various ways. In general, at lab scale vacuum is maintained on the permeate side using a vacuum pump, while the permeate vacuum in industry is most economically generated by cooling and condensing the permeate vapor spontaneously creating a partial vacuum. The third possible way is to sweep the permeate side of the membrane with a counter-current flow of carrier gas. Carrier gas can then be cooled down to condense and recover permeate vapor [4].

Separation by pervaporation is based on the solution-diffusion mechanism of transport. The mass transport across the permselective membrane involves three successive steps: (a) upstream partitioning of the feed components between the flowing liquid mixture and the swollen upstream surface layer of the membrane according to their affinity for membrane material, (b) diffusion of the selectively absorbed components through the membrane, and (c) desorption of these

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components at the downstream surface of this membrane [5]. Dehydration of solvents, removal of volatile organic components from water (water purification) and organic/organic separation as an alternative to conventional distillation are the most common applications of pervaporation process.

Classified under inorganic membranes, metallic hollow fiber membranes exhibit superior mechanical and thermal stabilities in comparison to polymeric ones. In addition, their metallic nature bestows thermal and electrical conduction properties and higher mechanical strength than other inorganic membranes like ceramic ones. Furthermore, their electrical resistivity makes metals interesting materials for direct heating of the membrane by the Joule effect. This way, the enthalpy of evaporation in SGMD and pervaporation can be supplied directly at the membrane surface where the evaporation takes place. This direct heating can thus limit the temperature decrease on the membrane feed side (the so-called temperature polarization) and reduce the subsequent mass transfer decrease due to this phenomenon.

Moreover, such localized heating of membranes can be very interesting for the concentration or separation of thermal sensitive solutions, because the effectiveness of the global process can be maintained without a too important heating of the whole feed solution. This principle was recently successfully applied in some membrane fields, i.e., pervaporation and solvent resistant nanofiltration, using the photothermal effect [6–8]. In SGMD or membrane evaporation, Hengl et al. [9–11] have previously demonstrated that temperature polarization can be minimized and water permeate fluxes can be increased by using flat-sheet metallic membranes and heating them by infrared rays or by the Joule effect using them as electrical resistance. However, in this previous work, the process was limited by the hydrodynamic conditions that were imposed because of the design of the module and by the structural membrane properties (thickness, pore size, hydrophobicity). Furthermore, flat-sheet membranes have a very low packing density that increases their footprint in comparison to hollow fiber membranes.

In more recent work [12] a multidisciplinary approach was presented that includes the development of macro-porous metallic hollow fibers giving hydrophobic properties to the surface with polydimethylsiloxane (PDMS), and finally the study of the SGMD process. Experiments were conducted with pure water, and effects of different process parameters on permeate flux, such as sweeping gas velocity and feed temperature, were investigated. A second set of experiments was conducted with sucrose solutions of different concentrations in order to assess the possibility of using this new metallic membrane system for the concentration of thermally sensitive/biological solutions.

Only few existing studies have reported alternative approaches to supply energy necessary for evaporation during pervaporation. Applying microwave heating for hydrophilic pervaporation through PVA-PAN cross-linked membrane was reported [13], as well as pervaporation using hollow fiber membranes in the electromagnetic microwave field [14]. Localized membrane heating was also established by means of photo thermal heating of silver nanoparticles dispersed in the PDMS layer supported on PVDF [7]. In this perspective, using metallic membranes could give immense opportunity to bring energy required for evaporation directly to the membrane surface in the course of the pervaporation process. This approach is both less energy intensive and is also of interest in applications such as recovery of valuable heat sensitive products or aroma compounds. In our study, the possibility of doing this is demonstrated by carrying out preliminary hydrophobic pervaporation experiments using ethanol-water feed.

This work presents the preliminary results of an innovative and multidisciplinary approach starting from the selection and the modification of metallic hollow fibers by a hydrophobic treatment with PDMS and the use of such metallic membranes as electric resistance in order to improve SGMD and pervaporation performance by diminishing the effects of the temperature polarization. In the case of SGMD, experiments were carried out in a module with a bundle of hydrophobic macroporous metallic hollow fibers. A module with a unique metallic fiber covered with a dense layer of PDMS was used to study the pervaporation of aqueous solutions of ethanol.

2. Experimental

2.1. Materials

Stainless steel (SS) powder (316L) with particle size of 4.17 µm (D50 by the manufacturer) was purchased from Epson Atmix Corporation (Japan). Polyetherimide (PEI), N-methylpyrrolidone (NMP, 99.5 wt%), polyvinylpyrrolidone (PVP K95) were bought from Aldrich. The stainless steel powder and PEI were dried before use; all other chemicals were used without further treatment. Polydimethylsiloxane (PDMS)-615 kit (General Electric) consisted on a vinyl terminated pre-polymer (RTV-A) and a platinum (Pt)-catalyzed cross-linker (RTV-B) containing a polyhydrosilane component. Ethanol ($\geq$ 99.8%) and hexane ($\geq$ 97%) were also purchased from Sigma Aldrich.

2.2. Methods

2.2.1. Preparation of hydrophobic stainless steel hollow fiber membranes for SGMD and pervaporation

Hydrophobic metallic hollow fibers for the SGMD were prepared as described in previous work [12]. They were manufactured through the non-solvent induced phase separation (NIPS) technique using SS particles (68 wt%) dispersed in N-methylpyrrolidone (25 wt%). After homogenization and outgassing the spinning dope was pressurized with nitrogen from a feed vessel through an spinneret, while simultaneously de-ionized water was pumped through the inner tube of the spinneret. The hollow fibers leaving the spinneret passed through brief air gap before a free fall into the external coagulant bath composed of tap water. The whole process was carried out at controlled room temperature of 269 °C K. Hollow fibers precursors (green fibers) were dried and stretched under ambient conditions for overnight. Then the fibers were fired at 1348 °C under nitrogen. After cleaning and drying, native fired stainless steel fibers were impregnated with a 2% of PDMS pre-polymer and cross-linker in a 10:1 weight ratio in hexane before being cured at 373 K overnight to evaporate the solvent and to complete the crosslinking reaction. The metallic grains forming the fibers were then covered through all membrane thickness with a very thin layer of PDMS that gives it excellent hydrophobic surface properties while maintaining an important macro-porosity as required for SGMD process. The characterizations of these membranes in terms of hydrophobic properties (water pressure intrusion and contact angle) have been reported in a previous work [12].

Pervaporation membranes were prepared using the same native fired stainless steel fibers [12], but their external surface was covered with a fine dense layer of PDMS without intrusion into the pores. For this purpose, the pre-polymer and cross-linker solution in hexane was prepared in a similar ratio as above, but at a concentration of 10% (M1) or 20% (M2). The cross-linking reaction was initiated by placing the solution into a water bath maintained at 60 °C with constant stirring for 2 h. This initial cross-linking time is important in order to obtain PDMS solutions with required viscosity [15]. Before coating hollow fiber supports, they were immersed in hexane for 4 h to saturate the pores with the solvent in order to prevent the intrusion of the coating solution into the porosity. Both open sides of the supports were plugged with a paste and immersed into a pre-crosslinked PDMS solution for 5 min. The supports were then dried at room temperature for 10 min followed by curing at 110 °C at least for 1 h to complete the cross-linking. This method allows having a thin dense PDMS layer on the external surface of the fibers without intrusion inside the pores.

2.2.2. Characterization of the membranes

The total pore volume, the mean pore diameter and the percent