J. of Supercritical Fluids 103 (2015) 105–114

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Optimization of flat sheet hydrophobic membranes synthesis via supercritical CO_2 induced phase inversion for direct contact membrane distillation by using response surface methodology (RSM)

Ali Zaherzadeh [a], Javad Karimi-Sabet [b,*], Seyed Mohammad Ali Mousavian [a], Sohrabali Ghorbanian [a]

[a] Department of Chemical Engineering, Faculty of Engineering, University of Tehran, Tehran, Iran
[b] NFCRS, Nuclear Science and Technology Research Institute, Tehran, Iran

ARTICLE INFO

Article history:
Received 15 February 2015
Received in revised form 28 April 2015
Accepted 30 April 2015
Available online 12 May 2015

Keywords:
Supercritical CO_2 phase inversion
Hydrophobic membrane
Ternary phase diagram
Response surface methodology
Membrane distillation

ABSTRACT

Flat-sheet hydrophobic polyvinylidene fluoride (PVDF) membrane was prepared by supercritical fluid induced phase inversion technique. The effects of initial polymer concentration, pressure, and temperature of supercritical fluid on the final membrane structures and surface hydrophobicity were investigated. The morphologies and hydrophobicities of PVDF micro porous membranes were analyzed by means of scanning electron microscopy (SEM) and contact angle (CA) measurement, respectively. The ternary theory phase diagram will evaluate the thermodynamic aspects of the membrane precipitation process for difference $ScCO_2$ pressure and temperature. This phase diagram was constructed by theoretical calculation, based on Flory–Huggins solution theory. Response surface methodology (RSM) was used to optimize the characteristics of membrane structural by setting the parameters of membrane synthesis process (temperature, pressure and polymer concentration) to be used in direct contact membrane distillation (DCMD). Analysis of variance shows significant effects of each variable on the responses. The membrane is optimized under the following conditions: 14.76 wt.% PVDF concentration, 35 °C temperature and pressure of 10 MPa. The fabricated optimum membrane, compared to membrane prepared by conventional wet phase inversion method exhibited a better permeate flux.

1. Introduction

In recent years, the hydrophobic porous membrane has largely been applied in membrane distillation (MD). MD is a non-isothermal separation process, based on the transmission of volatile compound especially water in vapor phase through a micro porous hydrophobic membrane from the hot side toward the cold side. Direct contact membrane distillation (DCMD) is a type of MD configuration in which the hot solution (feed) and cooled permeate are in direct contact with both sides of the membrane. MD is generally used for desalination, removal of trace, volatile organic compounds from waste water and concentration of ionic, colloid, or other relatively non-volatile aqueous solutions. Also, MD can be used for liquid low-level radioactive waste treatment [1,2]. In the MD process, pores of the membrane should not be wetted by the aqueous solutions. Thus, the used membrane should be hydrophobic [3].

The morphology of the membranes used in the MD process, has a strong effect on the MD process performance. To obtain a high permeability, the surface layer which controlling the membrane mass transport must be as thin as possible. Moreover, the membrane surface porosity must be large as possible and a high porosity in the cross section. The optimum range for average pore size in surface membrane is 0.01 μm to 1 μm for MD application [4]. In addition, membranes must have good thermal stability and excellent chemical resistance to feed the streams. Polyvinylidene fluoride (PVDF) has received great attention as a membrane material, having excellent properties such as high hydrophobicity, high thermal stability, chemical resistance and mechanical strength in comparison to other commercialized polymeric materials [5].

Phase inversion is a method widely used to prepare micro porous polymer membrane. Phase inversion it pertaining to the process in which a homogenous solution of a polymer and solvent is immersed into the non-solvent bath, inverting a single phase to a two-phase system in total equilibrium with each other. Water is frequently used as non-solvent, a technique called wet phase inversion [6,7]. Recently, an alternative technique has been proposed

* Corresponding author. Tel.: +98 2177797714.
E-mail address: j_karimi@alum.sharif.edu (J. Karimi-Sabet).

http://dx.doi.org/10.1016/j.supflu.2015.04.030
0896-8446/

that uses supercritical CO_2 ($ScCO_2$) as the non-solvent to induce phase inversion [8–24]. In the phase inversion compared to other non-solvents, $ScCO_2$ has liquid-like density and gas-like diffusivity; hence it removes the solvent from the membranes in a short time almost completely without any additional post-treatment. Other advantages of this technique over the wet phase inversion method is that by changing operation parameters such as polymer concentration, $ScCO_2$ pressure and temperature the membrane morphology can be adjusted effectively tailored to our needs. Also, CO_2 is not toxic or flammable and it is cheap [11,19,22].

The membrane precipitation is persuaded by mechanisms of liquid–liquid de-mixing and/or crystallization [25]. In fact, for membranes synthesized from semi-crystalline polymers such as PVDF, the structure of the membrane was impressed by a sequence of these phase inversion mechanisms [6].

Depending on operating conditions such as the temperature and pressure of carbon dioxide as well as polymer concentration, the rate of these mechanisms may change in comparison to one another. When liquid–liquid de-mixing dominates the precipitation process, the nascent membrane usually comprises a dense skin and a porous bulk packed with cellular pores or macro voids. In contrast, when crystallization dominates the precipitation process, a porous membrane packed by embellishments of interlinked crystallites is produced. In intermediate cases, the membranes displayed mixed morphologies, characterized both by crystalline particles and cellular pores [26,27]. In liquid–liquid demixing mechanism, the two-phase system consists of a solid phase (polymer-rich phase) that forming the matrix membrane as well as a liquid phase (polymer-poor phase) which forming the pores in the final membrane [28].

The phase diagram is a convenient tool to study the thermodynamic aspects and mechanism of the membrane formation process. The phase diagram of a non-solvent/solvent/polymer system can be constructed by theoretical calculations based on Flory–Huggins theory [29]. The Flory–Huggins theory for polymer solutions was extended to a three-component system and was widely used to describe the ternary phase diagram of the membrane casting system (i.e., polymer/solvent/non-solvent) [30]. The ternary phase diagrams of water/DMF/PVDF and 1-octanol/DMF/PVDF systems have been studied by some researchers. This diagram for semi-crystalline is included in binodal and crystallization curves [31,32].

Flory–Huggins theory involves a series of parameters namely the data of non-solvent/solvent, solvent/polymer and non-solvent/polymer interaction parameters which must be determined to compute the phase diagram. By changing the operating conditions such as the temperature, the $ScCO_2$ pressure and polymer concentration, the membrane morphology was controlled in turn improving the surface hydrophobicity. Response surface methodology (RSM) is a statistical technique used to evaluate the effect of multiple factors on one or more response variables [33]. The hydrophobic property of PVDF membrane can be enhanced with roughness and porous surface. The top surface of the sponge-like porous PVDF membrane showed greatly enhanced hydrophobicity [34].

The present study discusses the effect of operating conditions such as temperature and $ScCO_2$ pressure on the membrane morphology by using phase diagrams and it has been attempted to present the correspondence between theoretical phase diagrams and the morphology of the formatted membranes.

The objective of the research was to appropriate the adjustment of the quantity of $ScCO_2$ temperature and pressure along with the concentration of polymer to optimize the micro porous membrane. The membranes prepared in this study were characterized by their hydrophobicity, surface average pore size and porosity. The Box–Behnken design of the experiments present a mathematical correlation between the temperature and pressure of $ScCO_2$ as well as polymer concentration to obtain maximum porosity and surface hydrophobicity by setting the surface average pore diameter between 0.1 and 1 μm for usage in MD [35]. In order to measure the permeate flux and separation factor of fabricated optimum flat sheet hydrophobic PVDF membrane, it was tested in DCMD.

2. Experimental

2.1. Materials

PVDF (Mw 530000, Aldrich Chemical Company, Inc.) was obtained in pellet form. Dimethylformamide (DMF, Aldrich, HPLC grade) was used as the solvent. Carbon dioxide with the purity of 99.99% was purchased from Farafan Gas Company, Iran.

2.2. Membrane preparation

To prepare the casting solutions, an appropriate amount of PVDF pellets was dissolved in DMF. The components were capped and magnetically stirred at 60 °C until the polymer solution became homogenous. In order to remove the air bubbles, the polymer solution was to be placed under the vacuum for 12 h at ambient temperature. A thin film was cast onto a glass microscope slid using a doctor blade with a 250 μm gap. Fig. 1 schematically shows the experimental setup for the formation of PVDF membrane by $ScCO_2$ phase inversion. Initially, the casting solution was put inside the vessel with internal volume of 200 ml which got closed quickly. The inlet valve was opened and the vessel was filled with CO_2 up to the desired pressure using a high pressure pump (OPET CO Model TB 160-65-2/u/v). This pressure inside the vessel was fixed for 45 min by pumping and afterwards the vessel's outlet valve got opened to dry the phase-separated membrane at the constant pressure and temperature with a CO_2 flow rate of 1.5 kg/h for 45 min. Then, the vessel was slowly depressurized for another 45 min.

2.3. Membrane characterization

Structures of the membranes in the surface and cross-section were observed with a scanning electron microscopy (SEM, Seron Technology-AIS2100). The mean pore diameters at the top surfaces of the samples were analyzed by image j software. Contact angles were measured using an OCA40 Micro Tensiometer (Data Physics Corp., Germany) to evaluate membrane hydrophobicity. The volume of the water droplet used in the measurement was 5 μL. The value of contact angle is greater than 90° the material is considered hydrophobic.

The porosity (ε) can be determined by Eq. (1).

$$\varepsilon = 1 - \frac{\rho_m}{\rho_{pol}} \quad (1)$$

where ρ_m and ρ_{pol} are the densities of membrane and polymer material (ρ_{pol} = 1.78 g/cm^3), respectively. The density of the PEI membrane was obtained by measuring its volume and weight.

2.4. Experimental design and optimization by RSM

Response surface methodology (RSM) which is based on factorial design is a mathematical and statistical technique to design experiments, fitting the models and determining the optimal operating conditions in the target response.

RSM uses an experimental design such as the Box–Behnken design to evaluate the relation between experimental outputs (or responses) and factors, called X_1, X_2, X_3, etc. Adopting Box–Behnken designs can sharply reduce the number of experimental sets without ever decreasing the accuracy of the optimization, in contrast to