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Performance characterization of polyamide reverse osmosis membranes upon supercritical CO_2 processing

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ABSTRACT

Stability is one of the most important criteria while selecting the proper membrane for a targeted separation. Use of supercritical carbon dioxide (SC-CO_2) as a solvent during the separation of solute molecules by polymeric membranes requires knowledge of the stability of membranes, considering the well known polymer–CO_2 interactions. In this study, the effects of different temperature (40, 60 and 80 °C), transmembrane pressure (10, 20, 30 and 40 bar), depressurization rate (0.1 and 5 bar/s) and processing time (0–24 h) at 120 bar on the performance of two commercial polyamide membranes were investigated. Performance of the membranes was evaluated by measuring CO_2 flux and oleic acid retention factors at 120 bar and 40 °C following processing with CO_2. High transmembrane pressures (30 and 40 bar) did not exhibit a linear increase in CO_2 flux and showed higher oleic acid retention factors whereas high temperature processing and depressurization resulted in higher flux and lower retentions. Each of these effects increased with processing time at each processing condition. The findings demonstrated that the covalently cross-linked polyamide membrane was more robust under supercritical conditions compared to the second polyamide membrane with a high level of hydrogen bonding in its structure.

1. Introduction

Supercritical carbon dioxide (SC-CO_2) has been widely used for extraction and recovery of high-value components for many years. In the past two decades, there has been a significant progress in terms of the commercialization of this technology associated with its advantages over the use of organic solvents [1]. Low viscosity and high diffusivity, low process temperature, adjustable solvation properties, ease of removal from extracted components, low cost and availability are some of the main advantages giving rise to numerous applications of SC-CO_2. On the other hand, the cost of recompression of gaseous CO_2 to supercritical conditions is high and powerful compression equipment is required with a refrigeration step [2]. Integration of a membrane separation system with the SC-CO_2 extraction process targets elimination of the depressurization step and reducing the recompression costs.

Membrane separation processes are relatively mature and currently utilized in many industrial applications. They are easy to scale up and economically favourable over energy intensive conventional processes. Membrane separations can be carried out under moderate pressure and temperature conditions. Some of the most common membrane applications are water desalination, enzyme purification, separation of thermolabile substances, concentration of whey and fruit juices and clarification of beverages [3,4]. The main problem associated with membrane separation processes is the low permeate flux when high selectivity is required. Use of SC-CO_2 as a solvent has been proven to increase the flux via reducing the viscosity during transport through the membrane [5].

Many applications of solute component separations, including essential oils, fatty acids and caffeine have been investigated along with separation of ethanol and processing of petroleum products using integrated SC-CO_2 extraction – membrane separation processes over the last decade, employing both organic and inorganic membranes [2,5–13]. The viscosity effect and transport of SC-CO_2 through the membrane network were also evaluated [14–16]. Most of these studies have focused on the permeability and selectivity of membranes under extreme processing conditions associated with the use of SC-CO_2. Although stability is one of the most important factors affecting membrane performance, reports on the stability of membranes processed under supercritical conditions are scarce. Since the use of organic membranes is very popular due to their availability and low cost, stability is even more important when polymeric membranes are employed in coupled SC-CO_2 extraction – membrane systems.

Interactions between CO_2 and polymer structure can adversely affect the membrane performance depending on the polymer material and processing conditions. These interactions were reported previously, targeting different functional groups associated with

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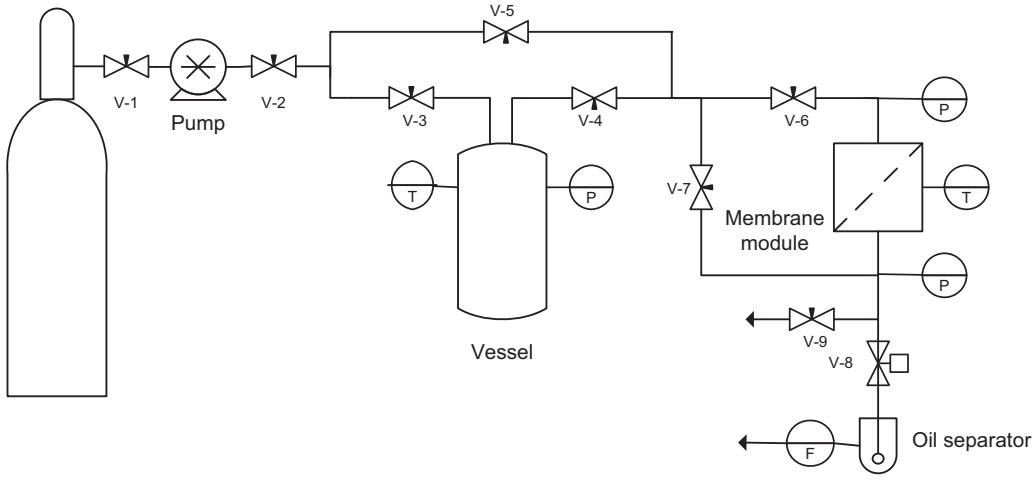

Fig. 1. Flow diagram of the supercritical CO_2 extraction – membrane separation coupled system (V, valve; T, temperature indicator; P, pressure gauge; F, flow meter).

different polymer materials [17–27]. The effect of SC-CO_2 on the polymer membrane structure can be considered in two different parts: swelling behaviour during processing and reorganization of the polymer network upon depressurization. Changes in the physicochemical and morphological properties of two polyamide membranes upon SC-CO_2 processing were previously characterized [28]. The objective of this study was to investigate the effect of those morphological and physicochemical changes on the performance of the same two commercial polyamide membranes (AK and SG). The effects of different temperature, transmembrane pressure, processing time and depressurization rate employed during processing were assessed by measuring CO_2 flux and oleic acid retention as indicators of performance and stability.

2. Materials and methods

2.1. Membranes and materials

Two reverse osmosis (RO) membranes, AK and SG, were kindly provided by GE Osmonics Inc. (Minnetonka, MN) with NaCl rejection rates of 97% and 94%, respectively, as determined previously [29]. The virgin membranes were cleaned by soaking them in deionized distilled water (DDW) water for 24 h and then dried in a dryer at 45 °C for 12 h. After drying, they were placed in a desiccator for a minimum of 24 h. This protocol was found to be sufficient for removal of water from the membranes based on trials of different protocols. Detailed characterization of the membranes used in this study was reported separately, which demonstrated the fully aromatic polyamide structure of AK and the polyesteramide nature of the SG membrane [29]. Oleic acid was obtained from Fischer Scientific (Ottawa, ON, Canada). Bone dry, liquid withdrawal CO_2 was from Praxair Canada Inc. (Mississauga, ON, Canada).

2.2. Supercritical system

The flow diagram of the supercritical system is presented in Fig. 1. The system was modified from that reported previously [28] to be able to perform the oleic acid retention tests. A high pressure stainless steel extraction vessel (200 mL) was used to dissolve oleic acid. The system was pressurized using a syringe pump (Model D260, Teledyne ISCO Inc., Lincoln, NE). A dead-end type stainless steel membrane module (Millipore Corp., Bedford, MA) was used to accommodate flat plate membranes. The membrane module had 9.6 cm^2 active filtration area and was designed to accommodate one flat plate membrane (47 mm diameter) for each experiment. Pressure difference between up and downstream was adjusted by using a back pressure regulator (V-8) (TESCOM 26-1721, Mississauga, ON, Canada). The pressure differential was monitored by two pressure gauges (GE Druck, Leicester, UK). A flow meter (Alicat Scientific, Tucson, AZ) was used to monitor the CO_2 flow under ambient conditions.

2.3. Processing protocols

A two-step protocol was followed for the evaluation of membrane performance under supercritical conditions. In the first step, membranes were processed by passing pure SC-CO_2 through them at different temperatures (40, 60 and 80 °C) and transmembrane pressures (10, 20, 30 and 40 bar) for different lengths of time (0, 2, 8 and 24 h) at 120 bar. In the second step, the change in performance due to the initial CO_2 processing time and conditions was investigated. Oleic acid retention and CO_2 flux were determined in the second step as indicators of performance at 120 bar and 40 °C with a ΔP of 10 bar right after pure CO_2 processing with no depressurization in between the two steps.

In order to reveal the effect of depressurization, system pressure was released to ambient pressure after the first step of SC-CO_2 processing followed by repressurization of the system to 120 bar and setting the temperature to 40 °C for the second step of performance evaluation by flux and retention analysis at ΔP of 10 bar.

2.3.1. Protocol for SC-CO_2 processing

For SC-CO_2 processing of the membranes, flat plate membranes were carefully placed in the module. Valve V-2 was slowly opened, the system was filled with CO_2 and pressurized slowly (~0.2 bar/s) to avoid possible compaction in the membrane structure. When the target pressure was reached (120 bar), temperature was set using the heater around the membrane module and the controller it is attached to. Then, valve V-7 was closed to build up the transmembrane pressure (ΔP) by adjusting the back pressure regulator (BPR) (V-8).

Both AK and SG membranes were processed at different temperatures and transmembrane pressures for up to 24 h as indicated above. Membranes were kept under these conditions for up to 24 h. Membrane processing at each condition was performed in triplicate.

Variation in CO_2 flux with increasing and decreasing ΔP values was tested after the system was pressurized to 120 bar at 40 °C. ΔP was increased from 10 to 40 bar by 10 bar increments and 1 h processing at each step.