Separation of lipid mixtures using a coupled supercritical CO₂–membrane technology system

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A B S T R A C T

Supercritical CO_2 was used as a solvent for the separation of a triacylglycerol/oleic acid (TAG/OA) model mixture at different pressure conditions employing five commercially available polymer reverse osmosis membranes, AK, SG, HL, CE, and DL. Equal amounts of OA and TAG (%, w/w) were placed in the high pressure vessel. Contributions of SC-CO_2 extraction and membrane separation steps on the final OA concentration in the permeate mixture were investigated. TAG and OA separation factors for each membrane were determined at 120 and 280 bar. HL exhibited the best separation factors at 120 bar whereas both SG and HL had the highest OA separation factor at 280 bar. When the pressure was increased from 120 bar to 280 bar, total lipid yield in the permeate stream of SG membrane was increased by 7 fold. Feed pressure of 280 bar resulted in fouling of the membranes after 4 h of processing. Pure CO_2 addition did not delay the decrease in CO_2 flux. Feed pressure was found to be an important parameter affecting yield and final composition after separation by using the coupled SC-CO_2 extraction–membrane separation system.

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1. Introduction

Carbon dioxide is at supercritical state at temperatures and pressures above its critical point (31 °C and 74 bar). Supercritical carbon dioxide (SC-CO_2) is an environmentally friendly solvent and a great alternative to replace organic solvents used for the extraction and recovery of high-value components, due to its tunable dissolving power. SC-CO_2 has advantages over organic solvents regarding its low viscosity and high diffusivity properties. Easy removal upon depressurization from extracted components makes its use very attractive, especially for food and natural product applications.

Membrane technology is a relatively more mature process compared to SC-CO_2 extraction. The main advantages of membrane technology are its easy integration and elimination of the energy-intensive processes with relatively low capital requirements. Thus, attempts have been made to integrate membrane technology with supercritical technology in an effort to extend separation capabilities. The main motivation for the integration of these technologies is to minimize high energy and capital costs associated with the recompression of gaseous CO_2 to SC-CO_2 and the powerful com-pression equipment required. Besides, the use of SC-CO_2 was also found to increase the flux via reducing the viscosity during transport through the membrane [1]. Over the last decade, many applications using this coupled process, specifically, employing organic and inorganic membranes with subcritical pressurized CO_2 or SC-CO_2 as a solvent have been reported. The coupled process has been studied for the separation and purification of triacylglycerols (TAG) and free fatty acids (FFA) for the deacidification of vegetable oil [2,3], separation of squalene and oleic acid (OA) [4], structured lipids (modified TAG) [5], β-carotene from carrot seed oil and a highly unsaturated fraction from less saturated TAG in fish oil [6], nutmeg essential oil [7], lemongrass, orange, and nutmeg essential oils [8], ᴅ-limonene [9], polyphenols [10], and caffeine [11–13].

Polymer membranes are economically more feasible than inorganic membranes. Most of the polymer membranes used in the current investigations under SC-CO_2 conditions has been commercial thin film polyamide reverse osmosis (RO) membranes produced by interfacial polymerization [14]. However, there is no polymer membrane commercially produced specifically for SC-CO_2 applications. In order to maintain the highest efficiency throughout the separation for a particular process, the interactions among the polymer membrane, solute and solvent should be well understood. Especially, tunable properties of SC-CO_2 will most likely result in potential changes in such interactions depending on its density. Although there are a few reports on the characterization of commercial polymer membranes [14–17], studies

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focusing on the separation performance of membranes under SC-CO_2 conditions have been scarce. The fact that membrane fouling is still one of the major problems encountered during separations should also be taken into account.

In order to prove the advantages of the coupled process and demonstrate its potential not only for the separation of lipids from CO_2 but also for the separation of different lipid components, more information is needed regarding the use of SC-CO_2, lipids and polymer membranes to reveal the effect of different processing parameters on the efficiency of separation. Therefore, the aim of this study was to investigate the effect of different pressure (120 and 280 bar) conditions of SC-CO_2 at constant temperature (40 °C) during the separation of OA from a model mixture of OA + TAG using five (AK, SG, HL, DL, and CE) commercially available polymer membranes on membrane performance, which was assessed in terms of CO_2 flux, OA retention, TAG/OA separation factor, and total lipid yield in the permeate stream. The effect of pure SC-CO_2 addition on membrane fouling was also assessed during processing of lipid components.

2. Materials and methods

2.1. Membranes and materials

Five commercially available membranes, AK, SG, HL, DL, and CE were kindly provided by GE Osmonics Inc. (Minnetonka, MN, USA). Physicochemical and morphological properties of these membranes were characterized in previous studies [14,16,17]. The virgin membranes were cleaned by soaking them in deionized distilled 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 and initial FTIR and contact angle evaluations. OA was obtained from Fisher Scientific (Ottawa, ON, Canada). Canola oil purchased from a local store was used as the TAG source (>99% TAG content, containing oleic, linoleic, and linolenic acids, as the major fatty acids). CO_2 (purity of 99.9%, moisture content <3 ppm) with liquid withdrawal dip tube was from Praxair Canada Inc. (Mississauga, ON, Canada).

Sylon BFT (N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA)/trimethylchlorosilane (TMCS), 99:1) and pyridine were purchased from Supelco Inc. (Bellefonte, PA, USA). Dilaurin used as internal standard was purchased from Sigma–Aldrich (Oakwille, ON, Canada). Chloroform (analytical grade) was obtained from Fisher Scientific Ltd. (Ottawa, ON, Canada).

2.2. Processing procedure

The flow diagram of the supercritical system is presented in Fig. 1a, as reported previously [18]. For each experiment, a flat plate membrane (47 mm diameter) was carefully placed in the membrane module (Millipore Corp., Bedford, MA, USA), which was a dead-end filter module with 9.6 cm² active filtration area. With valves V-3, V-4, V-8, and V-9 being closed and V-5, V-6, and V7 being open, the system was filled with CO_2 by slowly opening V-1 and V-2 and pressurized using a syringe pump (Model D260, Teledyne ISCO Inc., Lincoln, NE, USA) slowly (~0.2 bar/sec) to avoid possible compaction in the membrane structure. When the system pressure reached the desired level, temperature was set using the heaters around the tubing and the membrane module and the controller they are attached to. Then, valve V-7 was closed to build up the transmembrane pressure (ΔP) by adjusting the back pressure regulator (V-8) (TESCOM 26-1721, Mississauga, ON, Canada). The pressure differential between the upstream and

downstream of the membrane was determined by two pressure gauges (GE Druck, Leicester, UK). A flow meter (Alicat Scientific, Tucson, AZ, USA) was used to monitor the CO_2 flow under ambient conditions. Flow rate was measured 15 min after CO_2 started to permeate at a given ΔP.

2.3. SC-CO_2 + OA experiments

2.3.1. Processing

For the OA retention experiments, 30 g OA was placed in the vessel (200 mL). The vessel was pressurized to the set pressure by opening valves V-1, V-2, V-3, and closing valves V-4 and V-5. OA + SC-CO_2 mixture was stirred for at least 3 h using a magnetic stirrer placed at the bottom of the vessel before it was fed to the membrane module at the operating conditions. Then, valves V-2, V-3, and V-4 were closed and V-5, V-7, and V-9 were opened to depressurize the lines except the vessel. The procedure described above to start CO_2 transport through the membrane was applied. System conditions were set at 120 bar, 40 °C and ΔP of 10 bar. OA + SC-CO_2 mixture in the vessel was fed to the membrane module 15 min after CO_2 started to permeate by closing valve V-5 and opening valves V-3 and V-4. At the end of the filtration period, depressurization of the system was achieved by closing valves V-2, V-3, and V-4 and opening V-5, V-7, and V-9.

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 with 1 h processing at each step. In order to investigate the effect of fouling, OA transport through the vessel was stopped after 2 h and 8 h of filtration by closing V-3 and V-4 and pure CO_2 was fed to the membrane module by opening valve V-5. CO_2 flux was measured before and after feeding OA to the system for all membranes upon 2 h and 8 h of processing. Then, ΔP was increased from 10 to 40 bar by 10 bar increments and 5 min processing at each step to determine the CO_2 flux at each ΔP. No cleaning was performed prior to the measurement of flux.

2.3.2. Determination of CO_2 flux and OA retention

In order to calculate the CO_2 flux (kg/m² h), the permeate volumetric flow rate was measured (at ambient conditions), multiplied by CO_2 density at those conditions [19] and divided by the area of the exposed membrane (9.6 cm²). Flux values were measured every hour for up to 8 h of processing.

OA retention was determined at 120 bar and 40 °C. Samples were weighed after being collected with and without the use of membrane until up to 50 L CO_2 (measured at ambient conditions) passed through the system during processing. When membranes were used, CO_2 flow rate corresponding to a flux of 50 kg/h m² was recorded by the flow meter and the same flow rate was applied during the process without the use of membranes. The change in OA retention was determined during 8 h processing similar to the previous step with 50 L CO_2 passing through as permeate to determine the initial OA retention for all membranes. Samples were collected, weighed and recorded hourly for up to 8 h of processing. Retention factor was calculated according to Eq. (1).

$$\%R = (1 - C_p/C_f) \times 100 \tag{1}$$

where C_p and C_f represent the total amount of OA collected with and without the use of membrane at the corresponding processing time, respectively. Binary mixture of OA + CO_2 was used to compare the theoretical and experimental OA amounts (C_f) at 120 bar and 40 °C using Chrastil's equation to confirm the acceptability of experimental methods during rejection and yield measurements [20].