# Polymeric membrane for the low energetic demand regeneration of supercritical $CO_2$ (sc-$CO_2$)

D.CHABNI [a], S. CAMY [a*], J.-S CONDORET [a], J.-C REMIGY [a]
[a] *Laboratoire de Génie Chimique, Université de Toulouse, CNRS, INPT, UPS, Toulouse, France*
**Corresponding author: severine.camy@ensiacet.fr*

## 1. Introduction

Use of membranes for supercritical $CO_2$ recycling is very promising from an energy saving point of view. A possible configuration consists in using membranes to concentrate the extracted products in the retentate and to recycle almost pure $CO_2$ in the permeate with a limited loss of pressure (a few tenths of bars compared to hundreds of bars in the classical process).
Such utilization of membranes has already been proposed for oils and fatty acids separation, *i.e.*, separation of nutmeg essential oil [1], the concentration of low volatile compounds [2], and for lipids purification [3].
One major reason to implement such a technology is to reduce the energy consumption of sc-$CO_2$ processes, which is crucial in the case of recovery of low and medium value-added products. To achieve this goal, the membrane should be both highly selective and permeable to $CO_2$ while showing good durability. In this work, commercial polyamide membranes were selected based on their selectivity and permeability observed with water and together with their mechanical resistance. Their permeabilities for pure sc-$CO_2$ were evaluated together with their performances in respect to the retention of vegetable oil, here sunflower oil.

## 2. Materials and Methods

The behavior of these membranes for a long time contacting with sc-$CO_2$ was studied by performing physical ageing tests, where membrane samples were left in an sc-$CO_2$ atmosphere (40°C and 200 bar) during 15 days. Mass transfer properties of these membrane samples were then assessed (by measurement of conventional permeability to gaseous $CO_2$ using the time lag technique) as well as by observing the evolution of their chemical surface properties (ATR-FTIR analysis).
Filtration tests of pure sc-$CO_2$ or (sunflower oil + sc-$CO_2$) mixtures were carried out using a home-designed dedicated filtration cell (88 cm² membrane area) as shown in Figure 1. The cell was operated using two high-pressure syringe pumps for pumping $CO_2$ feed and recovering permeate (Model D260, Teledyne ISCO Inc., Lincoln, NE, USA)). Use of these two syringe pumps ensured perfect control of flowrate and upstream and downstream pressures. The whole setup was temperature controlled. Sunflower oil was injected into the setup using a NEMESYS high pressure syringe pump (Cetoni, Korbussen, Germany) and mixed with the sc-$CO_2$ in a static mixer located upstream of the cell (Figure 1).

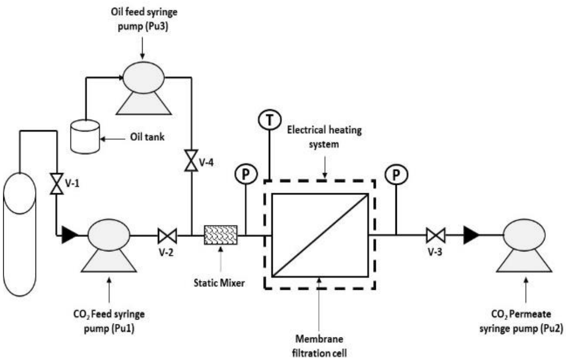

**Figure 1.** High pressure filtration system

## 3. Results and discussion

Ageing experiments showed that neither $CO_2$ gas permeability nor the chemical composition of the two tested polyamide composite reverse osmosis membranes (AG and BW30) were modified after contact with sc-$CO_2$ during 15 days.
Filtration tests of pure sc-$CO_2$ and (sc-$CO_2$ + sunflower oil) mixtures were realized using AG polyamide reverse osmosis membrane. Transmembrane pressure variation as a function of filtration time (Figure 2**Erreur ! Source du renvoi introuvable.**) at a feed $CO_2$ flow rate of 5g/min, temperature of 40 °C and permeate pressure ranging from 80 to 200 bar, have exhibited transmembrane pressures lower than 10 bar for all experiments, allowing obtaining higher than 80% energy saving.
Permeabilities variation, calculated using equation (eqt 1), as a function of sc-$CO_2$ permeate pressure is shown in Figure 3 and indicates that the permeability increases with pressure to reach a maximum value of 36 kg/(h.m$^2$.bar) (at a permeate pressure of 150 bar) and then this permeability slightly decreases. It can be

concluded that the permeability of the membrane in respect to sc-$CO_2$ does not depend only on the intrinsic properties of the membrane, but also on the sc-$CO_2$ properties, therefore on the total pressure and temperature of the filtration system.

$$\boldsymbol{P}_{\boldsymbol{erm}_{\boldsymbol{CO_2}}} = \frac{\boldsymbol{Q}}{\boldsymbol{A} * (\boldsymbol{f}_{\boldsymbol{e,co_2}} - \boldsymbol{f}_{\boldsymbol{p,co_2}})} \qquad \textbf{(eqt 1)}$$

Where $\boldsymbol{P}_{\boldsymbol{erm}_{\boldsymbol{CO_2}}}$ is the $CO_2$ permeability expressed in kg/(h.m$^2$.bar) , $\boldsymbol{Q}$ is the $CO_2$ mass flow rate in kg/h, $\boldsymbol{A}$ represents the membrane surface in m$^2$, and $\boldsymbol{f}_{\boldsymbol{e,co_2}}$ , $\boldsymbol{f}_{\boldsymbol{p,co_2}}$ are the fugacities (bar) of the sc-$CO_2$ at the feed and permeate sides respectively, calculated with Soave-Redlich-Kwong equation of state.

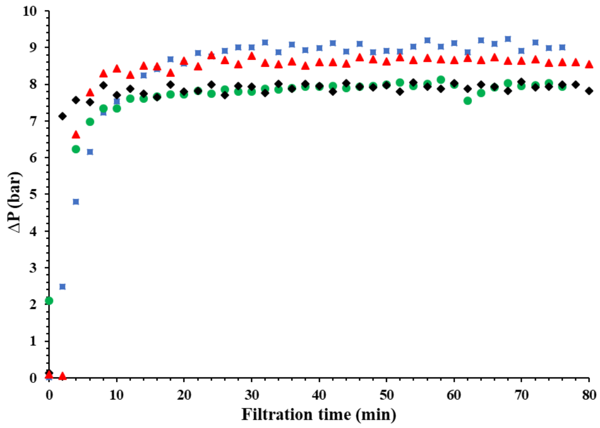


**Figure 2.** ΔP variation as a function of filtration time at different permeate pressure: (■) 80 bar ; (●) 100 bar ; (◆) 150 bar ; (▲) 200 bar, temperature ~ 40°C , feed flow rate : 5 g/min

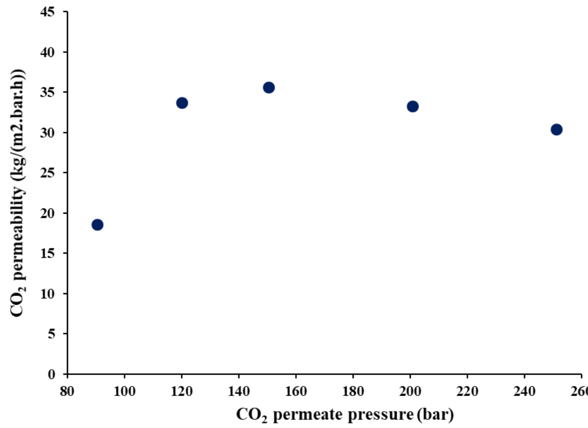


**Figure 3.** Pure Sc-$CO_2$ permeabilities variation as a function of permeate pressure, temperature ~ 40°C, feed flow rate: 5 g/min

Figure 4 shows the variation of pure sc-$CO_2$ permeability and sunflower oil retention versus filtration time during the (sc-$CO_2$ + sunflower oil) mixtures filtration. The results at time 0, 400 and 800 minutes correspond to the filtration of the pure sc-$CO_2$. The $CO_2$ permeability decreases over the filtration time, from 20 to 13 kg/(m$^2$.bar.h) after 680 minutes of filtration time. The retention of sunflower oil remained stable at around 90% over time.

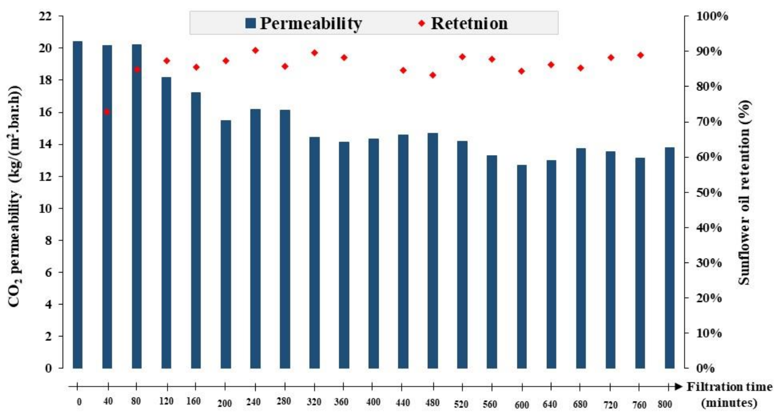


**Figure 4.** sc-$CO_2$ permeability and sunflower oil retention variations as a function of filtration time. Permeate pressure 150 bar, temperature ~ 40°C, $CO_2$ feed flow rate: 5 g/min, sunflower oil feed rate: 10 µg/min

## 4. Conclusions

Commercial membranes, such as polyamide reverse osmosis membranes, can be used for the separation of sunflower oil dissolved in supercritical $CO_2$. Tested membranes were shown to have good stability, a high sc-$CO_2$ permeability, and a good selectivity in respect to sunflower oil. Such results allow expecting significant energy savings in the solvent recycling step that is crucial for the development of industrial processing of low and medium value-added products using supercritical $CO_2$ as a solvent.

## References

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