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Membrane processes in Sc-CO_2 medium for low energy demand supercritical processes

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The implementation of a clean process requires the utilization of a green solvent, among which supercritical CO_2 (Sc-CO_2) is considered as an excellent choice for its modular transport properties (density, viscosity, diffusivity, ...) and its high solvent power towards non-polar compounds.
Despite the fact that the use of Sc-CO_2 is very promising from an environmental and safety perspective, the energy costs due to the compression of CO_2 to the needed high pressure are high and can discourage the adoption of Sc-CO_2 processes on an industrial scale, especially when dealing with moderate added value products.
The goal of our project is to reduce the energy cost of Sc-CO_2 processes by coupling them with membrane processes, allowing the CO_2 recycling at higher pressure, therefore with a limited energy demand for the recompression. The membrane should have a high selectivity and permeability to ensure a needed high CO_2 purity and high flux to achieve a high reduction energy cost. Also use of commercial membranes should be privileged and their durability in these conditions should be assessed.
In this study, selective reverse osmosis membranes based on their commercial specification for water treatment were tested because of their high selectivity (salt rejection > 99%) and high mechanical resistance (transmembrane pressure around 40-50 bar). However, their performances (selectivity, permeability, resistances or ageing) in Sc- CO_2 media are unknown and are the subject of this work.
Selected membranes are thin film composite membranes made of three layers of different materials:

- Separating layer: cross-linked aromatic polyamide, characterized by high resistance to chemical solvents and excellent mechanical properties.
- Support layer: porous polysulfone
- Substrate: non-woven polyester

The behavior of these membranes in contact with supercritical CO_2 is studied by performing physical ageing process at 40°C and 200 bar. The membranes are characterized by the measurement of their mass transfer properties (permeability to CO_2 gas using the time lag technique) and the chemical analysis of their surface properties (ATR-IRTF spectra) before and after contact with supercritical CO_2.
The results show that the permeability (see Table 1) or the chemical composition of two polyamide composite reverse osmosis membranes (AG and BW30) did not change significantly after contact with supercritical CO_2 (Table 1) during 15 days.

Table 1: permeability (mol/m^2. s. Pa) to CO_2 gas of two polyamide-TFC reverse osmosis membranes after 15 days of contact with supercritical CO_2 at 200 bar and 40°C

Membrane/Function/Material	Before Sc-CO_2	After Sc-CO_2
AG/reverse osmosis/polyamide-TFC	**7.03 10^{-7}**	**7.05 10^{-7}**
BW30/reverse osmosis/polyamide-TFC	**6.45 10^{-7}**	**6.43 10^{-7}**

The filtration tests of supercritical CO_2 + oil mixtures are carried out using a specifically made filtration cell and a setup (Top Industrie, France) (Figure 1) consisted of two syringe pumps for pumping CO_2 feed and permeate, a filtration cell for performing filtration tests on 10cm diameter membrane sample, a temperature regulator and a HPLC pump for oil injected using a static mixer.

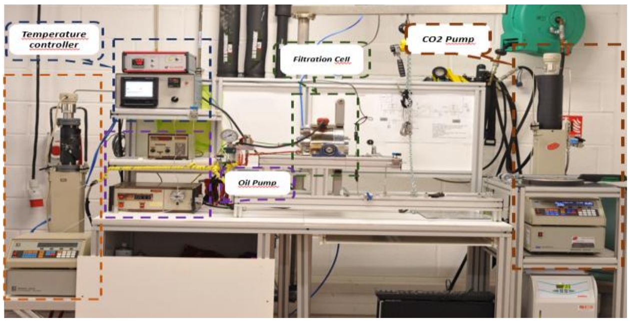

Figure 1: Setup used for the separation of supercritical CO_2 and oil mixture at high temperature and pressure.