USE OF REVERSE OSMOSIS MEMBRANES FOR THE SEPARATION OF LEMONGRASS ESSENTIAL OIL AND SUPERCRITICAL CO$_2$

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Abstract - Although it is still used very little by industry, the process of essential oil extraction from vegetable matrices with supercritical CO$_2$ is regarded as a potentially viable technique. The operation of separating the extract from the solvent is carried out by reducing the pressure in the system. Separation by membranes is an alternative that offers lower energy consumption and easier operation than traditional methods of separation. Combining the processes essential oil extraction with supercritical CO$_2$ and separation by membranes permits the separation of solvent and oil without the need for large variations in extraction conditions. This results in a large energy savings in the case of solvent repressurisation and reuse. In this study, the effectiveness of reverse osmosis membranes in separating lemongrass essential oil from mixtures with supercritical CO$_2$ was tested. The effects of feed oil concentration and transmembrane pressure on CO$_2$ permeate flux and oil retention were studied for three membrane models.
Keywords: supercritical extraction, reverse osmosis membranes, essential oils.

INTRODUCTION

The extraction of substances from solid materials with supercritical carbon dioxide (SCCO$_2$) occurs when the materials are brought into close contact with a flux of dense CO$_2$ (Brunner, 1994). Generally, the solid material constitutes a fixed bed in the form of a column, over which the solvent is passed to extract and draw with it the solute which, up on leaving the extractor, is precipitated by simple expansion of the solvent. Since there is no solvent residue to contaminate the extract, the extraction of natural products with SCCO$_2$ is considered to be an alternative to traditional extraction processes (Reverchon, 1992; Moyler, 1993). According to

Reverchon (1994), a volatile mixture of terpenes and their derivatives is generally responsible for the aroma of vegetable material. The extraction of essential oils from flowers and leaves represents an attempt to obtain a mixture of components in which the original composition of the extract is maintained intact. Unfortunately, the techniques generally adopted, such as distillation and extraction with liquid solvent, have various limitations in relation to preservation of thermolabile compounds, permitting hydrolysis of part of the solute, and contamination of the product by the solvent.

Of the separation processes that employ membranes microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (IO) are

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prominent. In the field of separation technologies, processes involving membranes are frequently preferred in over classical processes for economic reasons. Many of these processes can be developed under moderate conditions of temperature and pressure. Scaling up is easy and energy consumption is generally low. Numerous studies have reported the use of membranes in the processes of separation of $SCCO_2$ and a solute: ethanol (Semenova et al., 1992), light fractions of petroleum (Higashijima et al., 1995), fractionation of triglycerides in supercritical medium (Sarrade et al., 1999), and nutmeg essential oil (Spricigo et al., 2001), all achieving different degrees of separation in which a linear relationship was found between the permeate flux and the applied pressure differential.

Sartorelli and Brunner (2000) observed a characteristic common to many of the processes involving membranes that appears in some separations of $SCCO_2$ and certain types of extract: high selectivity of the membranes is characterised by low permeate flux or high permeate flux combined with low selectivity. This results from the phenomenon known as plasticisation by CO_2 (the CO_2 causes the plasticisation of the membrane, which increases its flux, mainly when high pressures are used). Plasticisation causes "swelling" of the polymeric structure of the membrane through which a large quantity of $SCCO_2$ as well as other components may pass, resulting in a poorly selective flux through the membrane. Even so, the association of the processes of separation by membranes and of supercritical extraction of essential oils from vegetable matrices with dense CO_2 could be an alternative in order to reduce the costs of recompression and reuse of the solvent. Sarrade et al. (2002) present a review of supercritical fluid and membrane coupled processes, such as CO_2 recovery by membranes in supercritical extraction processes, nanofiltration plus supercritical extraction processes applied to the purification of low molecular weight compounds, and supercritical fluid extraction assisted ultrafiltration.

The objective of this study was to investigate the use of commercial reverse osmosis membranes in the separation of lemongrass essential oil and $SCCO_2$.

MATERIAL AND METHODS

Equipment

The experiments in this study were carried out in an experimental unit schematised in Figure 1. This diagram shows part of a pilot extraction and separation unit in which two cells, (6) and (7), encased in and constructed of stainless steel with a unit volume of 30 cm^3 and an internal diameter of 2.3 cm were arranged in series. The membranes to be tested were positioned in one cell (7), whilst the other cell (6) contained quantities of essential oil corresponding to 5%, 10%, and 15% wt.% in relation to the CO_2 that occupied the two cells. The temperature of the cells was maintained by a thermostatic bath (11). The membranes in the cell (6) were placed on a perforated metal support held in place by polytetrafluorethylene rings. The filtration area of the membranes was determined to be 3.14 cm^2 and the dead-end flux regime was used during the experiments. The working pressure of the cells was monitored by a pressure transducer (5) (Model RTP12/BE53R, AEP, Italy) and controlled by a pneumatic valve (4) (Model 807, Badger Meter, USA). The working pressure in the surge tank (3) and in the cells was maintained by a booster (2) (Model DLE 15-1, Maxpro, Germany). The temperature in the surge tank was maintained the same as that of the cells through a thermostatic bath (11).

Membranes

The reverse osmosis membranes denoted CG, SG, and AG, were purchased from Osmonics (USA). The average retention of NaCl, as indicated by the manufacturer, was 85, 98.2, and 99.4%, respectively.

Carbon Dioxide

Carbon dioxide (99.95% purity) was obtained from White Martins (Brazil) and used as solvent.

Essential Oil

The lemongrass essential oil was obtained in this laboratory through extraction of vegetable matrix with supercritical CO_2 at 120 bar and 40ºC.

Experimental Procedure

The tests for characterisation of the membranes in relation to the flux of CO_2 were carried out when valves (17) and (14) were closed and valves (15) and (16) were open to produce equal pressurisation between the two faces of the membrane. After reaching equilibrium pressure, valve (16) was closed and the pressure differential across the membrane was applied using a back pressure valve (9). The pressure differential was monitored by a pressure

transducer (18), and the release of CO_2 was obtained via a flow meter (13). Transmembrane pressure differentials (ΔP) of 10, 20, 30, and 40 bar were applied and the corresponding CO_2 flux for each ΔP was measured until a constant value was obtained. The working pressure was maintained at 120 bar by a booster (2), monitored by a pressure transducer (5) and controlled by a pneumatic valve (4).

The tests for characterisation of the membranes in relation to their essential oil retention capacities and permeability to CO_2 were carried out with the equipment used in the pure CO_2 flux tests. Quantities of essential oil sufficient to maintain the concentrations of 5, 10, and 15% wt.% were placed in cell (6). Valve (15) was closed and valves (14), (16), and (17) were open. Once a pressure equilibrium had been established between the faces of the membranes, valve (16) was closed, and similarly to the procedure for the tests of pure CO_2 flux, the pressure differentials were established by the back pressure valve (9) and monitored by the

transducer (18). The quantities of essential oil permeate were measured by the mass collected in the separator (10). These measurements were taken until a constant flux had been achieved through the membranes. The concentration of essential oil retained by the membrane in the cell (7) was determined by the mass of oil collected in the separator (10) at intervals of approximately 30 minutes through periodic opening of the micrometer valve (8).

All the experiments were carried out at a feed pressure of 120 bar and 40°C. These conditions were used for the extraction of the essential oil that was employed in the experiments designed for the characterisation tests for membrane permeability and retention. Under these conditions, even after establishing a pressure differential of 40 bar, the solvent was found to be in conditions of pressure and temperature above its critical state (critical pressure = 73.8 bar and critical temperature = 31.06°C) on both sides of the membrane.

1 - CO_2 cylinder,
2 - Booster,
3 - Surge tank TP,
4 - Pneumatic valve,
5 - Pressure transducer,
6 - 7 - Cells,
8 - Micrometer valve,
9 - Back pressure valve,
10 - Collectors,
11 - Thermostatic bath,
12 - Personal computer,
13 - Flowmeter
14 - 15 - 16 -17 - Manual valves.
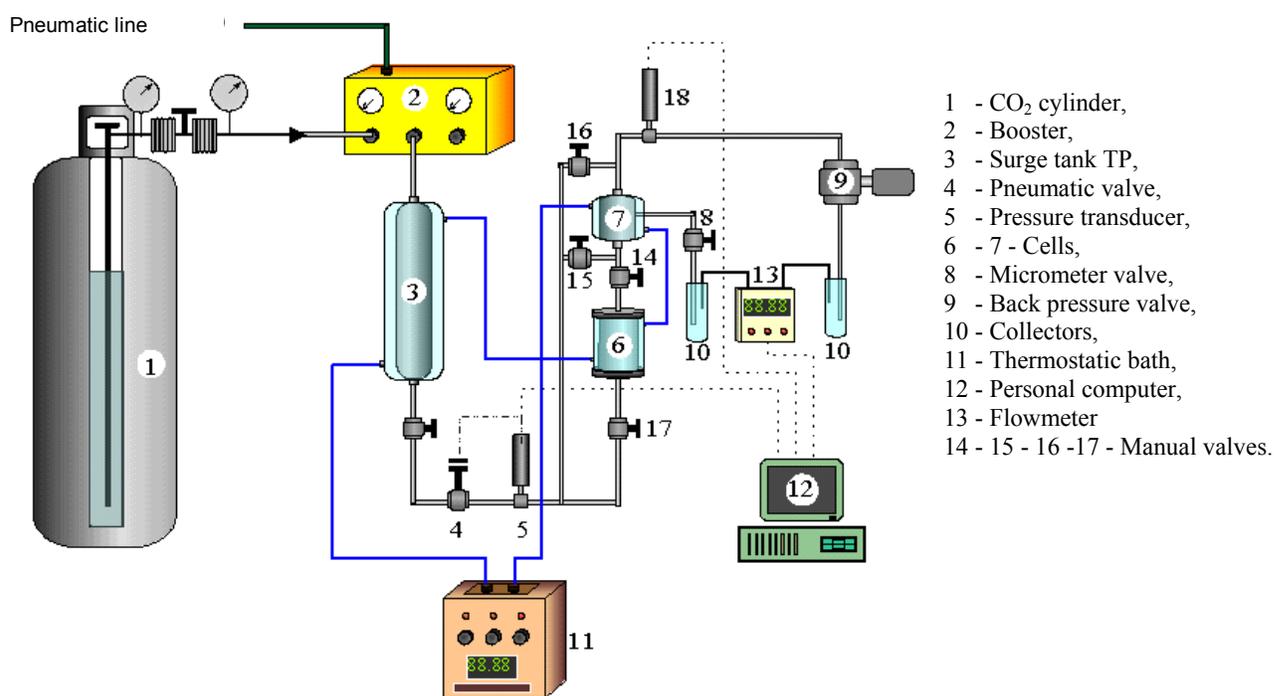
Figure 1: Experimental unit.

Analytical Procedure

Composition of the oil was determined by gas chromatography-mass spectrometry (HP 5971 MSD, Hewlett-Packard, USA) with a fused silica capillary column DB-5 (20 m × 0.188 mm internal diameter, 0.4 μm film thickness). The injector temperature was 280ºC and the flame ionization detector (HP 5890, Hewlett-Packard, USA) was maintained at 320ºC. Oven temperature increased at a rate of 3ºC/min from 60 to 310ºC. The sample volume injected was 0.15 μl of a 10% solution in CH_2Cl_2, with a split rate of 1:50. The carrier gas was hydrogen at a flow rate of 1 ml/min.

RESULTS AND DISCUSSION

Figure 2 presents the results of the characterisation tests for the SG, CG, and AG membranes in relation to flux of pure CO_2 at a feed pressure of 120 bar and transmembrane pressure differentials of 10, 20, 30, and 40 bar. The results demonstrate a linear variation in flux with the pressure differential and indicate that the AG membrane had the best flux rates with the lowest pressure differentials.

The permeabilities of the membranes, determined by the slope of the flux curves with the pressure differential in Figure 2, were 2.158, 1.048, and 3.048 kg h^{-1} m^{-2} bar^{-1}, respectively, for the SG, CG, and AG models.

In Table 1 a comparison between the CO_2 permeate fluxes arising from the CO_2 and essential oil mixture, through the membranes tested at a feed pressure of 120 bar and transmembrane pressure differentials of 10, 20, 30, and 40 bar is presented From this table, it can be seen that the CG membrane had the highest flux rates with the lowest pressure differentials.
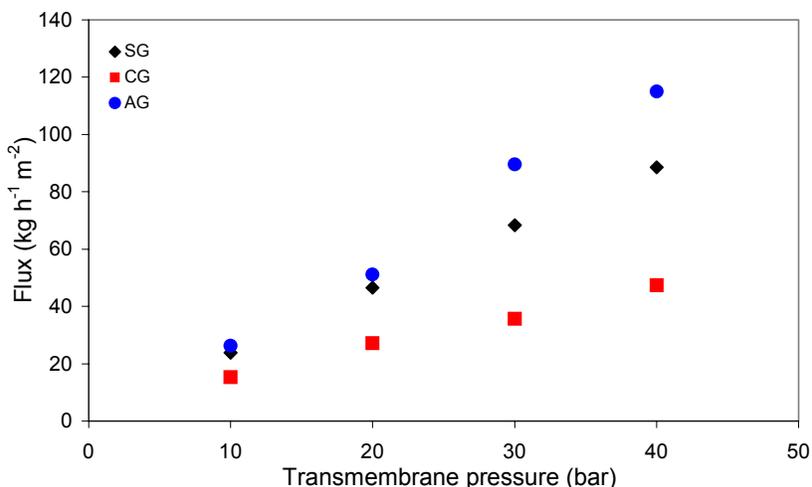
Figure 2: Flux of pure CO_2 through the membranes.

Table 1: CO$_2$ flux obtained with permeation of the CO$_2$ and essential oil mixtures through the membranes.

Flux (kg h^{-1} m^{-2})/Membrane								
	With 5% oil			With 10% oil			With 15% oil		
ΔP (bar)	CG	SG	AG	CG	SG	AG	CG	SG	AG
10	7.62	5.27	4.80	7.47	5.68	5.16	6.78	6.24	7.41
20	12.11	5.98	10.80	11.87	7.62	8.79	15.56	9.50	12.07
30	18.04	6.58	25.76	21.49	9.32	13.11	24.74	10.72	20.96
40	28.12	9.29	38.92	29.09	10.74	33.14	29.24	11.88	54.55

The retention tests were carried out by varying the concentration of essential oil in the feed as well as the applied pressure differential. The retention index (RI) was determined by Equation (1):

$$RI = (1 - C_p/C_i) \cdot 100 \qquad (1)$$

where C_p is the permeate concentration of essential oil and C_i is the feed concentration of essential oil.

In Table 2 a comparison of the essential oil retention indexes for the membranes tested, when exposed to pressure differentials of 10 to 40 bar and feed oil concentrations of 5 to 15% wt.% is presented. The results in Table 2 indicate that the SG membrane showed the best retention index at small pressure differentials, thus being the most suitable for the separation of lemongrass essential oil from supercritical CO_2, even though the fluxes maintained by this membrane were lower than those observed with the CG membrane. The latter, in turn, had the lowest retention index for lower pressure differentials.

Fractionation of the essential oil did not occur with passage through the membranes, and Table 3 presents the lemongrass essential oil composition as determined by gas chromatography-mass spectrometry.

The retention of the essential oil by the membranes was affected only by the pressure differential and did not show significant variation with the concentration of oil in the feed, as can be seen in Table 2. This indicates that, even when increasing the inlet essential oil concentration, membrane selectivity is not altered. The same results were obtained by Spricigo et al. (2001).

Table 2: Retention index of the essential oil by the membranes.

RI (%)/Membrane								
With 5% oil			With 10% oil			With 15% oil		
ΔP (bar)	CG	SG	AG	CG	SG	AG	CG	SG	AG
10	55	88	89	57	90	85	47	87	83
20	47	78	63	50	83	80	53	73	62
30	49	73	45	52	70	49	55	67	48
40	56	45	30	62	59	36	66	55	32

RI = Retention index

Table 3: Composition of lemongrass essential oil.

Component	Retention time (min)	Area (%)
6-Methyl hepten-2-one	8.5	0.3
Myrcene	8.7	2.8
Linalool	13.2	0.9
Citronellal	15.5	0.2
n.i.	16.0	0.4
n.i.	16.5	0.2
n.i.	16.9	0.7
Citronellol	19.3	0.4
Neral	19.8	29.3
Geraniol	20.3	3.5
Geranial	21.2	55.4
Bornyl acetate	21.7	0.2
2-Undecanone	22.1	0.6
Neryl acetate	24.8	0.2
n.i.	25.7	2.2
Geranyl acetate	26.2	0.6
2-Tridecanone	31.0	0.7

n.i.: not identified.

Figure 3 shows the behaviour of the SG membrane in relation to the flux of dense CO_2 before and after permeation by essential oil. The results indicate a reduction in the flux that may be the result of the formation of a film of oil over the filter face of the membranes, causing a greater resistance to the mass flux. Alternatively, it may have been caused by fouling, a common phenomenon when using a reverse osmosis membrane in dead-end filtration regime. The permeability of the SG membrane to pure CO_2 was 2.158 kg h^{-1} m^{-2} bar^{-1}. During the tests with 5, 10, and 15% wt.% essential oil in the feed, the values were 0.127, 0.167, and 0.181 kg h^{-1} m^{-2} bar^{-1}. There was no significant influence of feed oil concentration on membrane permeability. After permeation of the oil, the permeability was 0.903 kg h^{-1} m^{-2} bar^{-1}, indicating a low degree of reversibility

in the processes of resistance to mass flux that act upon the membranes.

In the tests of flux and of permeability to supercritical CO_2 and to the solvent-solute mixture, the pressure differential was increased from 10 to 40 bar, causing a linear variation in the flux before being reduced once again to the initial value of 10 bar. For each ΔP, the fluxes of pure CO_2 or of CO_2 arising from a mixture of CO_2 and essential oil were determined for at least 3 hours, until stationary values were achieved.

In Figure 4 the results for the flux of pure CO_2 during compression and decompression of the SG membrane are presented. Hysteresis was not observed, showing that there was not a significant influence of membrane compaction on permeate flux after submission to a transmembrane pressure of 40 bar.
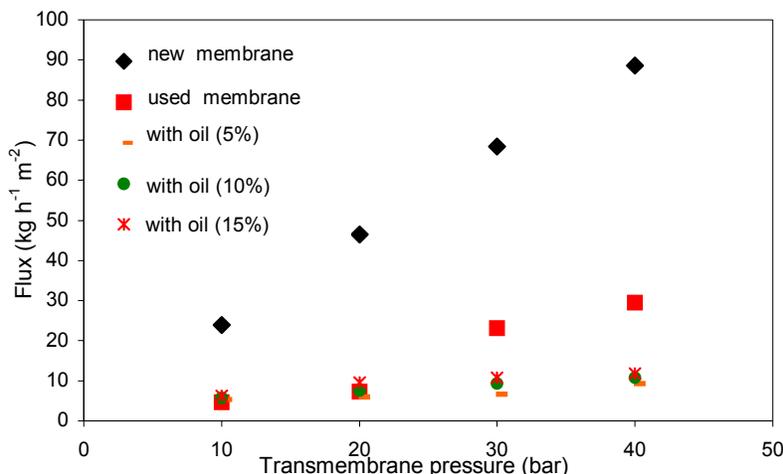
Figure 3: Flux through the SG membrane before and after 140 hours of use.
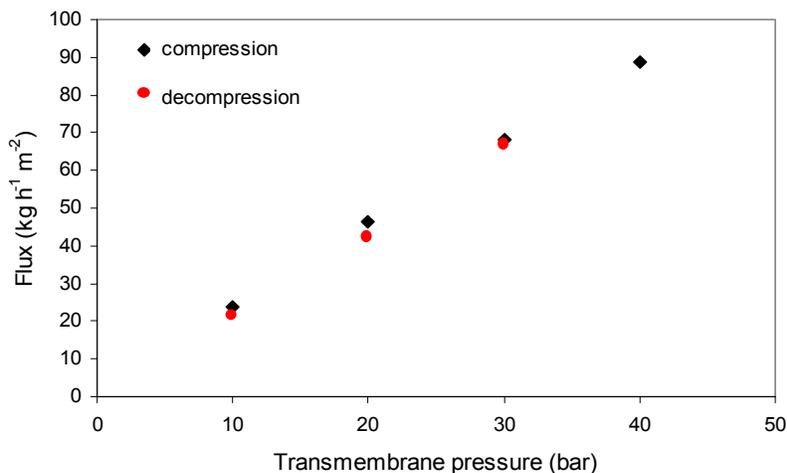
Figure 4: Flux of pure CO_2 during compression and decompression through the SG membrane.

CONCLUSIONS

The results presented in this study demonstrate the possibility of the use of commercial reverse osmosis membranes for the separation of lemongrass essential oil and supercritical CO_2 in the place of the commonly used depressurization step.

The SG membrane showed good resistance to the severe pressure conditions, resulting in a retention index of up to 88% of the essential oil, maintaining an average flux of 5.75 kg h^{-1} m^{-2} and an average permeability of 0.16 kg h^{-1} m^{-2} bar^{-1} for a difference in pressure of 10 bar. Under these conditions a large reduction in energy consumption is possible for the recompression and reuse of CO_2 as solvent, since it is not flashed to the gas phase, but rather is maintained as a supercritical fluid. Also, under these conditions the behaviour of the SG membrane was best with regard to the essential oil retention index.

Although the process of coupling membranes to supercritical extraction has been still, studied very little it was shown to have potential, on account of the resulting economy of extraction, mainly for products of high aggregate value.

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