DEVELOPMENT OF PLATE & FRAME MEMBRANE CONTACTORS

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INTRODUCTION

Membrane Contactors are an emerging technology in which the membrane is used as a tool for inter phase mass transfer operations. The membrane does not act as a selective barrier, as usual, but the separation is primarily based on the principle of phase equilibria. Virtually any adsorption, stripping or extraction process might be performed by membrane modules instead of conventional devices.

Gas membrane separations represent further class of separation processes based on the same idea. In that case a porous hydrophobic membrane is in contact on both sides with non wetting liquids at pressures lower than the pressure needed to displace the gas phase in the pores; gas-liquid interfaces are thus immobilised at both pore mouths and a gas phase is entrapped within the pores.

Membrane Distillation and Osmotic Distillation [1,2] are well known examples of gas membrane separations. O.D. is being considered with great interest as an alternative to evaporation for concentrating aqueous mixtures containing heat sensitive products, ex. vegetable juices or biological products. Concentrated brines are typically used downstream the membrane. Organic extractants, as Glycols or Glycerol, were recently proposed [3,4] in order to avoid corrosion and scaling associated with the use of brine; the process was called *Gas Membrane Extraction*, in that a solvent is used to remove water from the feed.

The use of hollow fibre in several membrane contactor operations have been commercially established [2]. Nevertheless flat sheet membranes might be better in many cases. First of all there is a wider chose of membrane type, secondly flat sheet membranes allow different module designs depending on the fluid properties and process characteristics; highly viscous fluids and streams containing suspended solids are difficult to handled in HF.

The paper will present the development of a plate & frame module suitable for viscous feeds containing also suspended solids. Same compromise has been made between mass transfer efficiency, easiness of construction and maintenance, membrane life etc. The module has been applied in a Gas Membrane Extraction process for concentrating vegetable juices.

OSMOTIC DISTILLATION AND GAS MEMBRANE EXTRACTION.

The physical mechanism of O.D and GME is the same: a porous hydrophobic membrane is in contact with the feed at one side and with a hypertonic solution (extractant) on the other side, at both pore entrances vapour-liquid equilibria are established giving rise to a water vapour pressure gradient through the gas phase entrapped within the pores.

The diffusion of water vapour through the stagnant gas phase can be described by the molecular diffusion model [5]:

$$v = K_m \frac{P_{w1} - P_{w2}}{P_{A_{lm}}} \qquad P_{w1} = P^{\bullet}_{w1} a_{w1} \quad ; \qquad P_{w2} = P^{\bullet}_{w2} a_{w2} \tag{1}$$

in which v is the transmembrane mass flux, P_{Alm} the logarithmic mean pressure of the air within the pores and K_m the membrane permeability depending on the membrane properties, mainly the thickness and porosity.

The description above gives a guideline for the selection of membranes and extractants. A crucial prerequisite for the process is represented by the ability of the membrane to sustain a gas phase within the pores; very important properties are thus the non-wettability of the membrane material, the pore size and the surface tension, which determine the penetration pressure. Pore sizes close to 0.2 µm seem to be adequate for the process. Indeed commercial membranes with 0.2 µm pore size exhibit a penetration pressure for water of nearly 3 bar [6]. Lower pore sizes give of course larger penetration pressure, but also lower permeability due to the Knudsen resistance to mass transfer.

As regard as the extractant, since the driving force for the water transport through the membrane is given by the difference between the water vapour pressures at the two membrane sides, a prerequisite of a good extractant is the high solubility in water. Other crucial properties to be considered are:- high surface tension (to get high penetration pressure), - negligible volatility (to avoid counter-diffusion towards the juice and loss during regeneration), - no toxicity. Based on the criteria above Propylene Glycol (PG),) and Glycerol (GLY) were identified as possible extractants. These compounds can be used in contacting with food, indeed they are allowed in the food as well as in the pharmaceutical industry also as additives. PG and Glycerol exhibit similar extractive power, in both case the driving force available is quite larger with respect to the driving force available with NaCl, especially for high juice concentration. The advantage is nearly 60% for dilute juice and over 200 % for concentrated juices (at 60°Brix).

Fig. 1 reports the fluxes observed in a capillary module made with PP membranes 0.6 mm inner diameter and 200 µm thickness. For comparison the maximum flux values observed in the same conditions with nearly saturated NaCl solution as extractant was only 0.7 kg/m^{2}h. Theoretical flux values were calculated by Eq. (1) using the Km value already measured [6]. Apparently for glycerol concentration lower than 60 wt % the agreement is quite satisfactory, that means that only for larger concentration values the polarisation effects play a role.

Experiments already reported [5] showed that the flux decreases as the water flow rate decreases, that behaviour was explained by the "thermal effect": the mass transfer through the membrane produces a cooling down of the feed and a warm up of the extractant. In the runs reported in Fig. 1 the flow rates of both streams were quite large, so that the thermal effect was negligible.

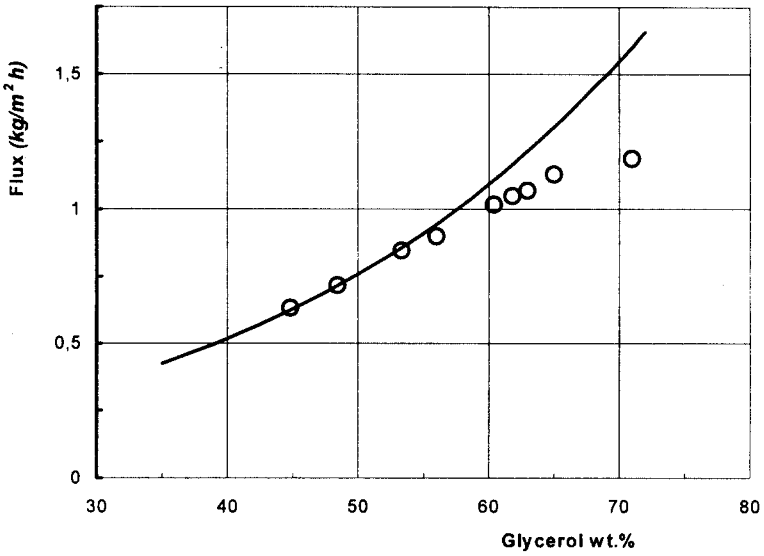

Fig. 1 *Flux vs. Glycerol concentration in the extraction of pure water with Glycerol through capillary membranes at 25°C. Theoretical values were calculated for Km=137.4 kg/m^{2}h.*

Fig. 2 reports the fluxes observed in a small module with flat sheet PTFE membrane 0.2 μm pore size and 60 μm thickness (TF200 by Gelman). Also in this case the flow rates were quite large to minimise the thermal effects. The feed was orange juice or a Glucose-Sucrose mixture in the weight ratio 2:1, whereas the extractant was glycerol 70 w t%. It is interesting to note that the difference between theoretical and experimental flux values is nearly constant up to 40°Brix, that means that the juice side concentration polarisation becomes important only for larger concentrations.

The use of organic extractants, as PG and GLY seems advantageous with respect to brine, however in order to accept GME as a reliable technique for juice concentration any solvent entrainment has to be excluded. Solvent entrainment can occur due to membrane defects, membrane wetting, or counter diffusion of the extractant through the gas membrane. Membrane defects, even not present in the new membranes, can arise from membrane failure during module assembling and operation. In the case of small defects solvent entrainment can be avoided maintaining a small overpressure in the juice side. Membrane wetting occurs if the hydraulic pressure prevailing in the liquid phase exceeds the penetration pressure of the membrane. On the other hand large pressure drop through the module are expected owing to the large viscosity of PG and GLY solutions, large penetration pressures are thus required for safe operation.

The penetration pressure of PG solutions in the capillary membranes used in the experiments, showed to be 1.25 bar at 65% wt and 1.1 bar at 80% wt. On the other hand the surface tension was 48 dyne/cm and 45 dyne/cm respectively, quite below the surface tension of water.

Glycerol solutions, on the contrary, exhibit surface tension, and thus penetration pressure similar to water.

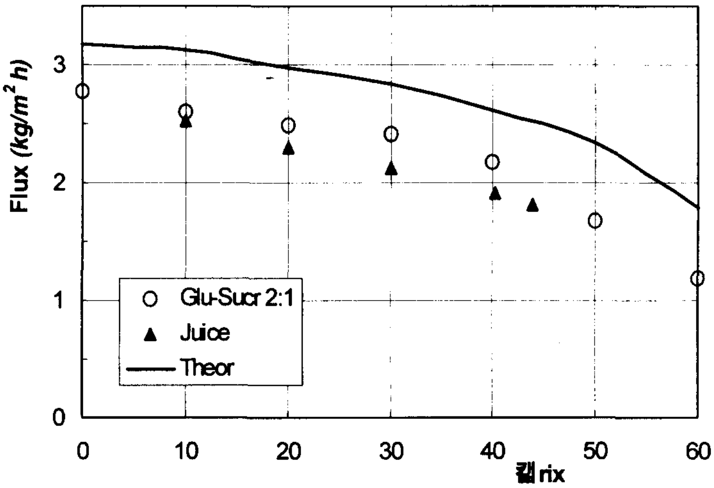

Fig. 2 *Flux vs. Juice concentration in the extraction of with Glycerol 70 wt% through PTFE membranes at 25°C. Theoretical values were calculated assuming Km=300 kg/m^{2}h.*

Counter-diffusion of the extractant towards the juice through the gas membrane is related to the volatility of the extractant, which in the case of PG is appreciable: at 25°C the vapour pressure of pure PG and Gly are 17.33 Pa and 0.026 Pa respectively.

Indeed appreciable quantity of PG was detected in the feed after experiments: the observed ratios of PG to water fluxes is nearly 7 g/kg, PG cannot thus be recommended as extractant in the juice concentration. In similar experiments performed with GLY solutions the GLY concentration in the feed after the experiment was not detectable with the analytical method used.

CONCENTRATION AND TEMPERATURE POLARISATION

As in all the membrane processes, the flux through the membrane can be limited by the concentration polarisation phenomenon. Since only water passes though the membrane, the solute concentration near the membrane is larger than the bulk value in the feed side, and lower than the bulk value in the extract side.

According to the well known film theory model we have:

$$v = k_{L1}\rho_1 \ln\frac{x_1^I}{x_1} \approx k_{L1}\rho_1 \frac{a_{w1} - a_{w1}^I}{\gamma_{w1} x_{1ml}} \tag{2}$$

$$v = k_{L2}\rho_2 \ln\frac{x_2}{x_2^I} \approx k_{L2}\rho_2 \frac{a_{w2}^I - a_{w2}}{\gamma_{w2} x_{2ml}} \tag{3}$$

In addition to the mass transfer through the membrane and through the boundary layers, also heat transfer is concerned, indeed the water transport implies evaporation at the feed side and condensation at the extract side. As a consequence a temperature difference is created through the membrane even if the bulk temperatures of the two liquids are equal (thermal effect).

The thermal effect has been analysed in a recent paper [5]. In a co-current apparatus an asymptotic value, ΔT_∞, of the temperature difference between the two streams is finally reached at which the convective heat flux through the membrane ($v\lambda$) is exactly balanced by the conductive heat back-flux ($h_m \Delta T$):

$$\Delta T_\infty = \frac{v\lambda}{h_m} \tag{4}$$

The effect of ΔT_∞ on the driving force for water transport can be evaluated by the Clausius-Klapeyron equation,. We finally have:

$$v_\infty = \eta_\infty K_m \frac{\Delta P_{wm}}{P_{Alm}} \tag{5}$$

in which ΔP_{wm} represents the vapour pressure difference evaluated at the average temperature, which in the symmetric case (equal inlet temperatures and heat capacities of the two streams) is equal to the inlet temperature. η_∞ is a sort of efficiency coefficient describing the thermal effect, in that it represents the fraction of the driving force really effective for the mass transfer through the membrane.

$$\eta_\infty = \left[1 + \frac{\lambda^2 M P_w^* a_{wm}}{R T^2 P_{Alm}} \frac{K_m}{h_m} \right]^{-1} \tag{6}$$

It is interesting to note that since both K_m and h_m are inversely proportional to the membrane thickness, η_∞ is independent of it. Essentially η_∞ depends on the void fraction and on the thermal conductivity of the membrane material. PTFE membranes with 60% void fraction showed nearly 70% efficiency at 25°C, whereas for Polypropylene membranes of similar characteristics the efficiency is nearly 60%.

The role played by the concentration polarisation can be easily evaluated considering the asymptotic conditions, at which the temperatures of the two streams have reached the asymptotic values. The situation can be analysed as a “pseudo isothermal” case in which the flux through the membrane is given by :

$$v = \eta_\infty K_m \frac{P_w^* (a_{w1}^I - a_{w2}^I)}{P_{Alm}} \tag{7}$$

Formally Eqs (2), (3) and (7) represent a purely mass transfer problem which can be analysed by the resistance in series concept:

$$v = K_O P_w^* (a_{w1} - a_{w2}) \tag{8}$$

The overall mass transfer coefficient is defined as:

$$\frac{1}{K_O} = \frac{\gamma_{w1} x_{1ml}}{\rho_1 k_{L1}} + \frac{\gamma_{w2} x_{2ml}}{\rho_2 k_{L2}} + \frac{P_{Alm}}{P_w^* \eta_\infty K_m} \tag{9}$$

Let's consider the special case in which the stream 1 is pure water and the stream 2 Glycerol 70 wt %. In this case the first term on the second side of Eq. (9) vanishes and we have to compare only the mass transfer resistance in the extract side and through the membrane. For a PTFE membrane with K_m = 300 kg/m^{2}h the extract side mass transfer resistance represents only 5% of the overall resistance if $k_{L2}=10^{-5}$ m/s, and 35% if $k_{L2}=10^{-6}$ m/s. Experiments and simulations with flat membrane modules with different spacers showed that the extract side resistance represents, on average, 20% of the overall resistance; this figure is related to the glycerol viscosity and cannot be appreciably reduced by changing the spacer shape or increasing the glycerol velocity.

Experiments and simulations with orange juice and glucose/sucrose mixtures showed that the feed side mass transfer resistance is quite small up to 40°Brix and rapidly increases with concentration, at 60°Brix it represents over one half of the overall resistance.

MODULE DESIGN

A pilot plant with plate & frame modules of 30 m^2 overall membrane area is under construction with PTFE membranes. The module design is similar to a dialysis unit; attempts were made to minimise polarisation effects, however many other factors were more important in the final design. As an example, in order to process juices containing appreciable quantity of pulp, the feed spacer was eliminated, as a result the expected flux with concentrated juices will be far from the ideal one, on the other hand with a good spacer the operation would be impossible at all.

The plant will be tested in the next season with grape juice and, after, with tomato juice, in both cases no particular pre-treatments are foreseen.

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