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Membrane Distillation Process Design Applied to Highly Concentrated Brines: Mathematical Model and Operating Conditions Analysis

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Water scarcity is an important problem in many countries that is expected to worsen with demographic increase. The world population should increase by 2.5 billion people by the year 2050 [1], and considering that about 70% of all freshwater withdrawn from natural resources around the globe is destined to agriculture [2], the cost of freshwater for the chemical processing industry (CPI) is going to experience a steep increase in the next decades. To illustrate the magnitude of this problem, a modern petroleum refinery consumes about 1 to 2.5 m^3 of water for each cubic meter of finished products produced [3]. For that matter, a large number of aqueous effluent reduction discharge projects are being implemented throughout the CPI.

The aqueous waste stream of a well-designed effluent treatment plant in the CPI, after the conventional primary, secondary and tertiary processing steps, is comprised mainly of inorganic species (salts) dissolved in water. Partial recovery of the water content in these saline effluents is frequently achieved by means of desalination processes like reverse osmosis and electrodialysis. However, 20 to 40% of the water is not recovered by such processes and comprise concentrated brines that are normally disposed in evaporation ponds, deep wells and coastal waters [4]. Not only is this water wasted but the disposal of concentrated brines imposes hazards to the environment [5] and is becoming very restricted by environmental protection agencies worldwide. Therefore, zero liquid discharge (ZLD) is becoming a necessary objective of many water recovery initiatives.

Recovery of the water contained in concentrated brines is, on the limit of a ZLD objective, a separation problem that will most likely consider a crystallization step. A prerequisite to promote crystallization of saline species dissolved in water is the supersaturation state, which may be achieved either by cooling or solvent evaporation, depending on the solubility behavior of the salts with respect to temperature variations. For brines containing significant amounts of sodium chloride (it is the case of industrial effluents in many CPIs), which display a high and temperature invariant solubility, conventional thermally driven crystallizers are the most suitable choice (forced circulation and draft-tube-baffled crystallizers have been widely used for production of sodium chloride from seawater [6]). These conventional technologies require relatively hot heat sources as evaporation takes place at the boiling point of the saline solution, and although the boiling point is occasionally lowered by means of vacuum application, evaporative crystallizers generally operate at temperatures higher than 70°C, with specific energy consumptions in the range of 30 kWh/m^3 of distillate produced [7].

Membrane distillation (MD) is an alternative thermally driven process that was developed in the late 1960s but did not attain commercial status at the time, mainly because of difficulties to obtain suitable membranes at reasonable costs [8]. Recent developments in membrane manufacturing technology allied to the research of less energy intense processes favored a rebirth of the MD process. The use of MD as the supersaturation promoter in a crystallization system was first proposed by Curcio et al. [9] in a process named membrane distillation crystallization (MDC). In MDC,

the high contact area provided by hollow fiber microporous hydrophobic membranes allows the achievement of reasonable evaporation fluxes at moderate temperatures (40-60°C) at atmospheric pressure, with an average energy consumption that ranges from 15-20 kWh/m^3 [7]. Also, the moderate temperatures involved in MD processes allow the utilization of low-grade waste energy sources (frequently readily available at oil refineries and petrochemical processing complexes) and/or alternative sources such as solar, wind and geothermal energy [10, 11].

The aim of the present work was to develop a mathematical model to assist the design and the establishment of optimum operating conditions of MD processes in applications where well soluble salts like sodium chloride are involved, which implies in concentrated solutions that require a rigorous approach for the water activity prediction in order to correctly estimate the vapor pressure depletion in the retentate side. The direct contact membrane distillation (DCMD) configuration was modeled because it is the most simple, economical and efficient configuration for the concentration of aqueous inorganic streams [9, 12, 13]. Also, regarding the membrane module geometry, the hollow fiber type was modeled due to its large specific contact area (about 10^4 m^2/m^3) and consequent better suitability for industrial applications when compared to its flat sheet type counterpart, normally found in laboratory apparatus [9, 10].

In DCMD, as depicted in Figure 1, hot saline solution is fed to one side of a microporous hydrophobic membrane (normally made of polymeric materials). The other side of the membrane is fed with pure cold solvent (in the present case, water). The vapor pressure difference established across the membrane air-filled pores drives the evaporation of solvent from the hot side to the cold side, with subsequent vapor condensation. The small size of the pores, in the range of 0.1 to 1.0 µm, prevents liquid to flow across the membrane pores (due to surface tension). Hence, only vapor is transferred from the hot side to the cold side, which causes the saline solution to become more concentrated in the hot side (the so-called retentate) and pure water to be recovered in the cold side (permeate).

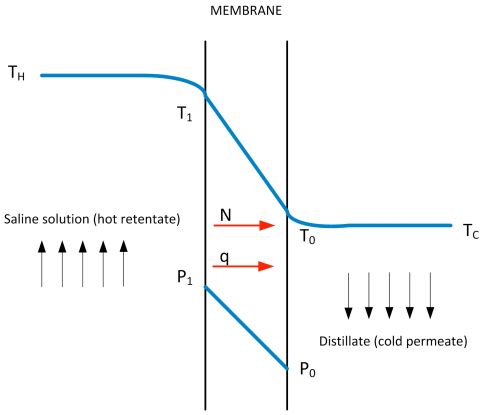

Fig. 1: Temperature and vapor pressure profiles across a hydrophobic membrane in a DCMD configuration.

In order to model the simultaneous heat and mass transfer phenomena that take place across the hydrophobic microporous membrane, the theory developed by Schofield and co-workers [14] for DCMD was employed. The water activity in the retentate side was rigorously modeled according to a Pitzer-based thermodynamic method [15], due to the significant role that water activity plays in the vapor pressure depletion of the resultant highly concentrated solution, specially in MDC applications where the retentate operates close to saturation or even at supersaturated conditions. The model also accounted for the temperature polarization effects due to heat transfer resistance across the membrane, which ultimately influences the process driving force (the temperature difference between the hot and cold fluids fed to the membrane module). Likewise, concentration polarization

that takes place on the hot side of the membrane is estimated by the model and considered in the net vapor flux calculation. A differential mass and energy balance performed for the hollow fiber module, which is similar to a shell and tube heat exchanger configuration, allowed the model to predict the concentration and temperatures profiles along the module and ultimately predict the required module dimensions (length, number of tubes, total area) and most suitable fluid dynamics (circulation flowrates, pressure drop, liquid entry pressure) for a given set of conditions (available feed temperatures of the hot and cold fluids, feed solution concentration, available commercial membrane characteristics as pore size, thickness, material etc.). Figures 2, 3 and 4 are model outputs for an arbitrary design case.

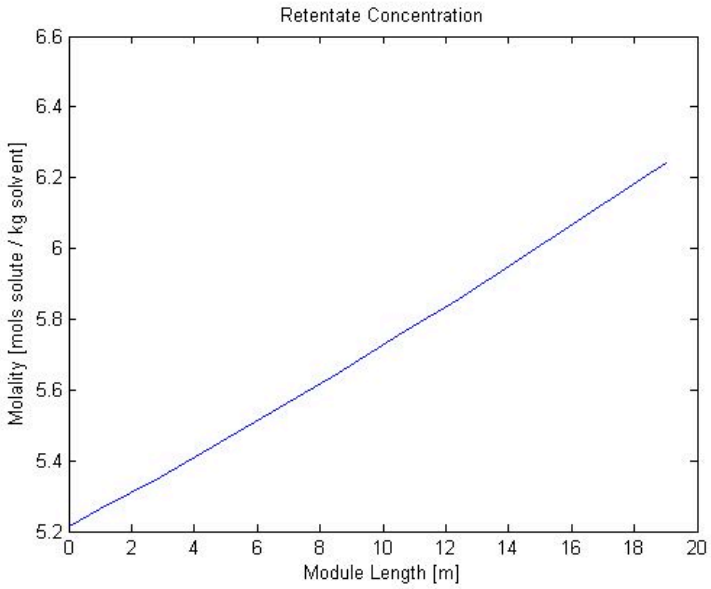

Fig. 2: Concentration profile across a DCMD membrane module.

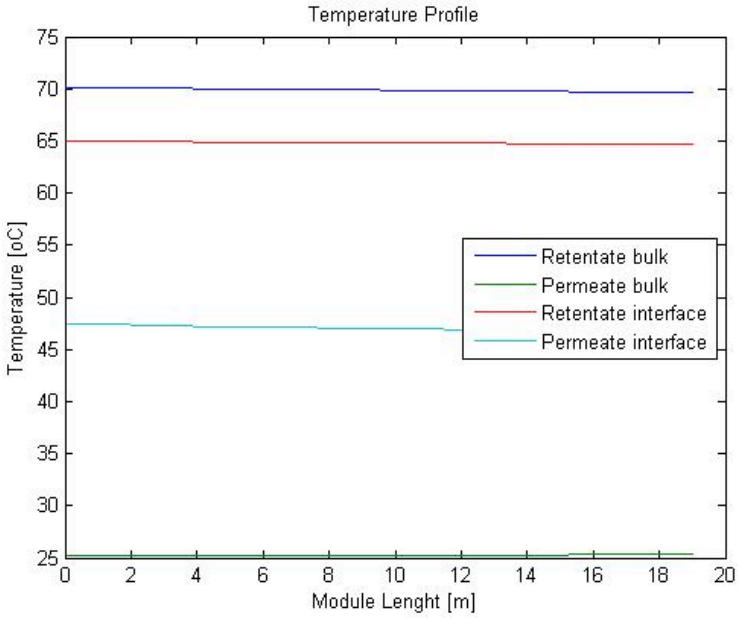

Fig. 3: Temperatures profiles across a DCMD membrane module.

The knowledge of concentration and temperatures profiles along the membrane module might be necessary, for example, in a MDC process design where the degree of saturation or supersaturation

of the retentate must be closely controlled in order to prevent crystallization on the membrane surface (which could cause its clogging).

Finally, as the present model is intended to assist the process design of membrane distillation processes as a whole, which comprises not only the determination of the membrane module dimensions but also the optimum process conditions (although both tasks are related), as previously mentioned, a hierarchical design approach [16] based on heuristics, experimental information and qualitative theoretical considerations was developed in order to be used alongside the model itself as a design tool. The full paper will present both the model and the hierarchical design approach in detail.

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