Membrane-assisted crystallization: Membrane characterization, modelling and experiments

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ABSTRACT

A hollow fiber membrane module was assessed for its potential in assisting crystallization processes. The membrane module was characterized in the sweeping gas membrane distillation configuration considering various solution and sweeping gas flow rates, temperatures and solution concentrations. A model, coupling mass and heat transfer, was developed to predict the membrane flux. The effect of the process conditions on the membrane flux was experimentally determined and the results were used to validate the model. Feed temperature and air flow rate were found to have a significant effect on the membrane flux. Having found the optimal process conditions for membrane distillation process, batch seeded crystallization experiment were performed to confirm the potential of membrane distillation in the generation of adequate rate and level of supersaturation. Since the desired supersaturation level could be maintained in the crystallizer while seeds were growing, it is confirmed that membrane distillation can be an efficient alternative to conventional super-saturation generation processes. Finally, comparing the modelling results with experiments confirms the acceptable accuracy and predictability capability of the developed model.

1. Introduction

Crystallization is one of the oldest and the most widely applied separation process in the chemical and pharmaceutical industries (Drioli et al., 2012). supersaturation is the driving force for the crystallization. Generation of supersaturation can generally be achieved by either reducing the solubility of solution (eg cooling) or by removing the solvent from the solution by evaporation (Lakerveld et al., 2010; Curcio et al., 2001). However, evaporation in a crystallizer is limited by the area available for evaporation and the entrainment of liquid droplets in the condenser. Furthermore, it is challenging to produce thermally labile compounds by evaporative crystallization, because of the high investment cost involved in evaporating the solvent at a lower temperatures (Kuhn et al., 2009).

A viable alternative to evaporation can be found in the desalination industry. Membranes are being widely used to substitute evaporation for obtaining the solvent (pure water) from the solution (saline water) (Khayet et al., 2003, 2000a, 2000b). Membranes can perform the similar task to concentrate a solution thereby generating supersaturation required for crystallization. Such an innovative combination of membranes and crystallization, Membrane-assisted Crystallization (MaC), has the potential to overcome the previously mentioned limitations of evaporative crystallization. MaC of several compounds

has been investigated (Kuhn et al., 2009; Curcio and Drioli, 2005; Gryta, 2002), and in a theoretical study it has been suggested that MaC can be applied to a large variety of systems (Lakerveld et al., 2010).

Among the various membrane processes, Reverse Osmosis (RO), Osmotic Distillation (OD) and Membrane Distillation (MD) are the most commonly used processes in MaC. The high potential of MaC-RO and MaC-OD to control the generation of supersaturation and to concentrate a solution was found in the precipitation and crystallization processes (Curcio and Drioli, 2005; Azoury et al., 1986). The potential of using MaC-RO process was investigated by optimization of final mean size with minimal energy conversion for adipic acid (Kuhn et al., 2009). MaC-RO was successfully used for NH_4SO_4/water and adipic acid/water systems. It was observed that selectivity and membrane flux depend on the level of solubility and dependency of solubility on temperature (Lakerveld et al., 2010). In case of temperature sensitive compounds OD is most often used to remove water from liquid foods since the driving force for OD is the concentration difference and it can be operated in relatively low temperatures (Gryta, 2005; Warczok et al., 2007).

MD is a promising alternative for compounds with high osmotic pressure. It is a thermally driven process in which the volatile components are transported across a porous hydrophobic membrane due to the difference in the vapor pressures across the membrane

List of symbols

Symbol Unit Properties

a	[Dimensionless] Activity coefficient
A_m	[m^2] Membrane total area
A_{ant}	23.1964 Antoine constant
B_{ant}	3816.44 Antoine constant
C_{ant}	−46.13 Antoine constant
C_1	1.2 Activity coefficient constant
C_2	0.003 Activity coefficient constant
C_p	[J/kg K^{-1}] Specific heat
d_m	[m] Membrane module diameter
d_t	[m] Membrane central tube diameter
d_i	[m] Tube inner diameter
d_o	[m] Tube outer diameter
d_c	[m] Cell diameter
d_h	[m] Hydraulic diameter
$d_{h,f}$	[m] Hydraulic diameter of shell side
$d_{h,a}$	[m] Hydraulic diameter of lumen side
D_{kn}	[m^2/s] Knudsen coefficient of diffusion
D_{mol}	[m^2/s] ordinary molecular diffusion coefficient
D_{mem}	[m^2/s] Diffusion coefficient of combination
h_f	[W/K m^{-2}] Heat transfer coefficient of feed side
h_a	[W/K m^{-2}] Heat transfer coefficient of air side
h_m	[W/K m^{-2}] Heat transfer coefficient of membrane
h_v	[W/K m^{-2}] Heat transfer coefficient related to MD flux
h_{fluids}	[W/K m^{-2}] Heat transfer coefficient of fluids
h_{tot}	[W/K m^{-2}] Total heat transfer coefficient
J	[kg/s m^{-2}] Membrane flux
k_a	[m/s] Mass transfer coefficient of air side
K_{mem}	[m/s] Mass transfer coefficient of inside the membrane
k_{tot}	[m/s] Total mass transfer coefficient
L	[m] Membrane length
m_w	[kg/mol] Molecular mass of water
N	[Dimensionless] Membrane number of fibers
Nu	[Dimensionless] Nusselt number
P	[Pa] Pressure
$P'_{v,f}$	[Pa] Vapor partial pressure of feed interphase
$P^o_{v,f}$	[Pa] Vapor partial pressure of pure water
$P_{v,a}$	[Pa] Vapor partial pressure of permeate side
Pr	[Dimensionless] Prandtle number
Q_f	[W/m^2] Heat flux of feed side
Q_a	[W/m^2] Heat flux of air side
Q_m	[W/m^2] Heat flux of membrane
Q_v	[W/m^2] Heat flux due to MD flux
R	[J/K mol^{-1}] Gas constant
r	[m] Membrane pore size
Re	[Dimensionless] Reynolds number
Sc	[Dimensionless] Schmidt number
Sh	[Dimensionless] Sherwood number

T_f	[K] Bulk temperature of feed side
T'_f	[K] Membrane interface temperature of the shell side
$T_{f,in}$	[K] Inlet temperature of lumen side
$T_{f,out}$	[K] outlet temperature of shell side
T_a	[K] Bulk temperature of shell side
T'_a	[K] Membrane interface temperature of lumen side
$T_{a,in}$	[K] Inlet temperature of lumen side
$T_{a,out}$	[K] outlet temperature of lumen side
u_a	[m/s] Linear air velocity
u_e	[m/s] Effective feed velocity
x	[m] Location on membrane length
x_s	[kg solute/kg solvent] Weight fraction of L-ascorbic acid in solution
x'_s	[kg solute/kg solvent] Weight fraction of L-ascorbic acid at the interphase
ΔH_v	[kJ/kg] Heat of vaporization of water
ΔH^o_v	[kJ/kg] Heat of vaporization of water at 0 ºC
δ	[m] Membrane thickness
ε	[Dimensionless] Membrane porosity
ϵ_p	[Dimensionless] Membrane packing fraction
ρ_f	[kg/m^3] Feed density
λ_{mm}	[W/m K^{-1}] Membrane material thermal conductivity
ω	[Dimensionless Air humidity
ϕ_a	[m^3/s] Volumetric flow rate of air
ϕ_f	[m^3/s] Volumetric flow rate of feed
π	[Dimensionless] Pi number
τ	[Dimensionless] Membrane tortuosity

Subscripts

f	Feed
s	Solute
a	Air
mol	Molecular
mem	Membrane
c	Cell
i	Internal
o	External
t	Central tube
m	Module
p	Packing
in	Inlet
out	Outlet
tot	Total
w	water
e	Effective
v	Vapor
h	Hydraulic
Kn	Knudsen
ant	Antoine

(Khayet et al., 2000; Souhaimi and Matsuura, 2011). MD gets its name from the similarity with conventional distillation process. Both processes are based on vapor-liquid equilibrium for separation and both processes require heat supplied to the feed for achieving the latent heat of vaporization (Souhaimi and Matsuura, 2011). It can be carried out in various configurations, out of which Direct Contact Membrane Distillation (DCMD) is the most studied and the commonly used in MaC. However, DCMD suffers from severe heat loss due to conduction across the membrane resulting in high temperature polarization.

The objective of this work is to use a relatively less studied configuration of MD, Sweeping Gas Membrane Distillation (SGMD), to generate the required supersaturation to carry out crystallization in

an L-ascorbic acid/water solution system. In SGMD, an inert gas is used in the permeate side to sweep away the vapor transferred through the membrane. The use of the inert sweeping gas reduces the conductive heat loss and the mass transfer resistance (Khayet et al., 2003). SGMD remains the least studied MD configuration, as MD was primarily developed for the desalination industry, and hence would require an external condenser to condense the water vapor from the sweep gas, thus complicating the system (Souhaimi and Matsuura, 2011). However, this complication does not apply when the objective is to merely concentrate a solution, which means that SGMD is potentially favorable in MaC.

In order to successfully implement SGMD in MaC, a detailed study