Membrane Crystallization and Membrane Condenser: Two Membrane Contactor Applications

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Abstract

In recent years different new membrane processes have been designed and developed. In this paper two innovative processes (i.e., membrane condenser and membrane crystallization) will be described and discussed. Membrane crystallization can be used in desalination in combination with membrane distillation and pressure driven membrane processes (such as nanofiltration or reverse osmosis) to achieve high recovery factor combined to salt crystals production. The innovative membrane condenser can be used for the selective recovery of evaporated waste water and contaminants from industrial gases. This process can be also used for pre-treating gas streams that require further separation for the recovery of a defined species (such as pre-treatment of flue gas when used for CO2 capture, biogas for bio methane production, etc.).

The current status, the separation principle, the utilized membrane materials and membrane configurations, and the application fields are described and discussed. The future development direction of these two processes is also given.

Keywords: Membrane Crystallization; Membrane Condenser; Water recovery; Membrane Technologies;

Abbreviations

Acronyms

AGMCr air gap membrane crystallization
AGMD air gap membrane distillation
DCMCr direct contact membrane crystallization
DCMD direct contact membrane distillation
ECTFE ethylene chlorotrifluoroethylene
LEPw liquid entry pressure (water)
MCo Membrane condenser
MD membrane distillation
MCr membrane crystallization
NIPS non-solvent induced phase separation
NF Nanofiltration

http://www.journalofchemistry.net
OMCr | osmosis membrane crystallization  
OMD | osmosis membrane distillation  
PP | Polypropylene  
PTFE | polytetrafluoroethylene  
PVC | Polyvinylchloride  
PVDF | polyvinylidene fluoride  
SGMCr | sweep gas membrane crystallization  
SGMD | sweep gas membrane distillation  
RO | Reverse osmosis  
TIPS | thermally induced phase separation  
VIPS | vapor induced phase separation  
VMCr | vacuum membrane crystallization  
VMD | vacuum membrane distillation  
ZLD | zero liquid discharge

**Introduction**

In recent years membrane engineering has played a fundamental role in the industrial field [1–3]. At present, many different membrane processes are widely utilized (such as nanofiltration (NF), ultrafiltration (UF), reverse osmosis (RO)), and other are in the developing phase (such as, membrane distillation (MD), membrane crystallization (MCr), membrane condenser (MCo), membrane emulsifier (ME) and membrane drier (MDr)). Membrane processes have been applied in different sectors, such as seawater desalination, gas separation, minerals recovery as well as food and drug industries, or even in aerospace engineering fields.

For the production of fresh water, RO is the most commercially used process but, at the same time, it also produces dangerous brine [4]. The management of high saline brine from desalination processes is a critical issue that has a very negative impact on the environment.

Each membrane process has its own field of application. MCr allows concentrating the feed until super saturation thus recovering, at the same time, the precipitated crystals and pure water obtained. Controlling the operating conditions such as temperature and/or flow rate, crystals morphology and nucleation could be different [5]. MCr could be applied for the recovery of salts and for the recovery of additional clean water from seawater. Moreover, it could be used for the crystallization of drugs and high-quality protein crystals [6,7], for the extraction and recovery of minerals.

In addition to seawater, another possible clean water source could be from the water vapor condensation of various gaseous streams (such as the ones exiting from the power plants, cooling towers, stacks, etc.). For this reason, innovative Membrane condensers have been studied and developed in order to promote the water recovery from the vapor condensation [8–10]. In addition, it could also be utilized for chemicals as well as particulates removal from waste gaseous streams. The condensation of vapor water is due to the temperature difference between the gaseous stream and the membrane module.

Both MCr and MCo utilize hydrophobic porous membranes. The hydrophobic nature of the membrane prevents liquid from penetrating the pores of the membrane while volatile components can pass through.

The aim of this work is to collect the information of MCr and MCo processes based on the common separation mechanism by hydrophobic porous membrane, including their configurations, applications, limitations and future development.

**Membrane Crystallization and Membrane Condenser processes**

**Membrane Crystallization Process**

MCr is an interesting process for the extraction of additional freshwater and raw materials from high-concentrated solutions. MCr has the potential to recover clean water and valuable salts, like lithium, sodium, magnesium, barium and strontium, etc.[11]. This technique, as MD, is based on the evaporation of solvent from a solution in contact with a porous hydrophobic membrane in order to achieve the supersaturation of the feed solution. The evaporated water can pass through the porous membrane due to the vapor pressure gradient generated by the temperature gradient across the two membrane surfaces [12–14]. This process allows to control the crystal growth, to minimize deposition and growth of crystals on the membrane surface and to maximize the crystals production with specific crystalline morphologies and structures. These aspects are not easily achievable in conventional crystallization methods, while in MCr yes thanks to the chemical—physical properties of the membrane coupled with the control of the process parameters. These parameters are feed temperature and concentration, flowrate, solvent evaporation rate and hence supersaturation rate [15]. Usually, the high concentration of non-volatile compounds close to the membrane surface may influence the performance of the process by reducing the transmembrane flux due to the concentration polarization (CP) layer at the feed side. This layer might act as a mass transfer resistance to the water vapor molecules transport through the porous membrane. In principle, MCr could overcome not only the limits of thermal systems but also CP. In fact, CP does not significantly affect the driving force of MCr process and therefore it is possible to reach high recovery.
factors and high concentrations. The integration of RO with MCr/MD offers the possibility to produce high quality solid materials transforming the traditional brine disposal problem into a potential new profitable market [16]. MCr opens an interesting economic effect for the present and future applications, i.e. green economy and valuable salts production. The economic effect of this process is mainly determined by the price of the recovered salts. Recovering high valuable salts can enhance the economic value of MCr process (like lithium which is widely used in electronic batteries and the related equipment).

**Membrane Condenser Process**

Membrane condenser is based on the hydrophobic porous membrane which retains the liquid whereas the dehydrated gases could pass through the membrane to the permeate side. Therefore, the condensable liquids are blocked by the hydrophobic surface of the membrane and collected at the retentate side [9,17]. Fundamentals for these phenomena are the characteristics of the membrane and the temperature difference established between the gaseous stream and the membrane module. This difference allows the water vapor molecules contained in the gaseous stream to condensate [8,18–20]. The main advantages of membrane condenser are: low energy consumption and no corrosion phenomena. Traditional processes that can be utilized for performing similar operations are heat exchangers, liquid-solid sorption, and dense membranes [17,18,21–24]. MCo can be utilized also to remove condensable contaminants (such as SOx, NOx, NH3, HF, HCl, VOC, etc.) or particles contained in the gaseous streams [25,26]. The capability of retaining water from waste gaseous streams subsequently opened to other perspectives in the use of this technology, proposing membrane condenser also as a highly efficient pre-treatment stage of (waste) gaseous streams. When the gaseous streams require further separation for recovering a defined specie, such as the flue gas for CO2 capture, biogas for bio methane production, etc., if these separation stages are membrane-based, the reduction of water content allows a better performance of the separation unit, depleting phenomena such as formation of water clusters, swelling, etc. that usually affect the utilised polymeric membranes, for example in CO2 separation, with consequent reduction of permeability and selectivity.

**Membrane Materials**

In general, the membranes used in MCr are hydrophobic and porous, while those used in condensation can be hydrophobic or hydrophilic, porous or dense, depending on the separation principle of the process[11,27]. The hydrophobicity prevents the liquid phase to penetrate into the membrane pores preventing membrane wetting. Membrane wetting with fouling are two of the major problems in almost all membrane contactors processes. Surface roughness and surface pore size may contribute to membrane fouling. Other important characteristics for MCr and MCo are in general adequate porosity, membrane thickness, high chemical resistance (e.g. with respect to acids), good thermal conductivity, high LEPw and high mechanical strength [28,29]. The thermal losses are minimized when a high porosity and/or thicker membranes are used [28]. The membrane for MCr and MCo are often made of polypropylene (PP) [7,30–32], polyvinylidene fluoride (PVDF) [5,7], polytetrafluoroethylene (PTFE) [7], ethylene chlorotrifluoroethylene (ECTFE) [18], polyvinylchloride (PVC) [30,33]. Among all these materials, PP and PVDF membrane are the most used ones, due to the relatively low cost, high porosity and easy fabrication procedure [14]. PVC is seldom used because of the low porosity. PTFE has high chemical and thermal resistance but less used mainly due to the high cost. ECTFE is an emerging material that is less investigated and is just starting its application as flat sheet membrane in MD [34,35]. Table 1 summarizes the main parameters of some organic polymeric membrane utilized in MCr and MCo. It gives an indication for the selection of the hydrophobic porous membrane for these two processes.

To enhance the performance of these membrane processes, modifications such as special coating or functionalization can be applied on the membrane surface [36,37]. Today, one of the new materials used for water treatment and purification is Graphene. It has attracted considerable attention in recent years as it improves the membrane properties such as hydrophobicity, anti-fouling and water vapor transport properties, etc. [38–41]. Graphene shows great potential as filler material and is worth to be explored. In addition to graphene, other two-dimensional (2D) materials (such as zeolites, mixed-organic frameworks, molybdenum disulfide, transition metal dichalcogenides, etc.) act as potential membrane materials for liquid and gas separation to achieve high permeability. Figure 1 shows the SEM images of the cross-section and surface of some organic polymeric membranes.

Apart from polymeric membranes, inorganic membranes attracted attention in recent years, like the ceramic membranes for the crystallization of NaCl or LiCl solution [31]. The ceramic membranes are in principle not suitable for the application in MCr due to their high thermal conductivity and hydrophilic nature. However, these drawbacks can be overcome by reducing the membrane thickness for increasing the trans-membrane flux (according to Al-Obaidani et al [51]) and/or making a hydrophobic modification on the membrane surface (like Leger et al. did for pervaporation membranes [52]). Other researchers also made hydrophobic coating of polyvinylsilsesquioxane aerogels and Fluoralkylsilanes (FAS) (1H, 1H, 2H, 2H-perfluoroctyltriethoxysilane) on the alumina hollow fibers to obtain the composite membrane with stable MCo performance [53]. In MCo the ceramic membrane was used by Kim et al. for the recovery of clean water from power plant emission [54] via transport membrane condenser (TMC). On the contrary of the previous hydrophobic membranes used in membrane condenser, in TMC the water vapor can pass through the membrane via capillary condensation and is collected on the permeate side. The main
The difference between MCo and TMC is the use of hydrophobic and hydrophilic membranes, respectively. In the first case the liquid is collected on the retentate side of the hydrophobic membrane surface. In the second case the liquid water is collected on the permeate side with a counter-current of cold liquid water [27]. In general, this application can be used for water recovery from internal combustion engine exhaust gas [55], power plant [54] and heat recovery in carbon capture [56].

**Process Configurations**

**MCo configurations**

In principle, all the five different types of MD configurations, including DCMD, VMD, AGMD, SGMD, and OMD are valid for MCo. The membrane configuration determines the performance of the process since the water transferred from the feed side to the permeate side is due to different driving force and this influences the trans-membrane flux. The basic configuration set-ups are shown in Figure 2.

Direct contact configuration is the most commonly used configuration due to the simple set-up and effective separation ability. A hot feed solution and cold distilled water are circulated on the two sides of the hydrophobic membrane respectively; the temperature difference between the two solutions is the driving force which pushes the vapor and the volatile components to pass through the membrane.

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**Table 1:** Characteristics of some hydrophobic membranes with hollow fiber and flat sheet shape for MCr and MCo [2,7,8,19,42–50].

<table>
<thead>
<tr>
<th>Shape</th>
<th>Parameters</th>
<th>PVDF</th>
<th>PP</th>
<th>PTFE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Porosity (%)</td>
<td>50-83.4</td>
<td>40-73</td>
<td>30-50</td>
</tr>
<tr>
<td></td>
<td>Contact angle (°)</td>
<td>86-106</td>
<td>112</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>Pore size (μm)</td>
<td>0.034-0.26</td>
<td>0.04-0.2</td>
<td>0.08-0.2</td>
</tr>
<tr>
<td></td>
<td>LEPw (bar)</td>
<td>2.3</td>
<td>0.95-27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Outer Diameter (mm)</td>
<td>1.2</td>
<td>0.3-2.7</td>
<td>22?</td>
</tr>
<tr>
<td>Hollow fiber membrane</td>
<td>Porosity (%)</td>
<td>31-75</td>
<td>66-80</td>
<td>70-80</td>
</tr>
<tr>
<td></td>
<td>Contact angle (°)</td>
<td>144</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pore size (μm)</td>
<td>0.18-0.86</td>
<td>0.2-1</td>
<td>0.2</td>
</tr>
<tr>
<td>Flat sheet membrane</td>
<td>Porosity (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Contact angle (°)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pore size (μm)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Vacuum configuration happens when a vacuum is connected to the permeate side. A cold trap with liquid nitrogen is positioned between the membrane module and the vacuum pump in order to condense the water vapor passed through the porous membrane. The pressure applied in the vacuum side must be lower than the saturation pressure of the volatile molecules in the feed solution [57].

For sweep gas configuration, a cold inert gas (usually N2) is applied on the permeate side to drag the vapor passing through the membrane pores.

Air gap is another configuration in which an air layer is interposed between the porous hydrophobic membrane and the permeate side. The molecules from the feed side volatize across the membrane pores, pass through the air gap and finally condense in the permeate side. The air gap leads to a decrease in heat loss due to conduction. This type of configuration is also not explored for MCr in the literature.

In OMCr the driving force is a concentration gradient between the two sides of the membrane [48]. It is similar to direct contact configuration, and an osmotic agent (such as NaCl or MgCl2) is present in the permeate side instead of cold distilled water [6].

Another MCr configuration based on membrane process was developed by DiProfio et al.[58] in which crystallization is induced by using antisolvent. This approach might be done in two different ways: solvent/antisolvent demixing and antisolvent addition. In the first case, supersaturation is generated by removing the solvent at higher velocity from a mixture of solvent, antisolvent and solute; in the second case the antisolvent is gradually evaporated from the other side of the membrane in a solution in which the solute is dissolved. In any cases the process is based on solvent/antisolvent migration in the vapor phase, and not by forcing the liquid phase through the membrane. The dosage of antisolvent can be controlled by the porous membrane that allows controlling the crystallization process.

**MCo configurations**

In the case of membrane condenser, given the importance of

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**Figure 2:** Five basic membrane crystallization configurations: (a) DCMCr; (b) AGMCr; (c) SGMCr; (d) VMCr; (e) OMCr. Published with permission from [48]
ΔT in terms of efficiency of the process, a simple way to optimize the performance is to develop different configurations to cool and condense the gaseous streams [8, 19]. The simplest configuration is determined by an external coolant medium used before the membrane module inlet. In this configuration the amount of recovered water increases more than proportionally with the growing of ΔT and T feed [9]. A second configuration can be done by using a cold sweep gas flowing in counter-current with respect to the feed inside the membrane module. This second configuration allows to reduce the energy consumption because the condenser heat duty will only depend on the flow rate and temperature of the sweeping gas [9]. The last examined case provides a mix cooling between the two previous configurations.

Process applications

MCr Applications

Initially the research has been focalized on the protein crystallization [7]. Brito et al [59] applied MCr to the crystallization of pharmaceutical compounds. They concluded that MCr allows producing crystals of quality and cost comparable to the commercial ones.

The use of MCr for the recovery of salts is attracting attention [5, 60, 61]. Some synthetic sea water with different components was also investigated in the literature [60, 62]. It is sometimes mixed with CaCO3 and humic acid to investigate the fouling phenomenon [63, 64].

In recent years, recovering LiCl is also a research focus in MCr, since the growing demand of electronic equipment contains a lot of lithium batteries [48]. The recovery of Li from salt lakes, sea, and other brine makes MCr in vacuum configuration more applicable and approaching industrial level. Other inorganic feed like Na2SO4, KN03, MgSO4 were also investigated [65]. Na2SO4 and NaCl mixture as feed solution were also tested in MCr with PVDF membrane, and both crystals were recovered. Different MCr applications are summarized in the following table 2.

Table 2 also indicates the fluxes of each MCr test, which shows the higher fluxes in ceramic membranes than in the polymeric ones. This also shows the potential application of ceramic membrane in these two processes.

<table>
<thead>
<tr>
<th>Feed solution</th>
<th>Configuration</th>
<th>Membrane</th>
<th>Recovered compound</th>
<th>Flux (kg/m²h)</th>
<th>Productivity (kg/m³)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seawater RO brine (artificial)</td>
<td>---</td>
<td>PP (hollow fiber)</td>
<td>NaCl</td>
<td>0.972</td>
<td>17</td>
<td>[2]</td>
</tr>
<tr>
<td>Seawater RO brine (natural)</td>
<td>---</td>
<td>PP (hollow fiber)</td>
<td>NaCl</td>
<td>1.116</td>
<td>17</td>
<td>[2]</td>
</tr>
<tr>
<td>4.5 M NaCl</td>
<td>DCMCr</td>
<td>PVDF (flat sheet)</td>
<td>NaCl</td>
<td>16</td>
<td>---</td>
<td>[44]</td>
</tr>
<tr>
<td>2 M Na₂SO₄</td>
<td>DCMCr</td>
<td>PVDF (flat sheet)</td>
<td>Na₂SO₄</td>
<td>13</td>
<td>---</td>
<td>[44]</td>
</tr>
<tr>
<td>NF-pretreated waste-water</td>
<td>DCMCr</td>
<td>PP (hollow fiber)</td>
<td>Na₂SO₄</td>
<td>1.6</td>
<td>---</td>
<td>[65]</td>
</tr>
<tr>
<td>Seawater</td>
<td>DCMCr</td>
<td>PVDF (hollow fiber)</td>
<td>Epsomite</td>
<td>1.4</td>
<td>---</td>
<td>[67]</td>
</tr>
<tr>
<td>NF seawater retentate</td>
<td>---</td>
<td>PP (hollow fiber)</td>
<td>NaCl</td>
<td>0.45</td>
<td>35.5</td>
<td>[68]</td>
</tr>
<tr>
<td>NF seawater retentate</td>
<td>---</td>
<td>PP (hollow fiber)</td>
<td>MgSO₄•7H₂O</td>
<td>0.45</td>
<td>8.4</td>
<td>[68]</td>
</tr>
<tr>
<td>NF seawater retentate</td>
<td>---</td>
<td>PP (hollow fiber)</td>
<td>Epsomite</td>
<td>0.45</td>
<td>---</td>
<td>[68]</td>
</tr>
<tr>
<td>5.5 M NaCl</td>
<td>DCMCr</td>
<td>Ceramic composite</td>
<td>NaCl and LiCl</td>
<td>17; 3.2</td>
<td>---</td>
<td>[53]</td>
</tr>
</tbody>
</table>
**MCo Applications**

The Membrane Condenser process developed in FP7 project “CAPWA” (Capture of evaporated water with novel membranes) and subsequently, optimized in EU H2020 project “MATCHING” (Materials & Technologies for Performance Improvement of Cooling Systems performance in Power Plants) has been, principally, focalized on water recovery from synthetic streams. As previously described, the quantity of recovered water increases with increasing $\Delta T$. In general, when flue gas is used to feed MCo, $\Delta T$ lower than 20°C are sufficient to recover more than 65% of the water present in the gaseous waste stream [66]. The quantity of recovered water increases with the growth of the ratio of the feed flow rate ($Q_{Feed}$) and membrane area ($A_{Membrane}$) [8].

Other MCo applications, as mentioned before, may be the removal of contaminants from flue gas with the possibility to control the concentration of contaminants in the recovered liquid water or as pre-treatment for CO2 separation for minimizing the quantity of contaminants in the gaseous streams. For what concern the chemicals removal, recent studies have been established how $\Delta T$ (temperature difference between the plume and the membrane module) and the Q/A ratio will affect the concentration of the contaminants. In fact Macedonio et al. [20] have observed how the concentration of contaminants decreases with the growth of Q/A due to the growing amount of recovered water. On the contrary, the concentration of contaminants in the recovered liquid water increases with the growth of $\Delta T$. Tests were carried out considering the presence of NH3 in the gaseous stream. The choice of NH3 is due to the normally presence of this contaminant in various industrial wastes [20]. The concentration of NH3 in the recovered liquid water as a function of the feed flow rate at various $\Delta T$ is shown in Figure 3, where, the lines are referred to the simulations while the points to the experimental measurements. Here it is possible to observe a good agreement between the experimental and the theoretical results.

![Figure 3: NH3 concentration vs QFeed at various $\Delta T$. (Feed temperature = 54.7–56.8 °C, RH feed = 100%). Published with permission from [20]](http://www.journalofchemistry.net)

**Conclusions**

The basic process definition, membrane materials, membrane configuration, practical applications of membrane crystallization and membrane condensers have been summarized and discussed.

Membrane crystallization is one of the most advanced membrane technologies that can be used for the production of crystals from high concentrated feeds. Membranes used in this technology are hydrophobic and porous. Polymeric porous hydrophobic membranes have been initially explored; the inorganic hydrophobic membrane maybe a research direction in the future. Different configurations of membrane crystallization can be chosen according to the research purpose. Operation conditions can be adjusted to control the recovered crystals morphology. Feed in membrane crystallization varies from industrial wastes to brine of seawater desalination. Lithium is a possible important future research direction because of the economic value in the electronic market.

Three membrane condenser configurations were proposed and analysed. The achieved results confirmed that the simulation study was validated by experimental analysis and showed as parameters such as the temperature difference $\Delta T$ between the fed gas $T_{feed}$ and the membrane module, and the ratio of the feed flow rate ($Q_{Feed}$) with the interfacial membrane area ($A_{Membrane}$) are fundamental parameters to control the performance of membrane condenser in terms of amount and composition of the recovery liquid water. The concentration of contaminants depends also on $\Delta T$; the concentration increases with the growing $\Delta T$ because of the decrease of the contaminant solubility with the temperature.
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