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MARIA TOMASZEWSKA*

MEMBRANE DISTILLATION

The paper presents a separation process based on evaporation through the pores of a hydrophobic membrane known as membrane distillation (MD). Different process configurations were considered. Preparation of membranes for the MD, their properties, transport phenomena, modules design have been discussed. Application of MD to preparation of pure, desalted water was presented. The MD process was also applied to the concentration of different acids. The process can be used in a food industry. The concentration of sulfuric acid solution obtained after extraction of apatite phosphogypsum by MD in order to recover lantane compounds was presented. The other direction of MD application was concentration and recovery of HCl from metal pickling solutions.

1. INTRODUCTION

The driving force of membrane processes can be of a quite different character. Very often it is a pressure difference that effects the mass transport through a membrane. In the other cases, it is a concentration gradient or an electrical potential gradient.

Membrane distillation is a thermally driven process. Although thermally driven processes are known from many years, membrane distillation process is still considered as a new, promising membrane technique. An early form of MD was described by Bodell in a 1963. In 1967 Weyl was granted a U.S. Patent describing desalination as a new process using porous hydrophobic membrane [1]. Findley and Henderyckx were the first who published the results of their work in MD [2]. The membranes used by Weyl and Findley did not have suitable characteristics. Development in membrane manufacturing in the 1980's allows us to obtain commercial membranes with desired properties. Improvements in module design and better understanding of phenomena occurring in the layer adjacent to a membrane also contributed to the renewed interest in MD [3–5]. From the commercial standpoint MD has gained little acceptance even today, although its productivity can be described as competitive with the other techniques. In comparison with the other separation operations, MD has very important advantages: 100% rejection of dissolved, non-volatile species, lower operating pres-

*Institute of Inorganic Chemical Technology, Technical University of Szczecin, ul. Pułaskiego 10, 70-322 Szczecin, e-mail: mariatom@mailbox.chemo.tuniv.szczecin.pl.

sure than pressure-driven membrane processes, reduced vapour space (practically to the membrane thickness) compared to conventional distillation. The low operation temperature, considerably below boiling point of a feed enables the utilisation of waste heat as preferable energy source. The possibility of using solar, wave or geothermal energy is particularly attractive [7].

2. PRINCIPLE OF MD

MD is a process in which a microporous, hydrophobic membrane separates aqueous solutions at different temperatures and compositions [6–9]. A temperature difference on both sides of membrane results in a vapour pressure difference. Thus, vapour molecules are transported through the pores of the membrane from the high-vapour pressure side to the low vapour-pressure side. According to *Terminology for membrane distillation* [10], the term 'membrane distillation' should be applied to membrane operations having the following characteristics:

- the membrane should be porous,
- the membrane should not be wetted by the process liquids,
- no capillary condensation should take place inside the pores of the membranes,
- only vapour should be transported through the pores of the membrane,
- the membrane must not alter the vapour equilibrium of the different components in the process liquids,
- for each component, the driving force of the membrane operation is a partial pressure gradient in the vapour phase.

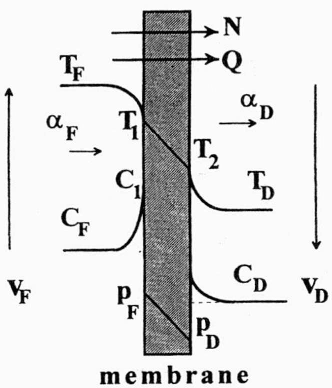

Fig. 1. The principle of direct contact membrane distillation

The principle of direct contact membrane distillation is presented in Fig 1. The process essentially involves the following steps:

- evaporation of volatile compounds of a feed at the warm feed/membrane interface,
- transfer of vapour through the membrane pores,
- condensation of the permeate at the membrane/cold distillate interface.

The hydrophobicity of the membrane used and maintaining a gaseous phase inside the membrane pores are the necessary conditions for MD.

Figure 2 illustrates different common MD configurations used for obtaining the required driving force. In all solutions, the membrane is directly exposed to the warm solution, but the ways of the permeate condensation are different. In the direct contact MD (Fig. 2A), the cold distillate is in direct contact with the membrane and vapour transported through membrane condenses directly in a stream of cold distillate. In the gas-gap MD system, the permeate is condensed on a cooling surface (Fig. 2B). In this case, the total length of vapour diffusion is the sum of membrane thickness and air gap. The condensed distillate does not have to be in a contact with the membrane. In low-pressure MD system, a low pressure is applied to the distillate side and the condensation of the permeate takes place outside the module. In the last system, a sweeping gas is applied and the permeate condensation occurs outside the module. Depending on MD system, the driving force in MD is a vapour pressure difference across the membrane, which can be caused by a temperature gradient across the membrane, or by a vacuum or a sweep gas on the permeate side of the membrane. If the term 'membrane distillation' is used without any specification, it applies to the direct contact membrane distillation.

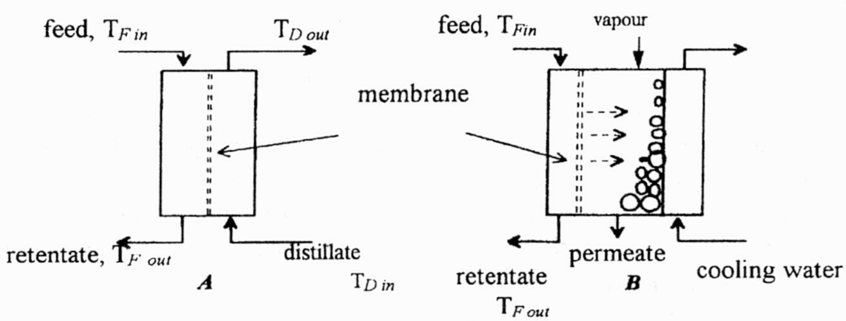

Fig. 2. Configurations of membrane distillation

The separation mechanism is based on the vapour/liquid mixture [9, 11]. This means that the component with the highest partial pressure will show the highest permeation rate. MD is a highly selective operation for non-volatile species like ions, colloids and macromolecules, which are unable to evaporate and diffuse through the membrane. The solutes are completely rejected and the permeate is then pure water. When volatile species are present in the feed they will also be transported through the membrane. According to vapour/liquid equilibrium, the permeate composition depends on a composition and temperature of a feed.

3. MEMBRANE CHARACTERISTICS

The membranes used in MD act rather as a physical support for a liquid/vapour interface, but their choice for the process is very important. The membranes have to meet several requirements simultaneously. The presence of only a vapour phase in the membrane pores is a necessary condition for MD. Thus hydrophobicity, i.e., its non-wettability preventing the bulk liquid from the transport across the membrane, plays an essential role in this process. Several polymers such as polytetrafluoroethylene (PTFE), polypropylene (PP) and poly(vinylidene fluoride) (PVDF) with low surface energy have the necessary hydrophobic properties [9–12]. Moreover, these polymers exhibit excellent chemical resistance and good thermal stability.

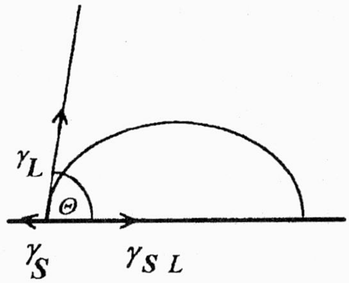

Fig. 3. The water droplet deposited on polymer film

The hydrophobicity can be determined by a contact angle. A droplet of water deposited on a hydrophobic surface gives the contact angle greater than 90° (Fig. 3), for example, the parameter measured on PTFE or PVDF membrane was 108° and 107°, respectively. Liquid entry pressure of water (LEP_w), a very important parameter determining the pressure, should not be exceeded. This is the minimum pressure at which pure water penetrates into the pores of a hydrophobic membrane.

The membrane porosity is the next parameter of the membrane influencing the permeate flux. The higher membrane porosity corresponds to a larger diffusion area inside the membrane, taking part in the vapour transport. Higher porosity reduces also the amount of heat lost by conduction. Thus a porosity higher than 70% is desirable [13].

The membrane with size of pores ranging from 0.1–1 μm should be used in MD for obtaining sufficiently high permeate flux. The pores must be small enough to prevent the liquid penetration across the membrane under the MD operation conditions. On the other hand, the pores should be large enough to facilitate the vapour transport.

The membrane thickness (from 50 to 150 μm) determines both mechanical strength of the membrane and the expected permeate flux. The permeate flux is inversely proportional to the membrane thickness.

4. MASS AND HEAT TRANSPORT

The transport of volatile components through microporous hydrophobic membrane can be described by equation in which the permeate flux (N) is proportional to the driving force, i.e. to vapour pressure difference (Δp) across the membrane, according to Darcy's law:

$$N = K\Delta p.$$

The proportionality factor K is determined by such membrane parameters as material, pore structure, porosity and membrane thickness. The partial pressure difference is mainly determined by the temperature difference and the composition of boundary layers adjacent to the membrane.

Mass transfer through the hydrophobic membranes may be explained by different mechanisms. The mechanism results from comparison of the mean free path of the gas/vapour and the mean pore size of the membrane pores [14]. In deareated system, either the Knudsen diffusion or Poiseuille's flow model can be involved. In the transition region both models must be considered [14]. In the case of the atmospheric pressure MD application, air is contained in the pores of MD membrane as a stagnant film, hence the molecular diffusion model applies. Taking into account the MD membrane morphology, we should consider both molecular diffusion and the Knudsen transport. The permeate flux is very often described as a function of the temperature gradient.

In order to analyse the water transfer, it is necessary to know the actual temperature at the solution/membrane interface. This temperature is different from the bulk temperature. Evaporation of water vapour occurs on the warm side of the membrane, whereas condensation of the vapour occurs on the cold side. The heat required for evaporation has to be supplied from the bulk solution which decreases the temperature of the layer adjacent to the membrane. Heat transfer through the membrane will deepen this effect. Due to heat transfer and vapour condensation, the temperature of boundary layer on the cold distillate side is higher than in the bulk solution. The difference between the temperature of the liquid in the bulk and the liquid in the boundary layer is called temperature polarisation. The temperature of the boundary layer cannot be measured directly, but can be calculated using suitable equations [15, 16]. Temperature polarisation phenomenon leads to a decrease in the temperature gradient and the driving force [17].

MD involves mass transfer of vapour through a microporous membrane which is coupled with heat transfer through the membrane and heat transfer to and from the membrane surfaces. Heat transfer in MD occurs by two major mechanisms. Firstly, there is latent heat transfer accompanying vapour flux, and secondly there is heat transfer by conduction across the membrane [4,18]. An increase in the volume flux and higher heat conductivity increase temperature polarisation, whereas an increase in membrane thickness reduces this effect. High flow rate of a feed and permeate streams inside the MD module will reduce temperature polarisation.

Contrary to the pressure-driven processes, the effect of concentration polarisation in MD is rather small, because the MD driving force is mainly due to the temperature gradient. Only at very high concentrations (near saturation) significant effects of concentration polarisation are produced.

5. MODULES

A different configuration of membrane modules has been designed and tested in MD systems. Generally, flat-sheets, capillary or spiral-wound modules have been applied [19]. A majority of the laboratory-scale modules are designed for use with flat sheet membranes, because flat sheet membranes may easily be removed from the module for examination, cleaning or replacement. However, from a commercial standpoint, capillary membrane modules are more attractive than the flat sheet modules. Capillary membranes do not require a support which decreases boundary layer resistance compared to flat sheet membrane modules, hence much higher membrane surface area to module volume ratio can be obtained. The module of the Swedish National Development Co. is commercially available. It is composed of MD cassettes working together in accordance with the filterpress principle. On an industrial scale, flat sheet modules have also been examined by Gore & Associates. The flat sheet module, presented in Fig. 4, is made much more compact by wrapping the channels in a spiral configuration [3]

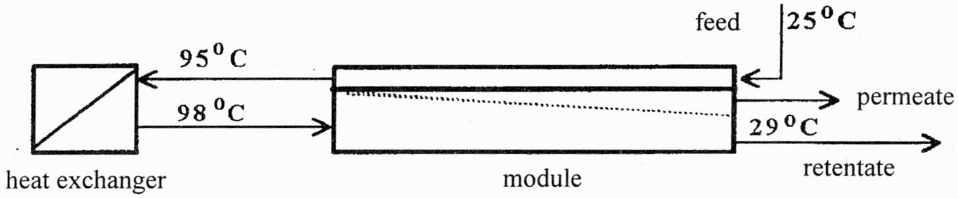

Fig. 4. The principle of Gore-Tex module performance [3]

The shell-and-tube module produced by Enka AG (Akzo) is a commercially available module with capillary membranes [13].

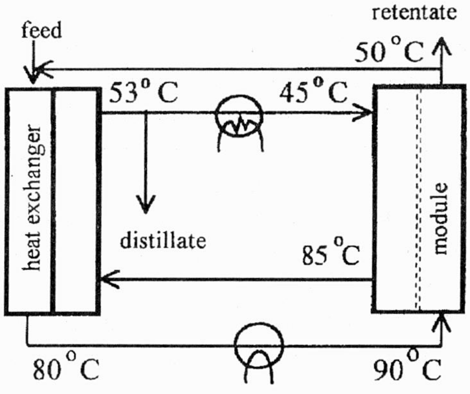

Fig. 5. The MD process with heat recovery [13]

In a number of cases, the problem of heat recovery and reuse was considered. In Gore device, the vapour which passes through the membrane condenses on the plate cooled by the entering fresh feed. In the direct contact MD the part of energy transferred across the membrane can be recovered using external heat exchangers (80% or more), which is presented in Fig. 5. There are applications where the heat transfer can be utilised, and thus heat recovery is not necessary – boiler feed water is an example [13].

A set-up for the membrane distillation studies in a laboratory is shown in Fig. 6.

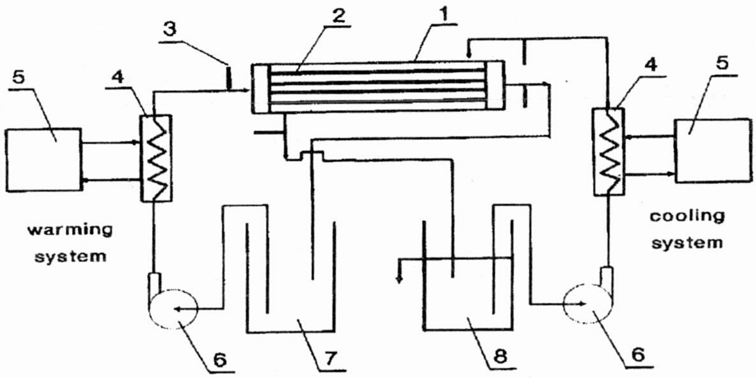

Fig. 6. Diagram of the MD set-up: 1 – MD module, 2 – capillary membrane, 3 – thermostat, 4 – heat exchanger, 5 – manometer, 6 – venting, 7 – pump, 8 – feed tank

6. EXAMPLES OF MD APPLICATION

MD has several limitations, which have resulted in the applications of the process. The primary limitation is due to MD definition – the process must proceed in aqueous solutions which should not wet a microporous, hydrophobic membrane. The very important feature of MD is the separation mechanism based on the liquid/vapour equilibrium. Hence, practical application of MD has three directions:

(1) preparation of pure, desalted or demineralized water from different sources,

(2) raising the concentration of non-volatile substance solutions up to high concentration,

(3) stripping the volatile compounds from a solution.

The main MD application is the production of high-purity water, fully demineralized, or fresh water from the sea. The retention coefficient of salt is practically 100%. The quality of the permeate does not depend practically on the feed concentrate. The purity of MD distillate is higher than that after conventional distillation, because in MD water droplets cannot pass through membrane pores and do not contaminate the distillate. The produced water is free of particles, bacteria and pyrogene, thus is suitable for medical and pharmaceutical purposes [13] or for semi-conductors' industry.

The permeate flux is mainly influenced by the feed temperature (Fig. 7). In direct contact MD the permeate fluxes are competitive with the fluxes typically observed in RO [20]. It is worth noticing that the rejection of salts, ions, colloids is higher than in RO, thus the MD permeate is of a higher purity.

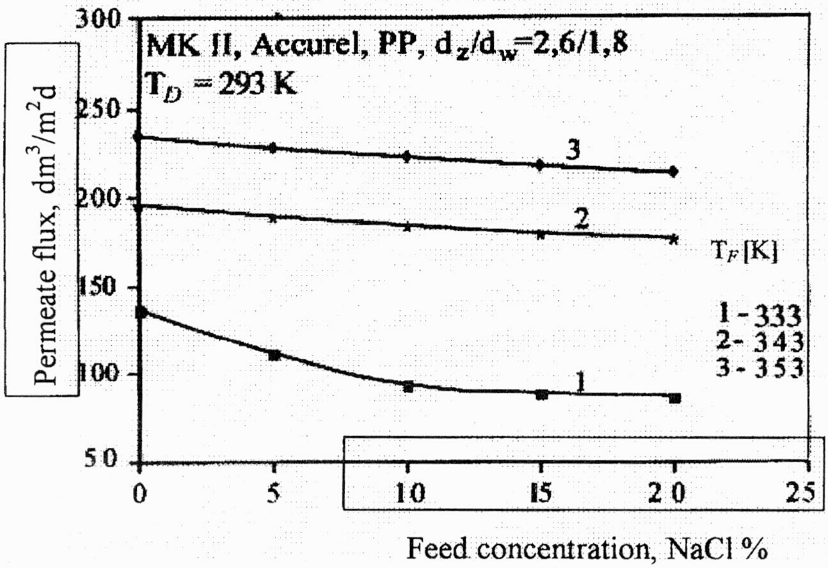

Fig. 7. The influence of temerature and concentration of the feed on permeate flux

The second direction of MD application is concentration of aqueous solutions. Relatively low feed temperature enables the application of the process to the food industry or to concentration of solutes sensitive to high temperature [21]. MD was successfully used for the concentration of citrus juices or the other fruit juices with low contents of pectic substances. Due to the low temperature of processing, the taste,

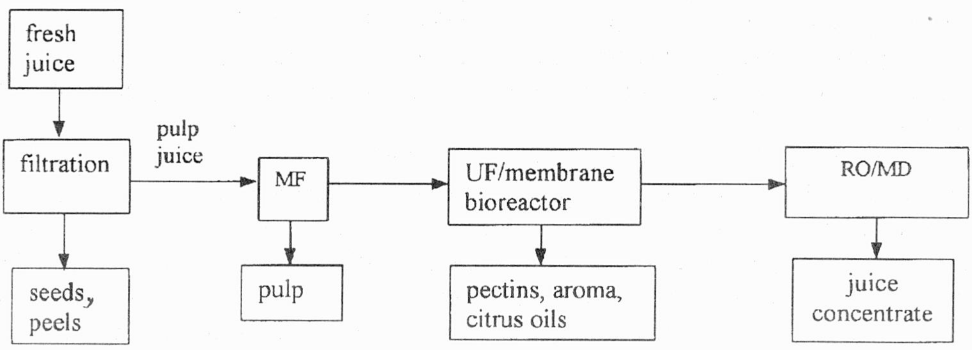

Fig. 8. Application of integrated membrane system in concentration of fruit juice [21]

colour and aroma of concentrated juice were very satisfactory. For concentration of juices rich in pectins, the integrated UF/MD membrane systems can be applied (Fig. 8), where UF is used as the juice pretreatment [21].

MD can be attractive method of concentration of palm sugar juice. Solar energy was proposed as the energy source [22]. MD was also effective in concentrating a blood [23] or bovine serum albumin solutions.

MD has also been applied successfully to wastewater treatment. The obtained permeate is very often harmless to environment, and the retentate can be concentrated into valuable chemicals. Moreover, some pollution problems may be solved, because the amounts of the effluents discharged may be reduced. MD is a promising method of the textile wastewater treatment. The dyes and pure water can be recovered and reused [24]. The solutions of non-volatile solutes can be concentrated to a very high level, even to a supersaturated state. The MD-crystallisation technique was investigated in order to recover taurine from wastewater during its production [25]. The investigations have shown the possibility of MD application to concentration of such diluted non-volatile compounds as sulfuric or phosphoric acids [26]. The results of experiments prove that the membrane distillation process can be applied to concentration of sulfuric acid solution obtained after apatite phosphogypsum extraction used to recover lanthane compounds [27]. The concentration process was carried out till the concentration of sulfuric acid in the solution reached about 40%. After cooling of the concentrated solution, lanthane compounds precipitated. The block system for this novel technology is presented in Fig. 9.

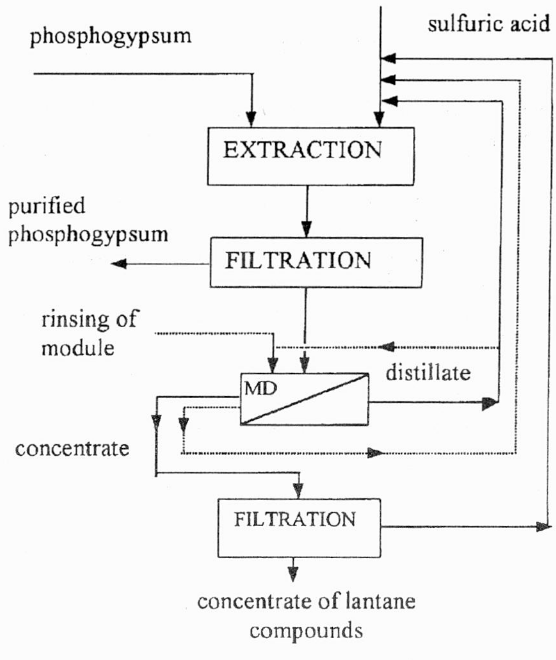

Fig. 9. The system for preparation of lanthane compounds' concentrate from phosphogypsum by MD

The membrane distillation process can be used for recovery of volatile compounds. The substances more volatile than water pass easier through a hydrophobic microporous membrane; therefore the permeate is enriched with these substances.

Ethanol preferentially vaporises from aqueous solutions. Traditionally, alcohol is produced by fermentation of biomass in the batch fermenter. The solution after fermentation contains 7–9% of alcohol. Unfortunately, the products of fermentation are also inhibitants of the process. With the increase in ethanol concentration, the rate of bioconversion falls to zero. This problem may be solved by integration of a fermenter and MD to continue separation of ethanol from the fermenting broth.

Different acids, e.g. hydrochloric acid, are used in the treatment of metal surface. Waste solutions after metal pickling contain non-utilised acid and heavy metals. Neutralisation procedure used traditionally not always allows us to obtain the results required. During the MD process, both water vapour and gaseous HCl are transported through pores of the membrane from the warm feed to cold distillate, whereas the salt is retained in the feed. It was found that the permeate was pure hydrochloric acid with a concentration significantly higher than in the feed. The results of the experiments show that MD may be promising method of HCl recovery from industrial effluent [18].

Taking into account the advantages of membrane distillation, especially possibility of using different sources of energy (waste, solar or geothermal energy), MD can be applied to the production of water of high purity and to solving various wastewater problems, e.g. the separation and recovery of valuable chemicals.

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