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MEMBRANE DISTILLATION BASED ON POLYPROPYLENE HOLLOW FIBERS: DEVELOPMENT AND TESTING OF LABORATORY UNIT

MEMBRÁNOVÁ DESTILACE ZALOŽENÁ NA TENKÝCH POLYPROPYLENOVÝCH MEMBRÁNÁCH: VÝVOJ A
TESTOVÁNÍ LABORATORNÍ JEDNOTKY

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ABSTRACT

In the face of the global water scarcity crisis, ocean water desalination and wastewater purification have become essential technological fields. This research aims to contribute to a future with no fresh water shortage by introducing a highly energetically efficient approach to water purification that produces high-quality product through the use of membrane distillation. This technology holds great promise to become a significant contributor to the water treatment industry. However, its full potential has not yet been realised due to the need for further research. This thesis provides a comprehensive overview of the membrane distillation process, including the principles of its operation and different membrane distillation types. In addition, this study highlights the challenges associated with the technology and addresses them in a scientific manner. An experimental study was conducted to identify the best operational conditions for a specific hydrophobic membrane type and mitigate the risk of membrane wetting. The analysis of the advantages and disadvantages of technology reveals that while membrane distillation has the potential to be highly effective in water purification, it faces limitations that need to be considered.

ABSTRAKT

V súvislosti s celosvetovou krízou nedostatku vody sa odsoľovanie oceánskej vody a čistenie odpadových vôd stali veľmi dôležitými oblasťami výskumu. Cieľom tejto práce je prispieť k budúcnosti bez nedostatku pitnej vody zavedením vysoko energeticky účinného spôsobu čistenia vody, pri ktorom sa pomocou membránovej destilácie získava vysokokvalitný produkt. Táto technológia má veľký potenciál stať sa významným prínosom pre priemysel úpravy vody, ale jej plný potenciál ešte nebol využitý z dôvodu nutnosti ďalšieho výskumu. Tento článok poskytuje komplexný prehľad procesu membránovej destilácie vrátane princípov jej fungovania a rôznych typov membránovej destilácie. Okrem toho táto práca poukazuje na problémy spojené s danou technológiou a rieši ich vedecky. Experimentálna štúdia bola vykonaná s cieľom identifikovať najlepšie prevádzkové podmienky pre konkrétny typ hydrofóbných membrán a zmierniť riziko zmáčania membrán. Z analýzy výhod a nevýhod technológie vyplýva, že hoci má membránová destilácia potenciál byť vysoko efektívna pri čistení vody, čelí obmedzeniam, ktoré je potrebné zohľadniť.

KEYWORDS

Membrane distillation, polypropylene hollow fibres, microporous membranes, membrane wetting, laboratory unit for membrane distillation, sodium sulphate, sodium dodecyl sulphate

KLÚČOVÉ SLOVÁ

Membránová destilácia, polypropylénové duté vlákna, mikroporézne membrány, zmáčanie membrán, laboratórna jednotka na membránovú destiláciu, síran sodný, dodecylsírany sodný

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Declaration

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1 INTRODUCTION

Freshwater shortage, high energy consumption and wastewater treatment difficulties are some of the most emerging topics nowadays. With the world's population rapidly increasing, the demand for freshwater is escalating, while the available supply is quickly depleting. This crisis requires innovative and sustainable solutions that can provide access to potable water without compromising the environment and energy resources.

One such solution that has gained significant attention in recent years is membrane distillation, a method of water purification that has the potential to provide potable water to arid areas while utilising renewable and waste energy sources for its operation. This technology is highly effective in removing contaminants, such as salts, microorganisms, and other impurities from water and can be applied in various settings.

Despite its potential, membrane distillation is still in its early stages of development and requires extensive research to be fully optimised. The process can be achieved using different principles, configurations, and equipment materials, each with advantages and limitations. The basic principle of membrane distillation involves a phase change of the feed solution, such as saltwater, to collect the high-quality product, i.e., freshwater.

Theoretically, membrane distillation's purifying efficiency can be up to 100%, making it an attractive alternative to traditional water treatment methods. However, the process also faces numerous potential issues, such as scaling and fouling, which must be addressed to ensure its long-term performance and sustainability. The potential applications of membrane distillation are broad, ranging from seawater desalination to wastewater treatment.

This thesis focuses on the hollow fibre membrane unit's effectivity and optimal operational parameters in membrane distillation. This study aims to investigate the impact of various parameters, such as feed solution temperature, feed solution concentration, and surfactants' effect on the performance of the hollow fibre membrane unit.

2 THEORETICAL PART

2.1 Water purification

Most of the water on the globe is present in oceans and seas. Only less than 3% of all water is not saline and exists in different reservoirs. Freshwater is present primarily in glacial form (around 68,9%). Secondly, approximately 29,9% of freshwater is categorised as groundwater and 0,9% as permafrost and soil moisture. Only 0,3% of freshwater is accessible to humans in freshwater reservoirs on the surface of the Earth (Benyahia, 2019; Drioli et al., 2015).

Freshwater scarcity has been a topic of interest to many scientists for decades. Urbanisation, increased waste production, and population growth have all been highlighted as the issue's root causes (Lee et al., 2016). Reportedly, 20 % of the population does not have daily access to fresh water, which is predicted to gradually increase in the following decades. Despite its scarcity, freshwater usage is growing in many fields. At least 70 % of the freshwater used globally is used by agriculture (Eliasson, 2015).

Current water purification technologies are well-established. However, their high costs and complexity are limiting for many applications and regions. Various new technologies have recently emerged, and water treatment is a hot topic for many researchers. Developing an approach for water treatment that is effective cost-wise and energy-wise is the main objective of the whole wastewater treatment and desalination sector (Lee et al., 2016).

Being the most abundant water form on earth, the oceanic water usage is faced with extensive research. Specifically, saline water desalination is an emerging topic. Many approaches have been developed and are generally classified by scientific society into three generations of technologies (Drioli et al., 2015).

The first generation mainly employed thermal desalination methods, whereas the 2nd generation gradually implemented the usage of membrane systems. One of the most widely used techniques (60%) for the removal of salts is reverse osmosis (RO) (Drioli et al., 2015; Greenlee et al., 2009). Most of the technologies based on the filtration method are facing a drawback of the formation of brine formed during the purification process. Another issue with conventional desalination techniques is high energy demands, which should be lowered to meet environmental restrictions (Drioli et al., 2015). Technologies used for water desalination nowadays are depicted in Figure 1.

Reverse osmosis is a desalination process utilised to water from a solution. It is the most widely used second-generation desalination technique. The process is divided into three main phases. The first phase involves pre-treating seawater using coagulation, flocculation, and filtration. The second phase involves the RO process, which separates the solvent from the particles using a semi-permeable membrane. The final stage requires the introduction of mineral ions and disinfection to make the water drinkable (Skuse et al., 2021).

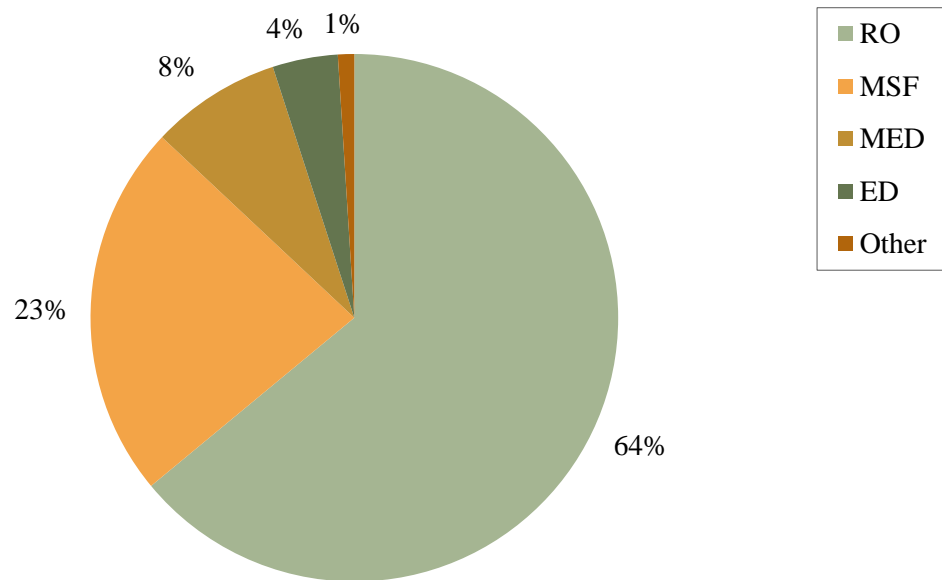


Figure 1 Percentual representation of water desalination techniques used nowadays (Reverse osmosis (RO), Multi-stage flash (MSF), Multi-effect distillation (MED), Electrodialysis (ED) and other) (AlMarzooqi et al., 2014)

Despite being relatively inexpensive compared to its predecessors, RO has a high energy demand and greenhouse gas emissions, limiting its implementation in some regions. One of the primary drawbacks of the technology is concentration polarisation, which leads to membrane fouling and reduces its efficiency. Additionally, RO has a low water recovery rate, producing high quantities of brine (Skuse et al., 2021).

To improve the efficiency of RO, researchers have been looking at other innovative techniques, such as forward osmosis and membrane distillation. These methods can enhance the recovery rate of water and minimise the environmental impact of RO by reducing the amount of brine produced (Ali et al., 2021).

Technologies addressing limitations of the second-generation desalination technologies are forming a 3rd generation. These technologies are giving rise to new membrane processes focusing on lowering energy demands and increasing effectivity. One area of interest in the development of third-generation desalination technologies is the incorporation of natural energy sources to reduce energy demands and increase effectiveness of new membrane processes. Emerging technologies such as forward osmosis, capacitive deionisation and membrane distillation can accommodate the requirements of this age. However, they are yet to be implemented in the industry (Drioli et al., 2015).

Forward osmosis (FO) is a water purification technique that utilises osmotic pressure to separate water molecules from saltwater using a draw solution effectively. The draw solution is specially formulated to contain a high concentration of a specific salt, which can be easily separated from the solvent. This process differs from RO because it utilises lower or no hydraulic pressure and lower temperatures, resulting in lower energy demands. Membranes used in forward osmosis have a high rejection range for many contaminants, making it a potentially effective method for removing various impurities from water. Although primarily used for desalination, forward osmosis has the potential to be used in other applications, such as concentrating landfill leachate and in the food industry. Overall, forward osmosis is a promising technology for water treatment due to its energy efficiency, high rejection range, and versatility in the application (Cath et al., 2006; McGovern & Lienhard V, 2014).

Capacitive deionisation (CDI) is based on ion adsorption and desorption, where both the cation exchange membrane and anion exchange membrane are immersed in an aqueous solution. When an electric field is applied, ions are attracted towards the electrodes. CDI can be used for the selective removal of targeted ions. Despite utilising an electric field, CDI is more energy efficient than most currently used desalination technologies. The energy demands can be satisfied using low-voltage sources (e.g., solar power). Additionally, the operation and maintenance are relatively easy too. These advantages decrease overall operational costs (AlMarzooqi et al., 2014). A comparison of main water purification requirements is depicted in Figure 2.

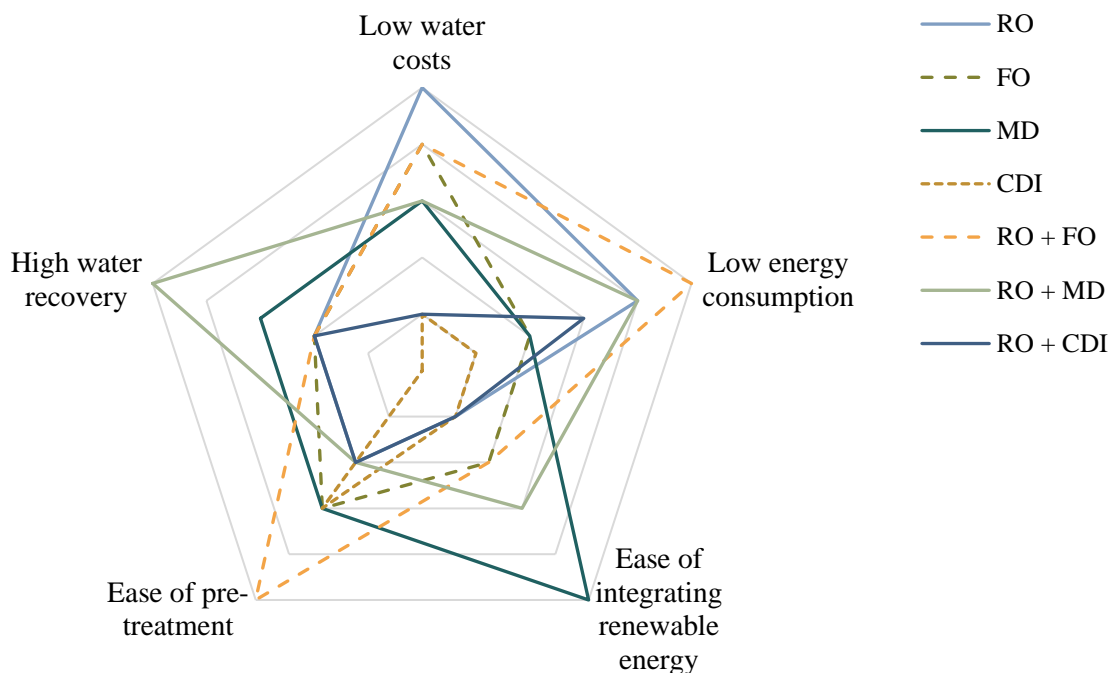


Figure 2 Graphical comparison of various water purification methods (Skuse et al., 2021)

2.2 Introduction to membrane distillation (MD)

Membrane distillation is a purification method that uses a hydrophobic microporous membrane to allow a liquid solvent, such as water, to evaporate and separate it from dissolved solids or other contaminants. The liquid feed solution is heated on one side of the membrane, while vapour is passed over to the other. During this separation process, temperature gradient allows vapour pressure difference to be the main driving force of the process. Membrane hydrophobicity prevents liquid solvent molecules with dissolved impurities from entering the membrane resulting in a high-purity permeate (Drioli et al., 2015; Khayet, 2011).

The membrane is an essential boundary component of a MD system designed to selectively permit or prevent the passage of specific substances based on their physical and chemical properties. Depending on their chemical composition, membranes can be classified as isotropic or anisotropic. Whereas isotropic membranes are symmetric and chemically homogeneous (e.g., microporous membranes, nonporous films, and electrically charged membranes), anisotropic membranes are asymmetric. They can be either homogeneous (Loeb-Sourirajan membranes) or heterogeneous (composite membranes). In addition to MD, membranes can be used in various separation processes, including reverse osmosis, nanofiltration, ultrafiltration, microfiltration, and distillation (Lee et al., 2016; Ulbricht, 2006).

2.3 History of membrane distillation

As a separation process used to purify water and other liquids, membrane distillation was first patented by Bodell in the 1960s. Despite its invention and continued research, membrane distillation did not receive much attention for decades. Bodell devised a method to desalinate water and make it potable. He circulated saline water through the system using silicone tubular membranes and demonstrated that liquid water could not permeate the pores. By introducing a gas into the tubing and heating the saline water, water vapours were directed through the tubular system and subsequently condensed. Additionally, Bodell proposed using a vacuum to transport air through the tubes but cautioned that this could harm the membranes (Bodell, 1968).

In the first ever published article about MD, Findley, in the late 60s, described the most basic configuration of MD (Direct Contact Membrane Distillation) and researched various materials for membrane coating. The reason for the lack of its industrial involvement throughout the following years was discussed to be its economic disadvantage over other water purification techniques (precisely reverse osmosis) (El-Bourawi et al., 2006; Findley, 1967; Khayet & Matsuura, 2011).

Around 20 years later, new membrane types started to be manufactured due to an improved understanding of the process, especially mass and heat transfer. The importance of MD in recent years encouraged its application into commercial use in desalination processes. After this, membrane distillation research gained momentum and new applications for MD were considered (Camacho et al., 2013).

At the beginning of the 2010s, MD started to be commercialised. The main application for MD was desalination. MD units were mainly produced by Memsys and Memstill. Throughout the following years, manufacturers showed high interest in creating new membrane systems and implementing them into technologies that could utilise waste heat or solar energy to drive the process of MD (Curcio & Drioli, 2005; Drioli et al., 2015).

2.4 Arrangement/configurations

MD can be generally set up in one of the four main configurations (direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), sweep gas membrane distillation (SGMD) and vacuum membrane distillation (VMD)) (see Figure 3). Adaptations to these for main configurations can be made resulting in formation of new configuration (material gap membrane distillation (MGMD), permeate gap membrane distillation (PGMD) and conductive gap membrane distillation (CGMD)). All these configurations secure effective permeation, mass transport and condensation of the permeate.

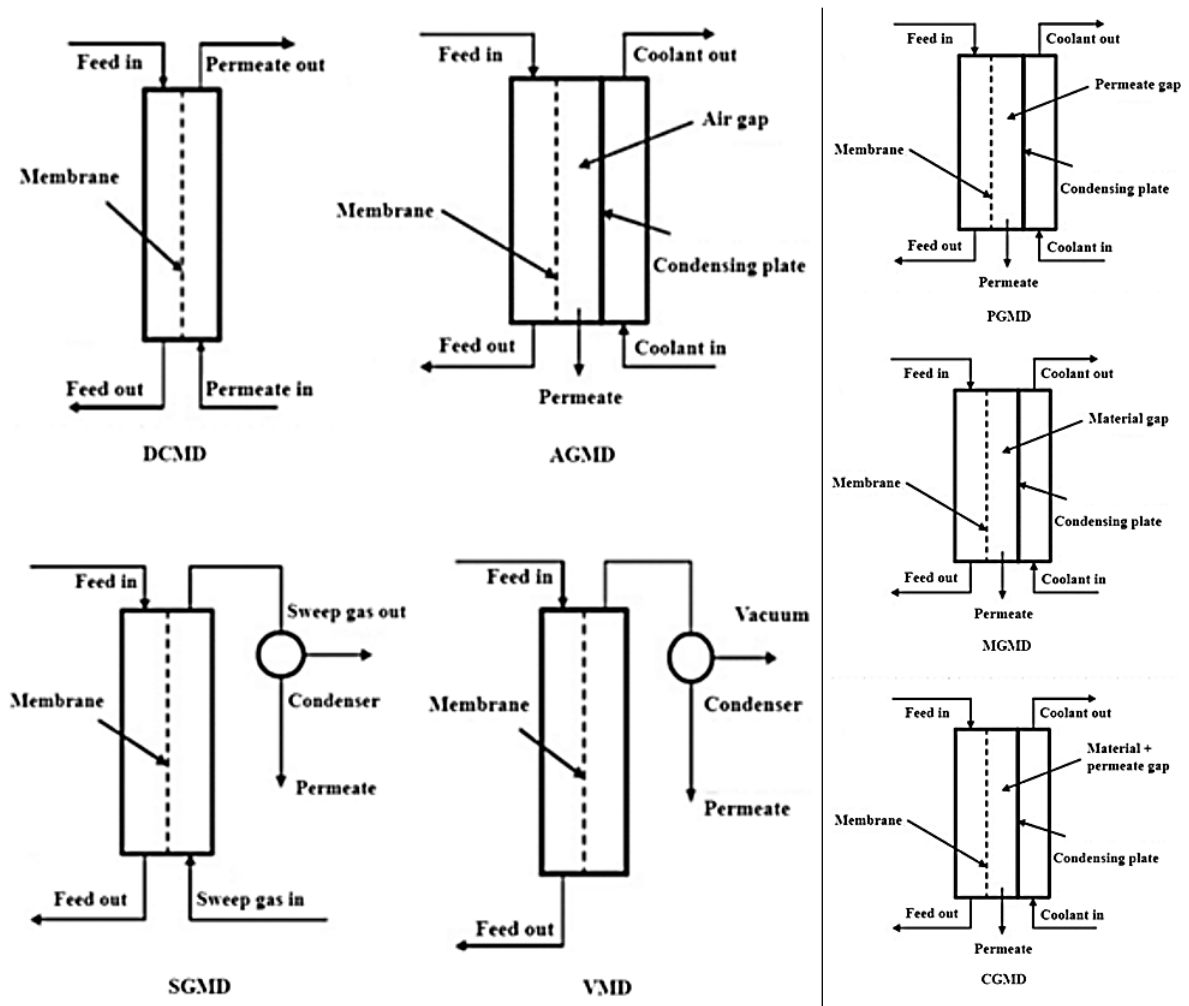


Figure 3 Configurations of MD (El-Bourawi et al., 2006), (Ullah et al., 2018)

2.4.1 Direct contact membrane distillation (DCMD)

Direct contact membrane distillation is a widely used MD configuration with diverse industry applications. It is commonly used in applications where the solvent is water, such as the desalination industry (Ashoor et al., 2016; Drioli et al., 2015; El-Bourawi et al., 2006; Ullah et al., 2018) and concentration of aqueous solutions (El-Bourawi et al., 2006; P. Wang

& Chung, 2015). DCMD has gained momentum across various industries, including food and beverage, wastewater (WW) treatment, drinking water treatment, pharmaceutical chemicals production, crystallisation of salts, biomedical industries, textile industries, and the oil and gas industry (Ashoor et al., 2016).

DCMD can perform well in a broad range of temperatures, making it applicable to technologies utilising temperatures above 100°C. It is relatively simple compared to other membrane distillation configurations and undemanding on the quality of the feed, making it possible to implement on-site water treatment in the oil and gas industry (Ullah et al., 2018). Additionally, it has a high gained output ratio, making it suitable for removing volatile organic compounds (VOCs) (Drioli et al., 2015). However, it is prone to membrane scaling, fouling, and wetting, and it has a lower flux than Vacuum Membrane Distillation (VMD) (Drioli et al., 2015; Ullah et al., 2018). It is also suitable for aqueous solutions only and has high thermal polarisation, leading to substantial heat loss because the membrane is the only barrier between cold and hot regions of the DCMD (El-Bourawi et al., 2006).

The energy consumption and distillation flux are closely related to process parameters, polarisation, membrane properties, and material (Ullah et al., 2018). The principle for the effective performance of the DCMD requires the feed solution to be kept at a higher temperature than the permeate to create the required vapour pressure difference for mass transfer through the membrane pores. The transmembrane temperature gradient is conditional to the vapour pressure difference, which drives the transfer of water molecules from the hot feed solution to the cold permeate solution. Therefore, careful temperature control of both the feed solution and permeate is crucial for optimal DCMD performance (El-Bourawi et al., 2006).

2.4.2 Air gap membrane distillation (AGMD)

Air gap membrane distillation is a separation technique that utilises an air gap to separate a condensation surface from a membrane. Due to the configuration preventing any contact between the permeate fluid and membrane surface, AGMD is well-suited for removing volatile substances. The substance being removed from the feed evaporates and passes through the membrane and air gap before condensing on a cooler surface (El-Bourawi et al., 2006). AGMD is less flux-efficient than other distillation methods, such as DCMD or VMD but has higher thermal effectiveness. It is used to treat industrial effluent, clean brackish water, and desalinate (El-Bourawi et al., 2006; P. Wang & Chung, 2015).

The condenser separates coolant from permeate, reducing heat loss and improving thermal efficiency (around 6% more efficient than DCMD). AGMD can recover heat without needing a heat exchanger, and heat is transferred from the feed to the membrane for efficient and effective distillation (Shahu & Thombre, 2019).

2.4.3 Sweep gas membrane distillation (SGMD)

Sweep gas membrane distillation is a separation process where a cold gas flow circulating through one chamber is passed along the permeate channel and collects vapour particles from the surface of the membrane (El-Bourawi et al., 2006; Khayet et al., 2000). The process also involves the introduction of an external condenser for collecting the permeate (Shahu & Thombre, 2019). The condensed vapours are typically collected outside the membrane module using an external condenser, which can result in additional equipment expenses (P. Wang & Chung, 2015).

Low thermal polarisation, compared to other configurations and reduced membrane wetting, is considered a significant advantage. On the contrary, this setup is relatively complex both from the involved equipment's point of view and the sweep gas's pre-treatment step. Additionally, this process does not provide sufficient heat recovery (El-Bourawi et al., 2006).

2.4.4 Vacuum membrane distillation (VMD)

VMD applies a vacuum to the permeate side of the membrane module. In order to accomplish the successful separation, the applied vacuum pressure needs to be lower than the saturation pressure of the volatile compounds in the feed solution (Shahu & Thombre, 2019). Whether condensation occurs outside the membrane module depends on the operational conditions. VMD and SGMD are generally used to remove volatile compounds (El-Bourawi et al., 2006).

The VMD process involves high flux, and the permeate quality is usually constant. On the other hand, the pores pose a risk of wetting, and the overall process requires a vacuum pump (VP) and an external condenser. This results in an overall increase in the system's complexity (Ding et al., 2006; Drioli et al., 2015).

2.4.5 Other configurations

In addition to the previously mentioned configurations, scientists agreed that other less commonly used arrangements have a potential. Some adaptations to the most common configurations can be made depending on the desired application of the MD, resulting in the formation of new set-ups. Permeate gap membrane distillation (PGMD), which is a configuration that resembles both the DCMD and the AGMD, consists of a three-chamber system with a permeate circulating through the gap and thus increases the thermal efficiency of the distillation process (Dharupaneedi et al., 2019; Shahu & Thombre, 2019). Secondly, Material gap membrane distillation (MGMD) engages a low-conductivity substance filling the gap and decreasing the heat transfer (Gude, 2015; Shahu & Thombre, 2019). Lastly, Conductive gap membrane distillation (CGMD) employs a metal filler, effectively increasing the heat transfer (Gude, 2015; Shahu & Thombre, 2019).

2.5 Applications of membrane distillation

The membrane distillation process has been widely studied and can be applied in various fields, including desalination, wastewater treatment, solution concentration, and food and beverage production. Compared to AGMD and SGMD, DCMD is more versatile. AGMD and SGMD have limited applications, primarily for desalination and chemical industries. VMD is similar to DCMD and more widely applicable.

One of the most significant applications of membrane distillation is in desalination. It was the first suggested application for MD; however, when they were first introduced for MD, the characteristics of membranes were unsatisfactory, and MD was significantly inferior to RO (Lawson & Lloyd, 1997). However, due to the emerging importance of desalination technologies, MD has been researched widely. The MD process effectively removes salt from seawater and brackish water, making it an attractive option for producing freshwater in regions where freshwater resources are meagre. The highest need for desalination technologies is located in arid and warm regions, where the atmospheric temperature can become helpful in applications such as MD. Since MD can function on renewable energy sources, solar energy can be satisfactory for obtaining desired purification results. Additionally, geothermal energy can also be used to drive MD desalination (Camacho et al., 2013; El-Bourawi et al., 2006).

MD (especially DCMD) also has great potential for applications such as wastewater treatment and removing contaminants such as heavy metals, organic compounds, and microorganisms. Renewable energy can be used as the heat source for retaining process energetical advantages. Moreover, waste heat from industrial processes has also proven to be an effective driver for MD. In addition to wastewater purification, MD can also be used for sludge concentration. However, wastewater MD has its limitations. If wastewater is rich in inorganic salts, MD can face undesired scaling. This encourages the use of antiscalants which can mitigate this issue (He et al., 2009). Additionally, MD can be used for wastewater treatment (WWT) if it does not contain VOCs. This can also be resolved easily by introducing a pre-treatment step for VOC removal; however, this would increase overall operational costs. MD can face membrane fouling if there is no other method for removing suspended particles. For this, several alternative pre-treatment steps can be used, including sieves, filtration membranes or even FO (Khayet, 2011; Lawson & Lloyd, 1997; Martinetti et al., 2009).

In the chemical industry, DCMD can be used to concentrate solutions and remove VOCs. DCMD has also been used for the separation of alcohol from azeotropic mixtures and crystallisation. The pharmaceutical and medical industries have utilised DCMD to concentrate blood and protein solutions. DCMD is particularly useful for the concentration of sensitive materials since it operates at low temperatures and pressures, minimising the

risk of denaturation or degradation of the material being processed (El-Bourawi et al., 2006).

Furthermore, since producing high-quality potable water, the process can be helpful if applied to the food industry for a concentration of juices and other liquid food products, resulting in a more concentrated and flavourful product. Lower operational temperatures compared to other concentration techniques prevent undesired loss of favourable properties of the product (Banat & Simandl, 1994; Galaverna et al., 2008; Lawson & Lloyd, 1997).

2.6 Principle

2.6.1 Membrane matrix properties

Membrane optimisation is a crucial step in ensuring the proper functioning of the MD system (Lee et al., 2016). The most important properties of the membrane are its hydrophobicity, which depends on a careful selection of membrane material (see 2.6.1.3 Membrane material), and effective and selective permeation, which is highly dependent on the properties of pores (Eykens et al., 2016a; Khayet, 2011). The parameters determining the process efficiency and their effect on the MD are depicted in Table 1 **Error! Reference source not found.**

Table 1 Summary of properties of MD system with their effect on MD performance (El-Bourawi et al., 2006; Khayet, 2011; Laganà et al., 2000; Sinha Ray et al., 2020)

	Effect on MD when high	Recommended value
Hydrophobicity	Liquid retention ↑	As high as possible
Chemical resistance	Membrane integrity ↑	As high as possible
Thermal conductivity	Energy efficiency ↓ and flux ↓	As low as possible
Thermal stability	Membrane integrity ↑	Stable up to 100 °C
Liquid entry pressure	Wetting resistance ↑	Higher than 250 kPa
Porosity	Energy efficiency ↑, flux ↑, mechanical strength ↓	30–85%
Pore size	Flux ↑ and liquid entry pressure (LEP) ↓	100 nm–1 μm
Thickness	Flux ↓, energy efficiency ↑	30–60 μm
Mechanical strength	Membrane integrity ↑	As high as possible
Tortuosity	Flux ↓	As low as possible

2.6.1.1 Membrane assembly

The membrane can be arranged in a single or multilayer structure. For a multilayer structure, at least one of the layers needs to be hydrophobic and porous (Khayet, 2011).

Over the years, many membrane assemblies have been proposed. These can be categorised into flat sheets and tubular membranes (capillary, hollow fibre modules, etc.). Their costs and operational effectiveness widely determine the selection of module type. However, different membrane assemblies can be preferable depending on the individual application.

2.6.1.2 Thickness

The thickness of the membrane is an essential parameter that affects the mass and heat transfer through the membrane, particularly for DCMD configuration. As the membrane thickness decreases, the mass and heat flux through the membrane increase. However, a

thinner membrane may also result in heat loss, necessitating careful consideration of the optimal thickness to balance distillation rate and energy efficiency. Mass flux for MD, where the solvent is water, is inversely proportional to membrane thickness, as depicted in the relationship (equation(1)).

$$N \propto \frac{\langle r^a \rangle}{\tau \delta} \quad (1)$$

Where N is the molar flux through the membrane, r^a is an average pore size, δ is the membrane thickness, and τ represents the membrane tortuosity (Lawson & Lloyd, 1997).

Therefore, the most effective membrane thickness for MD applications is typically between 10–60 μm . The optimal thickness of the membrane is closely related to the operational temperature and the influence of temperature on the system. Additionally, the membrane is critical in partially isolating the feed and permeate regions, affecting the MD performance. (Eykens et al., 2016b)

Airgap MD is less impacted by membrane thickness than DCMD is. For instance, the flow has no or minimal impact if the air gap space is greater than the membrane thickness. On the other hand, with vacuum MD, the flow decreases as the membrane thickness increases. Permeate gap MD requires the highest membrane thickness (up to 200 μm) to compensate for the loss of driving force obtained in this configuration.

In conclusion, the membrane thickness is a crucial factor in determining the performance of different MD configurations. Therefore, careful selection of optimal membrane thickness is necessary to achieve maximum extraction and energy efficiency while considering the specific operating conditions (Eykens et al., 2016b).

2.6.1.3 Membrane material

Material for membrane distillation should be selected carefully to obtain the best possible functioning of the system. Over the years, many scientists attempted to collect a set of membrane properties that would best suit specific applications. Due to the speed of developing of new distillation techniques, many membrane materials are reviewed (Qasim et al., 2021).

Three main criteria have been proposed. Firstly, material hydrophobicity is the most critical parameter because the material must have high retention towards liquid feed solution. Secondly, the material should have low thermal conductivity to decrease heat losses through the membrane matrix. Thirdly, the membrane should be chemically and mechanically stable to prevent overtime deterioration (Eykens et al., 2016a).

The most widely used material for membrane distillation is polymers. Their advantages over other types are sufficient to be the most interesting for water desalination or other MD

applications. Ceramic membranes are also widely researched and can compete with polymeric ones. In addition to ceramic and polymeric membranes, membranes can also be carbon nanotubes made membranes, hydrophobic/hydrophilic membranes (used for DCMD), mixed matrix nano-composite membranes, electro-spun membranes, modified polymeric membranes (Camacho et al., 2013).

The most widely used materials in MD are polymers. Polymers such as polypropylene (PP) polytetrafluoroethylene (PTFE), polyethylene (PE), poly(ether sulfone) (PES) and polyvinylidene fluoride (PVDF) have low surface tension, thus allowing for low wetting risks(El-Bourawi et al., 2006; Eykens et al., 2016b). Surfactants can affect the standard material properties by interacting with the membrane material and decreasing its hydrophobicity by wetting. Also, high transmembrane pressure can lower the membrane's ability to transfer only the desired vapour phase (El-Bourawi et al., 2006).

Ceramic membranes have shown highly satisfactory performance under critical conditions. Compared to polymeric membranes, ceramic ones are more expensive and harder to manufacture. Despite having higher thermal and chemical stability and being more resistant to wetting, ceramic materials are harder to modify and adapt for a specific application (Hubadillah et al., 2019; Qasim et al., 2021).

2.6.1.4 Thermal conductivity

The thermal conductivity of membranes is affected by the material choice as well as its porosity. It is calculated from the material's thermal conductivity and the gas occupying the pores. Most widely used membranes can conduct heat between $0,04 \text{ Wm}^{-1}\text{K}^{-1}$ to $0,07 \text{ Wm}^{-1}\text{K}^{-1}$. With increasing porosity, the thermal conductivity decreases. This is desired in MD since low thermal conductivity improves process efficiency by increasing mass flux and lowering energy losses. Thermal conductivity dependency on the material is also evident. Selected materials are tabulated with their thermal conductivity in Table 2 (Alkhudhiri et al., 2012; Eykens et al., 2016b).

Table 2 Membrane material thermal properties thermal conductivity (Alkhudhiri et al., 2012; Phattaranawik et al., 2003) thermal and chemical stability (P. Wang & Chung, 2015)

Material	κ_s (293K)	Thermal stability	Chemical stability
Polyethylene (PE)	0,33–0,52	Low	High
Polytetrafluoroethylene (PTFE)	0,25–0,27	High	High
Polyvinylidene fluoride (PVDF)	0,17–0,19	Moderate	High
Poly(ether sulfone) (PES)	0,13–0,18	High	High
Polypropylene (PP)	0,11–0,16	Moderate	High
Air	0,026		
H ₂ O (g)	0,020		

2.6.1.5 Strength and stability

The mechanical strength of a membrane is another parameter which requires attention. Generally, the mechanical strength of membranes is not well researched and tested; however, by some scientists, a wide variety of values is recorded. Strength is highly dependent on the material and pore distribution and, thus, should be evaluated for every membrane matrix separately. It also depends on the method of manufacture, and different membrane providers supply membranes with different mechanical characteristics. Reported values vary significantly. For instance, tensile strength for a specific membrane matrix is recorded to be 3,4 up to 57,9 in some publications (Eykens et al., 2016b).

In general, the stress test of the matrix shows membrane deformations before complete breakage. PTFE elongates almost twice compared to the size before rupturing. However, the membrane loses its functionality already in the deformed state and is unstable for MD. Mechanical rupture can be caused by applied pressure or by temperature increase. Membranes made of PP show ruptures when increasing the temperature of the feed to around 70 °C (Eykens et al., 2016a).

In addition to the ability to withstand mechanical stress, the membrane should be chemically and thermally stable. These properties can be obtained by careful selection of the membrane material and pore size and porosity. Membranes that are strong and resistant to chemical and thermal stress have a longer lifetime and are preferable for long-term applications (P. Wang & Chung, 2015).

2.6.1.6 Pore size

The selection of pore size is crucial for different separation processes in obtaining effectiveness. Pore size vary based on the specific application and separation stage, ranging from 0.1 nm to 1 mm. The largest pore sizes are typically found in macromembranes and micromembranes, which filter relatively large particles like sand, small rocks, pollen, and hair. Macromolecular membranes can separate particles, such as some bacteria and red blood cells, through microfiltration. For ultrafiltration, molecular pore sizes are used to catch certain viruses. Nanofiltration and reverse osmosis are used for particles smaller than 0.1 nm. In some cases, different membrane types can be arranged in a sequence, with the largest pore size membrane being used first to ensure absolute purification and prevent blockages (Lee et al., 2016). Therefore, selecting the appropriate membrane pore size for a given application is critical in achieving the desired separation efficiency.

For membrane distillation, desired pore size is between 0,1 µm to 1 µm (El-Bourawi et al., 2006; Lawson & Lloyd, 1997). The exact size of membrane pores is selected so the pores are large enough to allow for the desired flux but also must prevent liquid feed solution from passing through them (Lawson & Lloyd, 1997).

2.6.1.7 Porosity

Commercial membranes usually have porosities between 30% and 85%. Higher the porosity, the better for MD, but it still needs to have sufficient mechanical strength. Mass flux is linearly proportional to porosity. Additionally, the thermal conductivity of polymeric materials is higher than for air and water vapour mixture. Therefore, it was established, both theoretically and experimentally, that high porosity increases thermal efficiency and mass transfer (Eykens et al., 2016b).

2.6.1.8 Tortuosity factor

The tortuosity factor is a quantification of pore structure shift from cylindrical pores. For proper function of the membranes, tortuosity should be small. It affects membrane permeability in membrane distillation. Despite being difficult to measure accurately, many approaches allow for the estimation of tortuosity based on membranes' porous structures. In general, when calculating transmembrane flux, tortuosity is estimated to be 2 (Khayet, 2011).

2.6.1.9 Liquid entry pressure (LEP)

For membrane distillation, LEP is an important parameter to look at. It demonstrates the minimum transmembrane pressure at which the feed solution starts to penetrate the membrane in a liquid form (Smolders & Franken, 1989). During the membrane distillation, the applied transmembrane pressure must be lower than the critical transmembrane pressure. Otherwise, the system faces risks of membrane wetting and can deteriorate over time (Khayet, 2011; Yazgan-Birgi et al., 2018).

High LEP can be obtained using highly hydrophobic membranes. LEP depends on the material's surface energy and the small maximum pore size (Khayet, 2011). Several models can be used for estimating LEP. A widely used approach is to use the Young-Laplace equation:

$$LEP = \frac{-2B\gamma \cos \theta}{r_{max}} \quad (\text{Franken et al., 1987}) \quad (2)$$

Where B is the geometric factor representing irregularities in the pore system and curvature radius of the surface pores. For perfectly cylindrical pores, $B = 1$; for noncylindrical pores, $0 < B < 1$. r_{max} represents the maximum pore size of the membrane, θ stands for a contact angle between the liquid and the membrane and γ is a surface tension of a liquid (Guillen-Burrieza et al., 2015).

2.6.2 Process parameters

Membrane distillation is a thermal separation technique that employs porous membranes made of hydrophobic material to permeate gas over liquid selectively (El-Bourawi et al., 2006). The basic principle of operation is depicted in Figure 4. The MD system is divided into four primary units responsible for different parts of processing.

The first unit is the feed chamber, which holds the feed solution and should allow for easy regulation of its temperature. As the feed solution is heated to the desired temperature, distillate passes through the phase boundary as vapour. The second unit is the membrane barrier, which contains a porous system. The membrane placement within the technology depends on the type of membrane distillation configuration used. The third unit is the permeate region, where the incoming distillate condenses directly into liquid (permeate) or on an external condenser surface. The fourth unit is the collection tank, where the collected product is stored. The collection method varies depending on the type of membrane distillation used (Lawson & Lloyd, 1997).

Designing a membrane system requires consideration of several system parameters. The most basic principle for the process functionality is to limit the degree of membrane wetting and ensure that only vapour enters and passes through the membrane. This separates membrane distillation processes from techniques utilising the filtration method. Permeate selectivity can be secured by membrane matrix optimisation (see 2.3.2 Membrane matrix) (El-Bourawi et al., 2006).

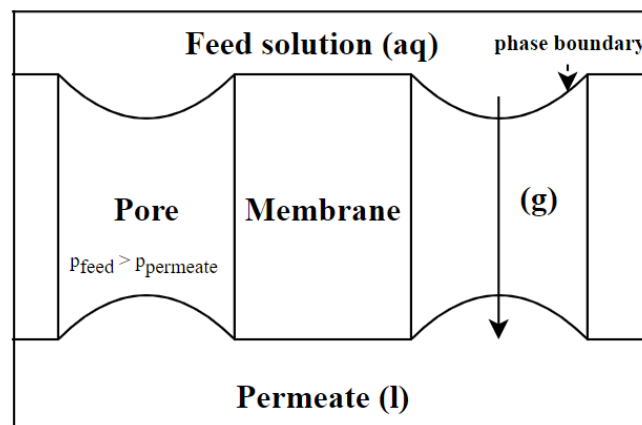


Figure 4 Membrane system (Eykens et al., 2016b)

The membrane acts as a separator between two phases. The membrane material is stable and does not interact chemically with either phase of the system.

Operating at lower temperatures and hydrostatic pressure compared to other separation techniques, MD is a suitable, energy-efficient method for water purification. The temperature of the feed should be held under the solvent's boiling point. For MD, where

the solvent in the feed is water, the boiling temperature is around 30 °C to 90 °C. This, however, is also dependent on the material properties of the membrane and other equipment. To prevent membrane deterioration, the temperature must be held below the temperature at which membrane material softens. The pressure used for the permeation is close to the atmospheric pressure to reduce the risks of membrane rupturing. This pressure is sufficient to allow MD to function correctly (Camacho et al., 2013).

The process engages mass and heat transfer through the membrane. The direction of the transfer is for both the same. The higher temperature of the feed compared to the permeate side encourages heat transfer from feed to permeate, and the mass flux is encouraged based on solvent vaporisation on the feed side to pass through the membrane in the same direction as heat (Qtaishat et al., 2008).

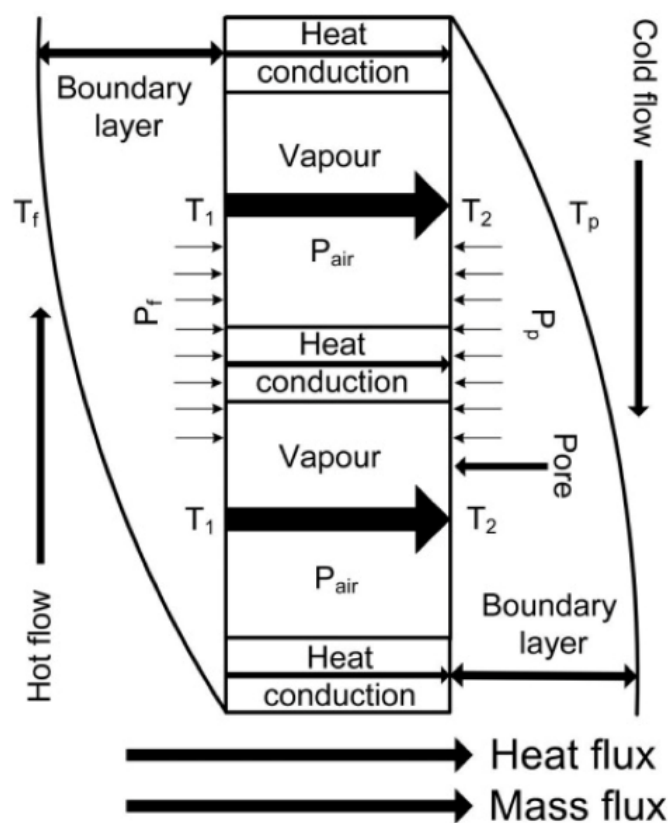


Figure 5 Membrane distillation principle, transfer of matter and heat (Camacho et al., 2013)

Figure 5 demonstrates the direction of heat and mass transfer in the DCMD configuration. It also illustrates the effect of heat conduction throughout the membrane boundary (Camacho et al., 2013). Temperature polarisation (TP) is established from the temperature differences as shown in equation (3), where, as depicted in Figure 5, T_1 is the temperature at the membrane surface on the feed solution side, T_2 is the temperature of the permeate on

the membrane surface, T_{feed} is the temperature of the feed, and T_{perm} is the temperature of the permeate (Schofield et al., 1990).

$$TP = \frac{T_1 - T_2}{T_{\text{feed}} - T_{\text{perm}}} \quad (\text{Schofield et al., 1990}) \quad (3)$$

2.6.2.1 Mass transfer

Mass transfer through the membrane has two major drivers. The first driver is the transmembrane vapour pressure difference (Δp), which is directly proportional to the mass transfer flux (J). The higher the difference in the vapour pressure difference between the two sides of the membrane, the higher the mass transfer rate. The second driver is the permeability (B) of the membrane, which determines the flux of mass transfer. This relationship is depicted in equation (4) (Sanmartino et al., 2016). A membrane with higher permeability allows for higher mass transfer rates and vice versa. Various membrane properties, such as porosity, pore size, tortuosity, and membrane thickness, influence the permeability coefficient.

$$J = B\Delta p \quad (\text{Sanmartino et al., 2016}) \quad (4)$$

Mass transfer through the membrane can occur through three main mechanisms. The first mechanism is Knudsen diffusion, which occurs when the molecules of the vapour bounce between the walls of the membrane pores without interacting with each other (Reinecke & Sleep, 2002). The second mechanism is Poiseuille flow, which is a symmetric flow through the membrane pore without any collisions. Its direction parallels heat transfer and the overall mass transfer vector (Camacho et al., 2013; Lawson & Lloyd, 1997). The third mechanism is molecular diffusion, which involves physical interactions between the molecules, namely collisions. Additionally, a transition mechanism can occur, where two or all three mechanisms may be involved in the process (Camacho et al., 2013).

2.6.2.2 Heat transfer

Heat can be lost and transferred in three ways in systems such as MD. Based on three regions of the MD system, heat is transferred either through the feed boundary, permeate boundary or membrane boundary. Heat flux through the membrane is defined as the overall conduction through the membrane matrix (solid membrane material and pores filled with gas (usually air) saturated with water vapour in their percentual compositions) and the heat of vaporisation (Sanmartino et al., 2016).

Heat transfer throughout the system is divided into two stages. First is the transfer of heat throughout the feed region where, as depicted in Figure 5 temperature of the feed inlet is higher than the temperature of the feed on the membrane surface due to convection. Secondly, heat transfer takes place through the membrane boundary in the form of sensible

and latent heat. Due to the two-staged heat transfer, the following relationship is applicable (equation (5) and equation (7) (Gryta, 2005; Schofield et al., 1990).

$$Q_1 = \frac{\lambda}{b}(T_1 - T_2) + JH \quad (5)$$

$$\lambda = \lambda_{air}\varepsilon + \lambda_{solid}(1 - \varepsilon) \quad (6)$$

$$Q_2 = \alpha(T_{feed} - T_1) \quad (7)$$

Q_1 and Q_2 equal and stand for the total heat flux. The combination of equations (5) and (7) can demonstrate the relationship between the two heat transfer mechanisms.

$$\frac{\lambda_{air}\varepsilon + \lambda_{solid}(1 - \varepsilon)}{b}(T_1 - T_2) + JH = \alpha(T_{feed} - T_1) \quad (8)$$

Where λ is the thermal conductivity of pores filled with air and membrane, b is the membrane thickness, ε is the membrane porosity representing the content of either air or membrane material, α is the convection heat transfer coefficient, J is the permeate flux, H is the enthalpy of the vapour, T_1 stands for the temperature at the membrane boundary on the side of the feed, T_2 is the temperature at the boundary on the side of the permeate and T_{feed} is the temperature of the bulk feed.

Heat transfer is conditioned by membrane pore size, porosity, and tortuosity. If the tortuosity is close to 1, the following relationship is applicable (equation (9))

$$Q = Q_{vap} + Q_{cond} \quad (\text{Sanmartino et al., 2016}) \quad (9)$$

Where Q represents the overall heat transfer, Q_{vap} stands for the latent heat transfer and Q_{cond} is the conduction heat transfer. Q_{cond} should be kept as low as possible to reduce any heat losses of the process.

2.7 Advantages vs drawbacks of membrane distillation (MD)

Over conventional distillation techniques, membrane distillation has numerous benefits. One of the most significant advantages is the high theoretical conversion of the solvent phase of the feed to permeate (above 90%), with no impurities passing through the membrane when the feed contains no volatile substances (Kiss & Kattan Readi, 2018). This makes it particularly beneficial in pharmaceuticals or food and beverage manufacturing sectors, where strict purity standards are crucial (Sanmartino et al., 2016).

Another asset is that it operates at much lower temperatures than normal distillation. It consumes relatively low amounts of energy and can be almost entirely powered by renewable energy sources or residual heat coming from the process. This low-grade heat can be supplied in the form of solar energy, or if MD is planted into a complex technology,

the waste energy can be utilised for driving the distillation (Lawson & Lloyd, 1997; Sanmartino et al., 2016; Skuse et al., 2021). Moreover, membrane distillation uses less hydrostatic pressure than other water desalination methods, such as reverse osmosis, which decreases the energetical demand and lowers the risk of membrane disruption (Skuse et al., 2021).

Individual parts of the system play a crucial role in separation processes, such as membrane distillation. Firstly, as opposed to other conventional desalination technologies, MD has lower material requirements for the membrane and the possibility of using polymeric materials that decrease the risk of corrosion. Moreover, stationary parts are used, simplifying the equipment design, and decreasing its robustness. Furthermore, unlike RO, membrane distillation is not a pore size exclusion process. The pores can be up to two magnitudes larger than those used in RO, which is beneficial for mitigating problems with membrane fouling. The overall maintenance costs are also reduced by mitigating fouling and prolonging the membrane's lifespan (El-Bourawi et al., 2006; Lawson & Lloyd, 1997).

Another benefit of MD is that it is not concentration-dependent, unlike RO, which relies on a specific feed solution concentration to operate. Hence, MD demonstrates greater operational flexibility than many other technologies used for water purification (Skuse et al., 2021).

Additionally, the compact design of MD membranes provides a low vapour area and enables the use of exclusively stationary equipment. Therefore, compared to reverse osmosis (RO), membrane distillation is more compact, making it a preferred option when space is limited. Additionally, unlike RO, MD produces low chemical sludge effluent (Lee et al., 2016).

As a result, membrane distillation is a cost-effective alternative to reverse RO for producing potable water. Unlike RO, MD has lower initial and maintenance costs, making it an attractive option for large-scale plants. Studies estimate the overall cost of drinking water produced by a large-scale MD plant to be between 0,46 and 1,07 €/m³ (Alobaidani et al., 2008). Additionally, MD exhibits a low risk of membrane fouling, necessitating minimal pre-treatment. Biodegradable antiscalants effectively prevent fouling in MD, which results in lower operational and maintenance costs than RO (Andrés-Mañas et al., 2018; Bindels et al., 2020).

Despite its numerous advantages, membrane distillation carries several drawbacks. One of the significant drawbacks of membrane distillation is the possibility of membrane wetting, which can reduce the process's performance. Pore wetting can be prevented by removing surfactants from the feed, but this requires complicated pre-treatment or developing anti-wetting membranes. Furthermore, commercial use is limited to relatively high component prices for the MD setup. Lastly, there is a decrease in the functionality of the membrane due to its deterioration over time (Skuse et al., 2021).

Additionally, the low flux in MD (1 to 4 L/m²) compared to the flux in RO (12 to 17 L/m²) is a significant limitation in desalination applications (Okamoto & Lienhard, 2019). This is, however, being addressed by many researchers who are attempting to improve the hydrophobicity of the membrane by doping polymers with nanoadditives (production of mixed matrix membranes) (Tijing et al., 2016). This approach increases the flux and energy efficiency of the membrane, making it more suitable for commercial applications (Eykens et al., 2016b).

Furthermore, despite having relatively low operational and maintenance costs, commercial use of MD is limited due to the relatively high prices of the components necessary for setting up the MD process (Lawson & Lloyd, 1997; Sanmartino et al., 2016). The membranes used currently lack specificity for MD. Additionally, the membranes have low mechanical strength, which makes them difficult to handle at a large scale, particularly if unsupported. To address these limitations, it is essential to reduce the production costs of the membranes and improve their performance (Skuse et al., 2021).

2.8 Design of laboratory units

MD process is still a relatively new approach to water purification. There are several possible MD applications, membrane types, and operational parameters that require close attention. For this reason, MD is still yet to be commercialised fully and requires higher interest from scientific society (Alkudhiri et al., 2012).

For this moment, MD modules are still being tested and researched. New adaptations are made so MD can overcome its disadvantages and become a superior water purification method, especially for water desalination. Its energetical advantages over other desalination methods (such as RO) have become highly significant, especially in areas that suffer from potable water shortages. These areas can take advantage of high temperatures and many cloudless days and use a renewable energy source to prepare potable water. For this purpose, research on MD is gaining on its importance. In general, laboratory tests are preferably undertaken on DCMD configuration. This is the simplest setup which can be accurately evaluated and tested in laboratory conditions. This setup is also preferable thanks to its high distillation rates compared to other configurations (El-Bourawi et al., 2006; Thomas et al., 2017).

However, other configurations are being tested as well. Despite requiring greater attention while using a more complex set of operational parameters, AGMD, PGMD and VMD can be preferable in specific cases and thus interest many researchers (Curcio & Drioli, 2005).

3 AIMS

The primary aim of this study is to optimise the membrane system setup for membrane distillation using a hollow fibre membrane matrix. The study aims to investigate the factors that influence the performance of the MD unit.

The operational factors' evaluation includes the selection of the optimal condenser for the MD unit; the resolution of the membrane floating problem using a membrane anchor; the comparison of the performance of the MD unit using different feed solutions, anchor types, and process conditions. The study aims to maximise the distillation efficiency and the distillation rate of the MD unit using hollow fibre polypropylene membranes, vacuum configuration, and an outside-in approach.

Another objective is to determine the surfactant concentration range at which the MD is effective. The surfactant concentration is a critical factor in the efficiency and performance of the MD unit. If the concentration is too high, surfactants can affect the integrity of the membrane, leading to membrane wetting and reduced performance. While regulating the disposal of surfactants as liquid waste is not easily manageable, the technological limits for wastewater treatment technology should be determined. One of the scopes of this thesis is to establish the maximum concentration of the surfactant at which the technology is unaffected. If present in higher quantities, surfactants must be removed from the feed solution by wastewater pre-treatment.

4 EXPERIMENTAL PART

4.1 Laboratory unit setup

The present study aims to optimise the setup of the membrane system. To achieve this goal, several adjustments were made. In contrast to the previous work conducted by Plachy, where the feed solution was circulated through the membrane system and mass transfer occurred in a direction from the membrane out (inside-out approach) (Petr Plachý, 2022), this thesis presents a study where the setup is constructed in a way where the membrane bundle is submerged in the feed solution. This adaptation involves airflow through the hollow fibres, where saturation occurs from the container into the membrane bundle (outside-in approach). Therefore, the mass transfer of this study happens inversely compared to Plachy's work (see Figure 6).

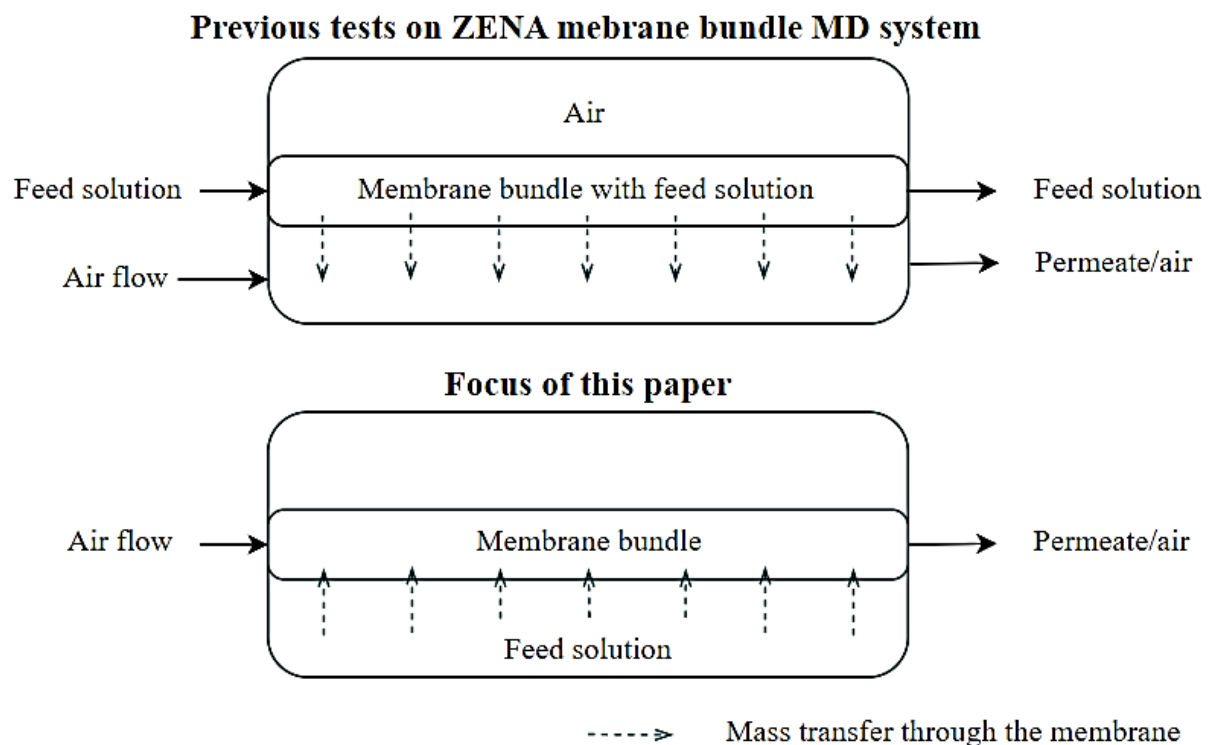


Figure 6 Comparison of the present research to its precede work conducted by Plachy (Petr Plachý, 2022)

The experimental setup for membrane distillation using a hollow fibre membrane matrix comprises several components essential for proper functioning. The setup has been divided into three distinct regions to attain simplicity and facilitate the understanding of the process. These regions include the feed region, the air/permeate region, and the permeate region, as illustrated in Figure 7.

The feed region is responsible for containing and transforming the feed solution. It consists of several pieces of equipment, including the membrane matrix, the feed solution, and associated setup components. The air/permeate region is responsible for transporting saturated air via tubing. The permeate region is where the product is condensed and collected.

The setup provides two main boundaries that divide the process phases. The first boundary is located between the liquid feed and the permeate vapour inside the membrane pore. The second boundary is between the air saturated with the vapour permeate and the liquid product and is located on the condensation surface.

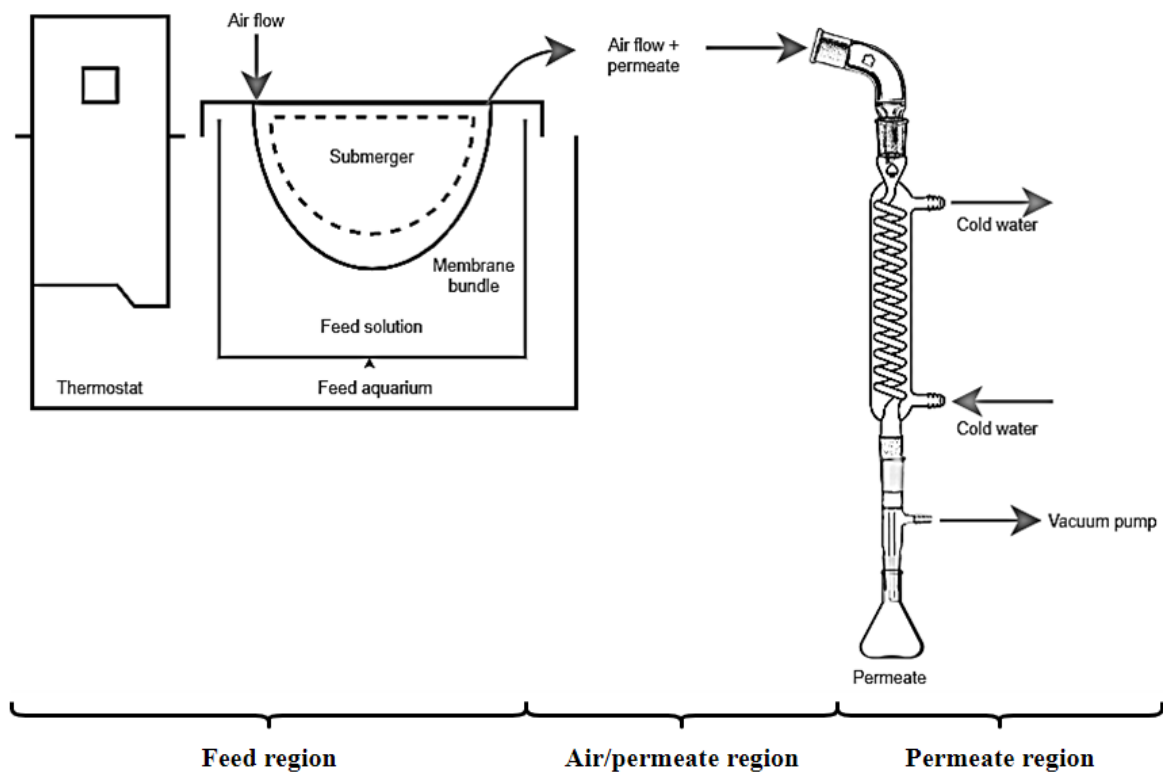


Figure 7 Schematic representation of the laboratory unit setup

The membrane bundle is the primary equipment that is a significant determinant of the study. It is attached in a way that allows inlet air to flow through the insides of the fibres and saturated air to flow out of the feed region.

The secondary equipment includes a heater, which is used to obtain the desired temperature of the feed solution. In this experiment, a water bath thermostat was used. The feed container, made of a material that is stable at experimental temperatures and pH, is another necessary component. For the conducted experiments, a glass aquarium was filled with feed solution and covered with a lid to which the membrane bundle could be attached. At the outlet of the membrane matrix, a barometer is included to measure the pressure of the

experiment. Permeate then flows through the condenser. The most suitable condenser type was determined by testing various options (see 5.1 Laboratory unit optimization). The product permeate is then collected in a conical flask. Lastly, the whole process is driven by a vacuum pump.

Tertiary equipment, including laboratory glassware, such as measuring cylinders, beakers, weighing boats, watch glasses, pipettes, etc., is utilised to prepare solutions and analyse product permeate. An analytical balance is used for solution preparation and extracted volume determination in some cases, and an electrical conductivity meter is used to determine the feed and permeate quality.

Instrumental adaptations have been necessary to achieve the highest possible operational efficiency, resulting in further adaptations of the tested unit. The laboratory unit setup is essential for conducting successful membrane distillation experiments, and the described components play a significant role in the overall process (see 5.1 Laboratory unit optimization).

4.2 Membrane bundle properties

The membrane type used in this particular application is a bundle of 1380 porous hollow fibrous membranes manufactured by ZENA Membranes s.r.o. The membranes are made of polypropylene and have an average pore size of 0,1 μm . The polypropylene material used in manufacturing these membranes is known for its high chemical stability, making it a reliable and durable option for use in challenging environments. The material can withstand a pH range of 2–11 and a temperature of 40 $^{\circ}\text{C}$, making it versatile and suitable for various applications. The membrane fibres are bundled in a cylindrical PVC casing with a polyurethane filling to hold the fibres. The casing has a radius of 10 mm.

The tested membrane bundle has a length of 30 cm, and fibre outer radius of 310 μm and an inner radius of 240 μm . The active surface area of the membrane bundle is 0,36 m^2 , making it suitable for use in various industrial and environmental applications (ZENAmembranes, 2023)

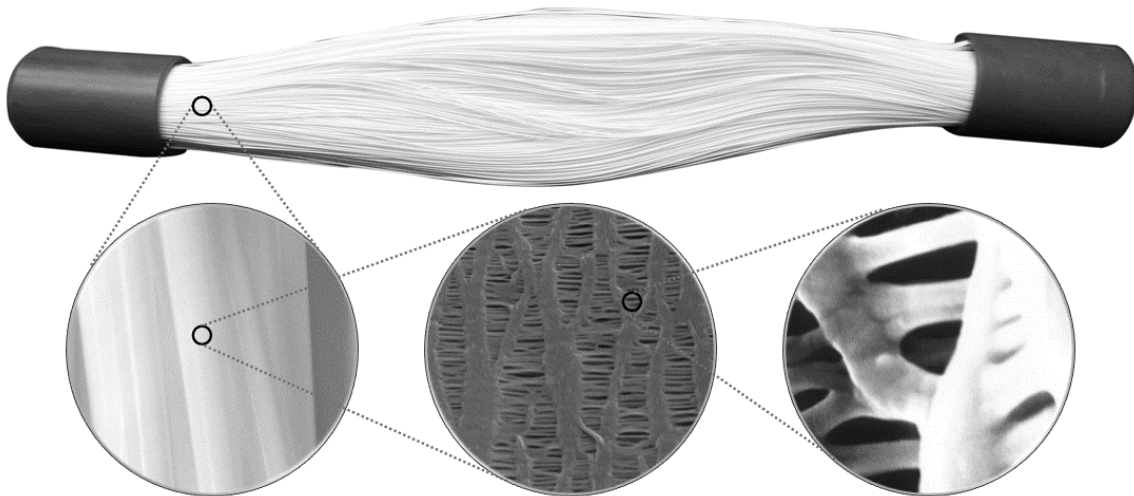


Figure 8 Membrane bundle used in the experimental testing with a close-up of the membrane fibre and pore structure (ZENAmembranes, 2023)

4.3 Analytical approaches

To ensure accurate results and precise evaluation of the technology, pre- and post-experimental testing was performed. Prior to the experiment, the feed solution was tested to determine its properties. This was necessary to allow for subsequent comparison of the permeate and the feed and evaluation of the effectiveness of the process. A calibration curve was generated for laboratory-prepared feed solutions with known concentrations to enable the identification of impurities in the permeate. This approach also served to assess the process effectiveness by comparing the feed and permeate concentrations.

Post-experimental testing was conducted on each collected permeate sample to determine both the permeate's quantity and quality and establish the process's overall efficiency.

4.3.1 Determination of the permeate quality

The permeate was subjected to an electrical conductivity test at room temperature (23 °C) using a HANNA electrical conductivity meter, and its conductivity was compared to that of the feed solution. In a successful distillation, all solutes should be removed from the distilled solvent, resulting in the permeate having the same electrical conductivity as the solvent.

In this study, tap water was initially used as the feed solution, but it was later replaced with a solution of known composition, namely sodium sulphate and deionised water (DI). The electrical conductivity of the deionised water (DI) was measured to ensure that the permeate's conductivity could be compared to that of the solvent. However, as the exact composition of DI is unknown, the permeate's electrical conductivity may be higher than the target conductivity of distilled water. The objective of the process is to obtain a permeate with an electrical conductivity lower or equal to that of the solvent used.

4.3.2 Determination of the permeate quantity

The distillation rate of MD under specific conditions was determined using volumetric measurement, which enables the evaluation of process efficiency and operational conditions. The equipment was saturated with DI before each test to enhance accuracy without sacrificing time efficiency to minimise product loss during volumetric analysis. However, the overall degree of uncertainty was not wholly eliminated.

4.4 Experimental approach

The performance of an MD unit largely depends on the selection of the optimal condenser and anchor types and the temperature and pressure conditions. In this study, a series of experiments were conducted to investigate the effect of different condenser and anchor types, feed solutions, and process conditions on the MD performance. The experiments were labelled A to K based on their aim and experimental setup.

Table 3 Test types conducted in this study, aim of the test, and general information on the test

Type	Condenser	Anchor	Test aim
A	Liebig	None	- Condenser selection - Initial system functionality test
B	Allihn		
C	Dimroth		
D	Graham		
E		None	- Feed solution change
F			- Pressure dependency on the process
G			C-type
H		- Temperature dependency of the process	
I		E-type	- Optimal setup operational effectivity
J			- Membrane wetting test
K			

Experiments A, B, C, and D aimed to select the optimal condenser for the MD unit and test the initial system functionality. In these experiments, Liebig, bubble Allihn, spiral Dimroth, and Graham condensers were used, respectively, with no anchor (see Figure 10). Experiments of type E compared the performance of the MD unit using two different feed solutions, tap water and sodium sulphate solution, with a Graham condenser and no anchor. Experiment F aimed to test the pressure dependency of the MD process with a Graham condenser and no anchor. Experiments G, H, and I aimed to select the optimal anchor type and investigate the temperature dependency of the membrane distillation process. In experiment G, a Graham condenser and no anchor were used, while in experiments H and I, a C-type and an E-type anchor were used, respectively, with a Graham condenser (see Figure 12). Experiment J aimed to test the operational effectiveness of the optimal MD setup using a Graham condenser and an E-type anchor (see Figure 14). Finally, experiment K aimed to test the membrane's resistance to wetting using sodium dodecyl sulphate solution as a feed solution for the MD, with a Graham condenser and an E-type anchor (see Figure 18).

Experiments conducted in this research were limited to the temperature region, which is acceptable by the equipment materials (PP and PLA soften or lose their properties in an

aqueous solution around 60 °C) (Ilyas et al., 2022). The experiments were conducted in the laboratory at surrounding conditions depicted in Table 4.

Table 4 Laboratory conditions (Weather & Climate, 2023)

Location of the experiments	The temperature of the surroundings/ inflow air temperature	The humidity of the surroundings/ inflow air humidity
Brno, Czech republic	23 °C	~ 75%

4.5 Experimental procedure

This study's experimental procedure for hollow fibre membrane distillation (MD) followed a standard protocol. The equipment was initially cleaned with propanol to avoid contamination. The medium was prepared, and its properties were measured and recorded before being placed in the aquarium with the membrane unit. The thermostat was set to a temperature typically 4 °C higher than the desired experimental temperature to account for temperature differences caused by placing the aquarium in a thermostat bowl.

After stabilisation of the temperature, the distillation was initiated, and the Erlenmeyer flask was emptied before recording the first test. A preliminary run was conducted to saturate the equipment with the distillate, ensuring accurate resulting volumes with minimal discrepancies and eliminating the need for a drying step between individual tests.

The setup was then reconnected, and the temperature and pressure were recorded at the start of the distillation. The experiment continued until sufficient product volume was collected for analysis. The vacuum was turned off, and the product was collected after disconnecting the setup. The volume of the product was measured, and the distillation rate was calculated. The product's electrical conductivity (EC) was compared to that of the feed solution. Finally, the experimental parameters were readjusted, and the instrument was prepared for the next test.

5 RESULTS AND DISCUSSION

5.1 Laboratory unit optimization

The experimental scope of this research involved applying predefined primary equipment (see 4.1 Laboratory unit setup) adjustments; however, optimisation of the secondary components was required to obtain the highest possible efficiency of the setup. The operation of the membrane distillation unit was tested, and adaptations were made. This primarily involved selecting the most suitable condenser and resolving the membrane floating problem.

5.1.1 Condenser selection

This involved examining four condenser types – Liebig, Allihn, Dimroth and Graham (see Figure 9). Despite having no effect on the quality of the collected permeate, condenser selection is an essential step in ensuring a high quantity of the product. A small contact area of condensation would result in product loss, and condensation would happen in the equipment between the condenser and vacuum pump; in the vacuum pump (VP) or gaseous permeate could be driven out of the system by air. Due to this, the incoming feed type is not a determining parameter in this setup optimisation step, so tap water was used as the feed solution because of its highest accessibility.

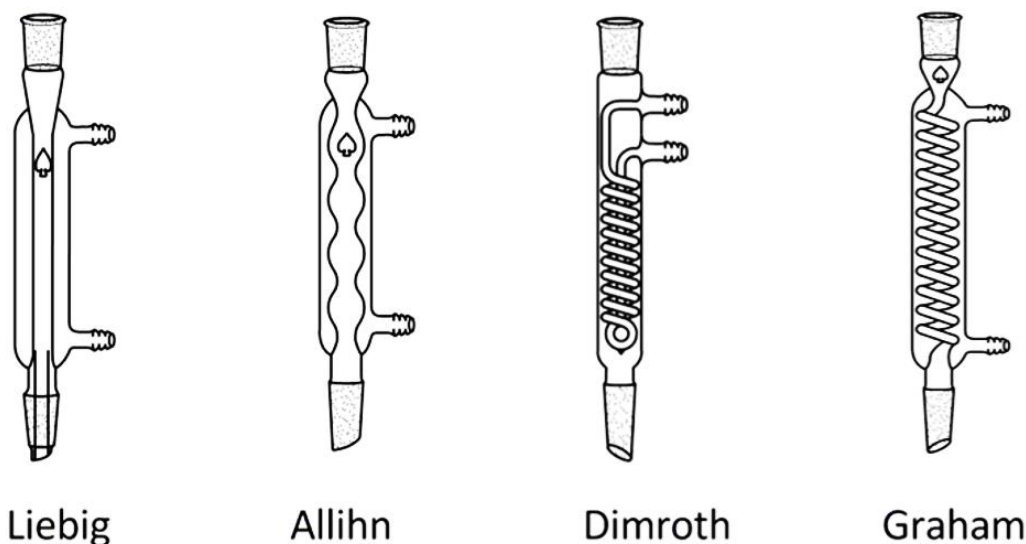


Figure 9 Condenser types used in the optimisation of the setup (Chemistry Forum, 2012)

Firstly, a Liebig condenser was used. The condenser was set up diagonally with cold water as a cooling medium. The results show a low distillation rate caused by insufficient surface area for cooling and condensation. Consequently, permeate condensation occurred in the vacuum pump instead of the condenser. Additionally, the VP outflow was highly saturated with water resulting in a loss of permeate.

Secondly, a bubble Allihn condenser was used to increase the surface area of the condensing site. It was set up vertically with cold water as a cooling medium. Even though this approach showed a promising improvement, there was still some condensation at the VP occurring. As per the previous approach, this would result in a loss of permeate product in the gaseous form through the VP, thus lowering the efficiency.

Thirdly, a spiral Dimroth condenser was utilised and showed a significant improvement in the quantity of the condensate. It was also set up vertically with water as a cooling medium. The increased surface area of condensation allowed permeate condensation to happen majorly inside the condenser. Condensation at the vacuum pump was eliminated entirely.

Lastly, spiral Graham was used and showed the best extraction rate relative to the other three condenser types. It was constructed in the same way as the Dimroth condenser, vertically with cold water as a coolant. Additionally, no condensation happened at the VP, similar to the Dimroth condenser approach. The highest distillation rate can be explained by the largest contact area between the permeate vapour and a condenser surface. These four condensers were tested at a temperature of 49 °C and a pressure of 0,7 bar. The results of the comparative study of the condensers for MD using hollow fibre membranes are depicted in Figure 10. The experiment involved repeatedly testing every condenser (5 tests) to ensure the highest possible accuracy. Due to its best performance, the Graham condenser was selected as the most effective for the purpose of this research and used for further experiments.

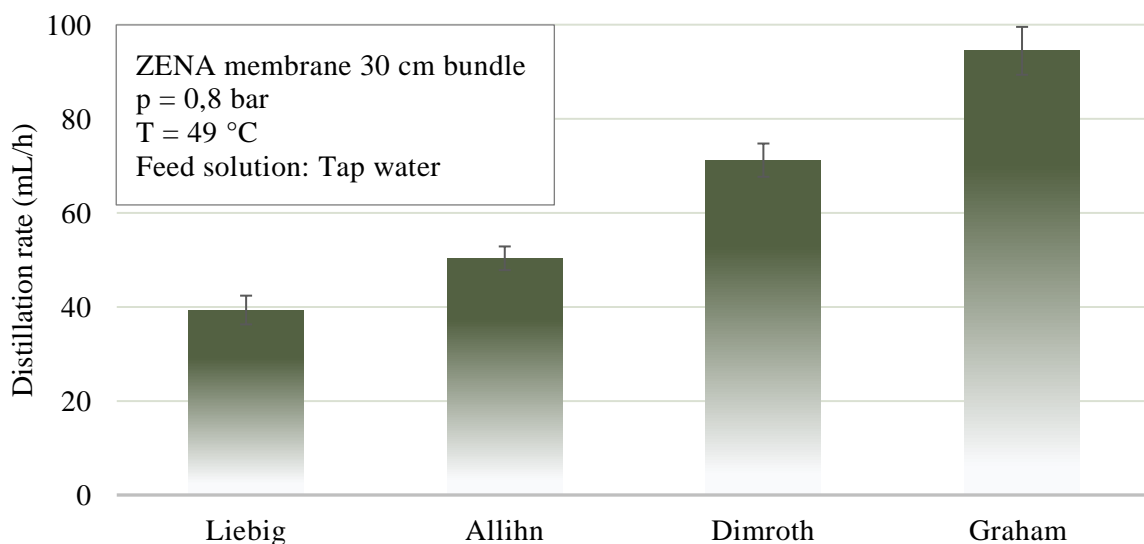


Figure 10 Distillation rates of various condenser types (Liebig, Allihn, Dirmoth and Graham) under identical experimental conditions (feed solution = tap water; the temperature of the feed solution = 49°C; pressure at the membrane output = 0,7 bar) and setup

5.1.2 Anchor selection

Membranes in this experimental setup tend to aggregate, emerge, and float atop the feed solution. This leads to a reduction in the overall active membrane surface area, consequently diminishing the effectiveness of the membrane distillation process. A membrane anchor has been suggested as a viable solution to address this challenge. The proposed mechanism effectively submerges and separates the membrane fibres, enhancing operational efficiency.

First, circular anchors A, B and C were proposed, and 3D printed (see Figure 11). Secondly, half circular anchors with longer separators D and E were proposed and 3D printed. All of the used anchors are 3D printed using a PLA filament. Polylactic acid is the most commonly used material for 3D printing. It has relatively high thermal allowances; however, when submerged in water, softening happens at 60 °C (Ilyas et al., 2022).

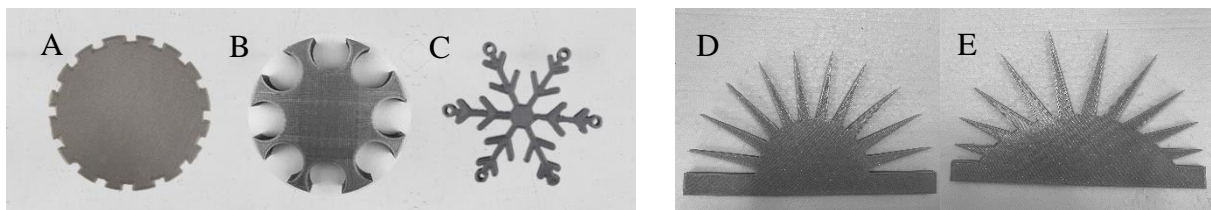


Figure 11 Five anchor prototypes 3D custom-printed for their purpose in the hollow fibre membrane distillation setup

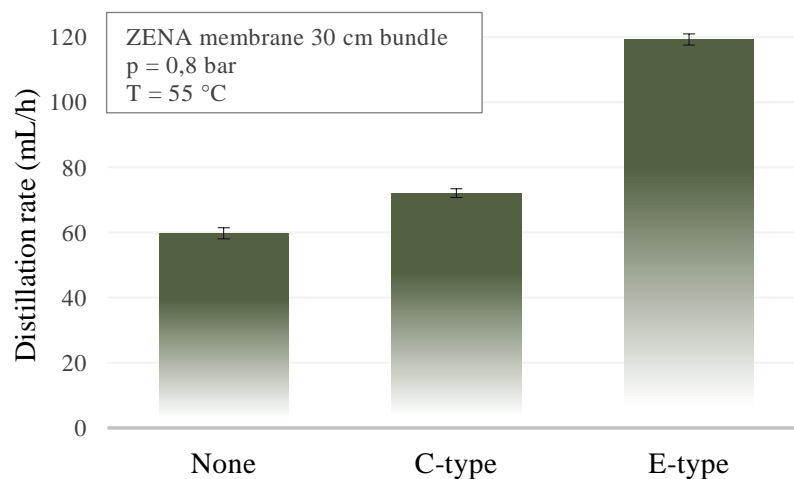


Figure 12 Comparison of performance of MD unit with none anchor, C-type anchor and E-type anchor at 0,8 bar and 55 °C with a Graham condenser

Out of the five prototypes for membrane anchors, two were selected as the most suitable and usable. Pre-experimental anchor application to the membrane unit showed that only C-type, D-type and E-type anchors could submerge the membranes. Anchors A, B and C did not show a good separation effect on the membrane. Their size also was not satisfactory and allowed the anchor to rotate in the solution. This resulted in membranes re-emerging

and the anchor's loss of purpose. Anchors D and E effectively separated the membranes. For comparison, the MD unit was tested using no anchor, C-type anchor, and E-type anchor at the same operational conditions (pressure of 0,8 bar, temperature of 55 °C, Graham condenser). The experimental results are depicted in Figure 12.

C-type and E-type showed promising permeate yields compared to the MD process using no anchor. However, a significant improvement in the distillation rate (120mL/h) could be observed when switching from the C-type to the E-type anchor. This can be justified by constants submerging and separation in the membrane distillation process using the anchor E. For this reason, anchor E was further used for the following experiments.

5.1.3 Selection of feed solution

Operational functionality is tested on different feed solutions. First, tap water was used as the most easily accessible medium. The medium was then substituted, and a solution of sodium sulphate of known concentration was used. Sodium sulphate is a crystalline white inorganic compound highly soluble in water (445,5 g/l at 20 °C). It is stable under the conditions of this experiment (Carl Roth, 2022).

The experimental testing was conducted on a sodium sulphate solution of different concentrations (4–5 mM). A calibration curve was constructed from the prepared control samples of the sodium sulphate solution (see Figure 13). Deionised water was used as a solvent for all the solutions in the experiments. The electrical conductivity of the DI was measured before the solution was prepared to allow for comparison with the distillate. The EC of DI ranged between 10 to 30 $\mu\text{S}/\text{cm}$ for all the experiments.

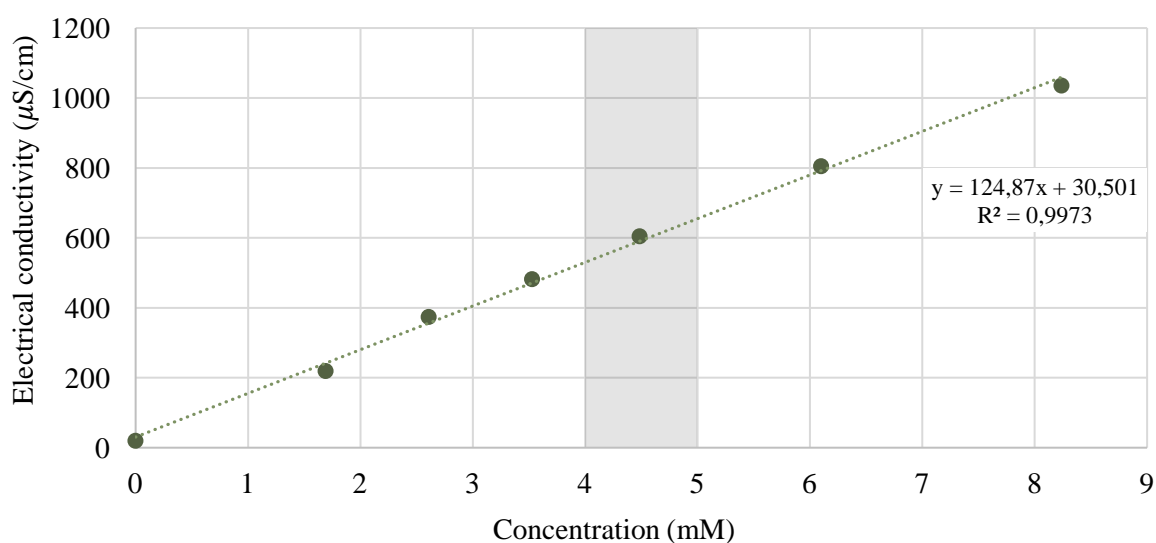


Figure 13 Calibration curve for control samples of sodium sulphate solution. Effect of concentration on the electrical conductivity for a solution at 23 °C.

5.2 Systems functionality

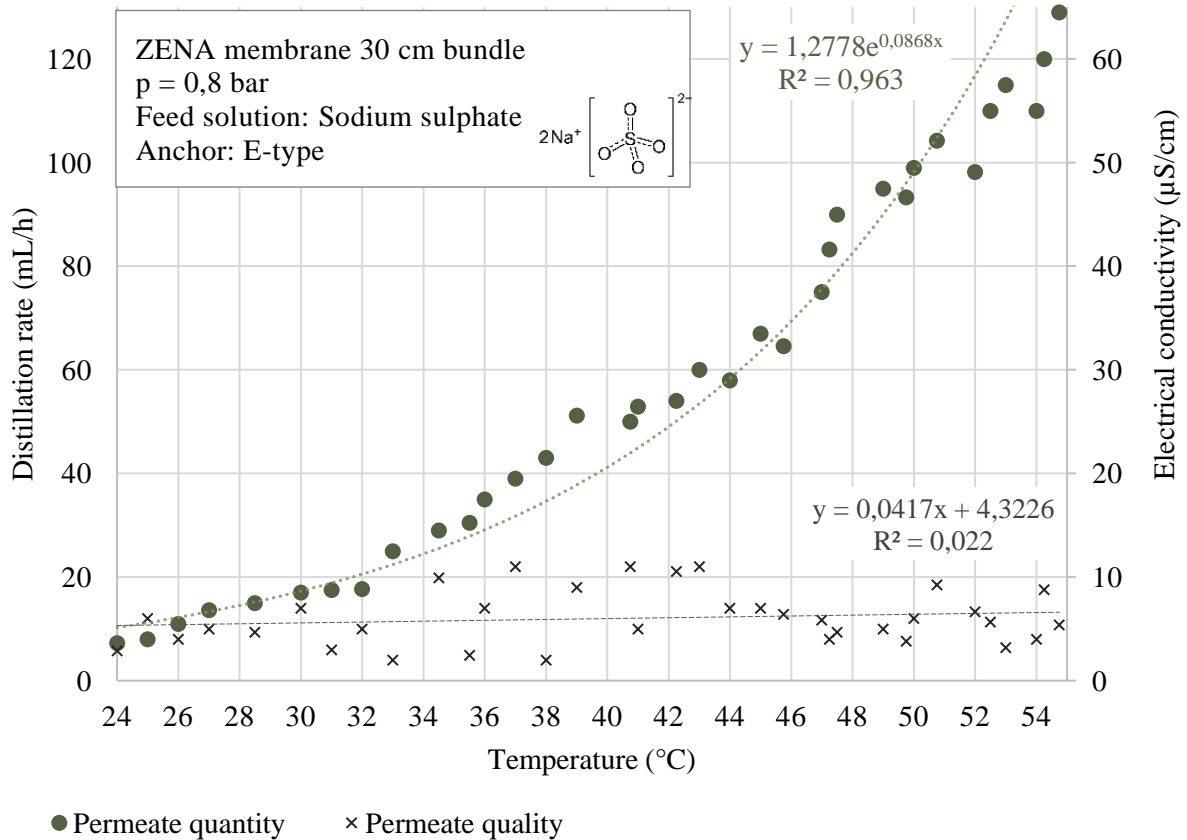


Figure 14 System functionality test by quantitative and qualitative analysis. Graphical representation of the relationship between the temperature of the feed solution and the quality and quantity of the permeate

The efficiency of a membrane distillation process determines the quality of the resulting permeate. Any degradation of the membrane can lead to a decrease in product quality. In the current experiment, conducted within a specific temperature range, membrane deterioration was not observed. The quality of the permeate was assessed using an electrical conductivity method. The feed solution used in the experiment had a concentration of 4mM and an electrical conductivity of approximately 600 $\mu\text{S}/\text{cm}$. The resulting permeate had an electrical conductivity of about 7 $\mu\text{S}/\text{cm}$, indicating a significant reduction in ionic content compared to the feed solution. The electrical conductivity of the deionised water used for preparing the solution was also higher than that of the permeate, measuring approximately 10–20 $\mu\text{S}/\text{cm}$. Therefore, the process demonstrated high effectiveness in reducing the ionic content of the feed solution.

After selecting the most effective setup, experimental analysis was conducted on the distillation efficiency. Samples were collected from measurements alternating the operational temperature and keeping the same vacuum pressure. The temperature was manipulated between the room temperature and the temperature of the materials' deterioration. The distillation rate increase is depicted in Figure 14. The relationship between the temperature and the hourly distillation rate shows an exponential trend in the range of experimental conditions. Whereas a temperature of 25 °C resulted in the distillation of 8 mL of permeate, a temperature of 50 °C already yielded 100 mL of product per hour.

The ZENA membrane testing results were compared to prior membrane testing conducted by Plachy, who investigated the effectiveness of distillation on the system by employing an inside-out operation. Table 5 and Table 6 present the results obtained at the same process conditions and are compared in Figure 15.

All measurements were conducted at a temperature of 50 °C. The first set of results were obtained during the practical phase of this research and include measurements at different vacuum pressures (0,68-0,80 bar). In the outside-in setup, the vacuum pressure is a critical determinant of the inlet air flow rate. The remaining measurements were obtained using an inside-out distillation configuration with feed solution flow rates ranging from 30 L/h to 150 L/h. The second dataset was collected using the VMD configuration at 0,45 bar and is referred to as VMD1. The VMD2 column corresponds to the second set of measurements at 0,3 bar vacuum pressure. VMD3 was obtained by applying a vacuum pressure of 0,6 bar to the configuration. Lastly, the SGMD dataset was obtained by conducting measurements on the sweep gas membrane distillation configuration (see Figure 15).

Table 5 Distillation rates of outside-in approach to VMD using hollow fibre polypropylene membranes; the operational temperature of 50 °C, tapwater as a feed solution

Pressure	0,68 bar	0,72 bar	0,76 bar	0,77 bar	0,80 bar
Distillation rate	0,099 L/h	0,097 L/h	0,120 L/h	0,095 L/h	0,097L/h

Table 6 Distillation rates of inside-out approach to MD using hollow fibre polypropylene membranes, operational temperature of 50 °C, tapwater as a feed solution (Petr Plachý, 2022)

Feed flow rate	30l/h	60l/h	90l/h	120l/h	150l/h
VMD1	0,026 L/h	0,032 L/h	0,034 L/h	0,039 L/h	0,042 L/h
VMD2	0,036 L/h	0,040 L/h	0,044 L/h	0,048 L/h	0,052 L/h
VMD3	0,018 L/h	0,022 L/h	0,024 L/h	0,024 L/h	0,024 L/h
SGMD	0,038 L/h	0,048 L/h	0,051 L/h	0,054 L/h	0,060 L/h

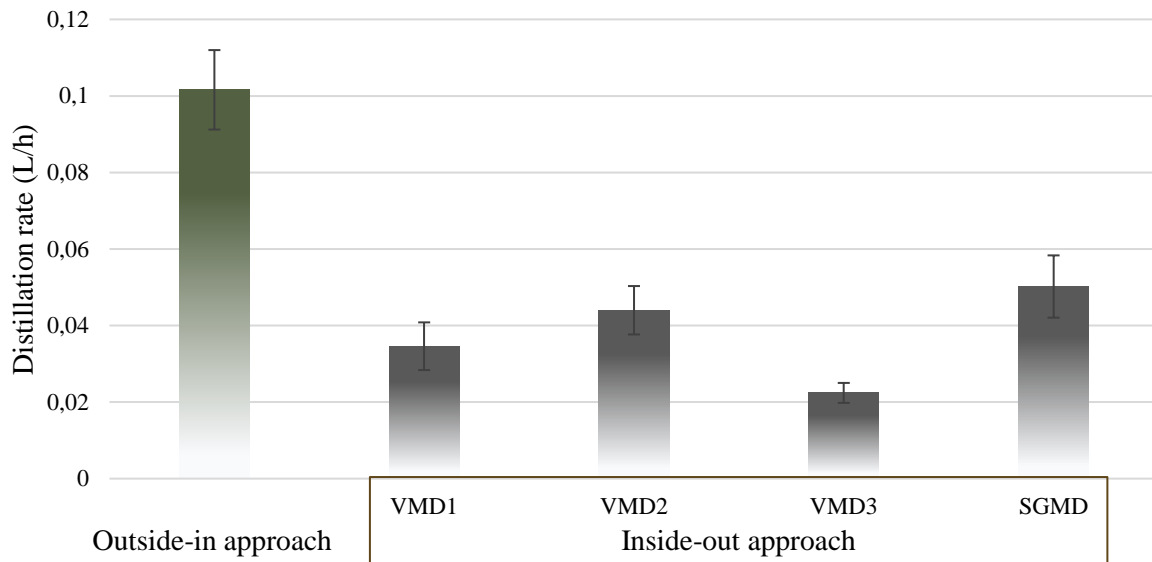


Figure 15 Graphical representation of the comparison of the results between the inside-out and outside in-approach (Petr Plachý, 2022)

The present thesis demonstrates that the outside-in approach exhibited higher distillation rates compared to the inside-out approach. Despite operating at higher pressures (weaker vacuum suction), VMD proved to be more effective in the outside-in process. This is due to the lower energy demand achieved by reducing the feed solution circulation and applying a smaller magnitude of vacuum pressure, which makes the outside-in approach highly advantageous. Moreover, operating at pressures closer to atmospheric pressure reduces the potential risk of membrane ruptures. In contrast, the inside-out approach, as discussed by Plachy, bears the risk of clogging the membrane entrance over time (Petr Plachý, 2022). This risk can be prevented by switching to the outside-in approach, where air is used as the circulating medium, and the partial pressure difference is achieved through suction that also drives the medium through the system. Consequently, the clogging of the membrane input is prevented, and the energetic efficiency is increased.

5.3 Membrane's resistance to wetting

In the membrane process, three main phase transformations should occur. First, a solvent in the feed solution must undergo evaporation to pass through the hydrophobic membrane pore. Secondly, the evaporated solvent diffuses and passes through the distillation unit until it reaches the condenser. Lastly, gaseous distillate condenses and can be collected and removed from the membrane distillation unit as a product. However, MD possesses a risk of membrane wetting. If that happens, there is no or little phase change, and the feed solution is filtered through the membrane pore contaminated. This can be caused by numerous reasons (e.g., the presence of surface-active substances dissolved in the feed solution, high transmembrane pressure, membrane degradation, condensation within the pores, etc.). Membrane wetting can also happen in both directions if the membrane is in direct contact with the liquid permeate

(DCMD). Then the liquid permeate can wet the pores from the permeate side, whilst the feed solution wets the pores from the feed region. This results in increased wetting risk (Chamani et al., 2021).

Wastewater treatment via membrane distillation has an exceptionally high risk of membrane wetting due to a huge variety of contaminants in wastewater. Namely, surfactants are the most problematic for WWT due to their amphiphilic nature. They increase the risk of membrane wetting by attaching their hydrophobic tail to the membrane's surface and creating a hydrophilic coating with their hydrophilic heads. This allows liquid feed to migrate through the pore and compromise the MD operation (Z. Wang et al., 2018).

Membrane wetting is closely related to the surface tension (γ). The relationship between the surface tensions of three different phases within the MD system (l, or liquid phase/feed solution; g, or evaporating permeate; s, or solid membrane surface) determines the contact angle between the phases and can be described by Young's equation (Equation 9) (Yildirim Erbil, 1996).

$$\cos \theta_Y = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}} \quad (9)$$

Where θ_Y is the contact angle defined by Young, γ_{sg} , γ_{sl} , and γ_{lg} are the surface tensions between two interfaces (solid-gas, solid-liquid, and liquid-gas, respectively).

Table 7 Effect of surface tensions between different interphases on the contact angle and the wetting of the membrane (Chamani et al., 2021)

Surface Tension Relationship	Contact angle	Predicted Wetting Degree
$\gamma_{sg} - \gamma_{sl} = \gamma_{lg}$	$\theta = 0^\circ$	Absolute wetting
$\gamma_{sg} - \gamma_{sl} > 0$	$0^\circ < \theta \leq 90^\circ$	High wetting
$\gamma_{sg} - \gamma_{sl} < 0$	$90^\circ < \theta < 180^\circ$	Low wetting
$\gamma_{sl} - \gamma_{sg} = \gamma_{lg}$	$\theta = 180^\circ$	No wetting

If the surface tension between the membrane and the evaporated solvent is higher than the surface tension between the membrane and the liquid feed solution, there is a high risk of membrane wetting. Conversely, low to no wetting is predicted to happen if the membrane-liquid surface tension is larger than the membrane-vapour surface tension. Surfactants are great at lowering surface tension, which can be problematic in applications such as membrane distillation. Decreasing the surface tension between the feed solution and the membrane reduces the contact angle θ and raises the risk of membrane wetting (see Table 7).

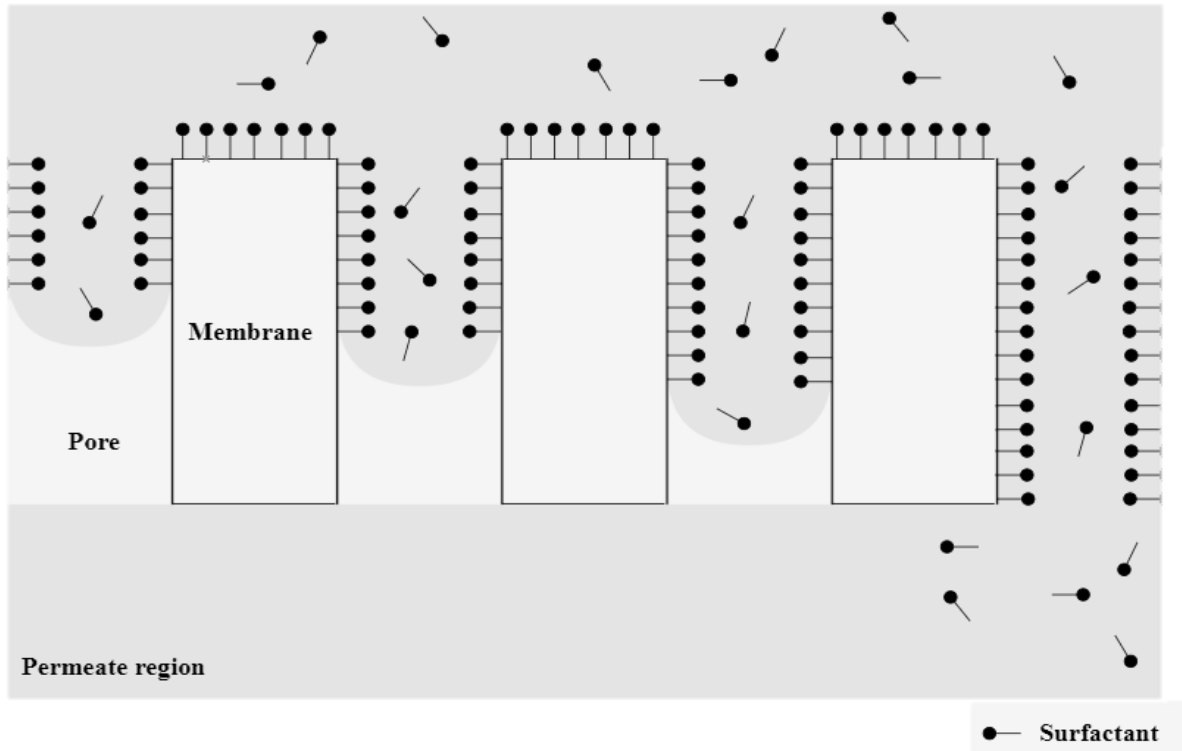


Figure 16 Model of the effect of surface-active substances on hydrophobic membrane

If present in the feed solution, the surfactant's concentration is a determining variable and is inversely proportional to the surface tension. Surfactants cause the wetting of the hydrophobic membrane pores until the pore is completely penetrable by a liquid. The feed solution then does not distillate but passes through the membrane with all the solute and contaminates the permeate (see Figure 16). The process is then not effective. Membrane wetting resistance should be sufficient until a specific concentration is reached. Above this concentration, the operation is ineffective.

Other membrane properties attributed to membrane wetting include surface roughness, pore size and distribution, contact angle, LEP, etc. These, however, are beyond the scope of this research.

The wetting resistance of a membrane bundle was tested by introducing a surface-active agent, sodium dodecyl sulphate (SDS), to the feed solution. SDS is an anionic surfactant found in many cleaning supplies. Its amphiphilic nature allows it to act as a bridge between hydrophobic and hydrophilic surfaces and substances. Unfortunately, SDS contaminates wastewater during disposal and cannot be removed by membrane processes, necessitating wastewater pre-treatment. SDS negatively affects the functionality of membrane processes such as reverse osmosis or membrane distillation by wetting the membrane, thereby enabling the penetration of contaminated feed solution. This contamination results in the permeate side being contaminated, reducing the effectiveness of the membrane process. The presence of SDS in

cleaning and hygiene products presents a challenge for wastewater treatment facilities, which must consider the impact of SDS on membrane processes (Ang et al., 2011).

A feed solution was prepared by dissolving SDS in the deionised water. The distillation process was then commenced. Step-based increase of concentration was conducted to accurately determine the concentration at the start of the wetting of the ZENA membrane bundle.

Firstly, a calibration curve of the surfactant's electrical conductivity dependency on the solution concentration was constructed. Solutions of different concentrations (ranging from 0 mM to the critical micelle concentration (CMC) (8 mM) were prepared. Their electrical conductivity was measured (see Figure 17). Electrical conductivities ranging from 21 $\mu\text{S}/\text{cm}$ to 480 $\mu\text{S}/\text{cm}$ were measured.

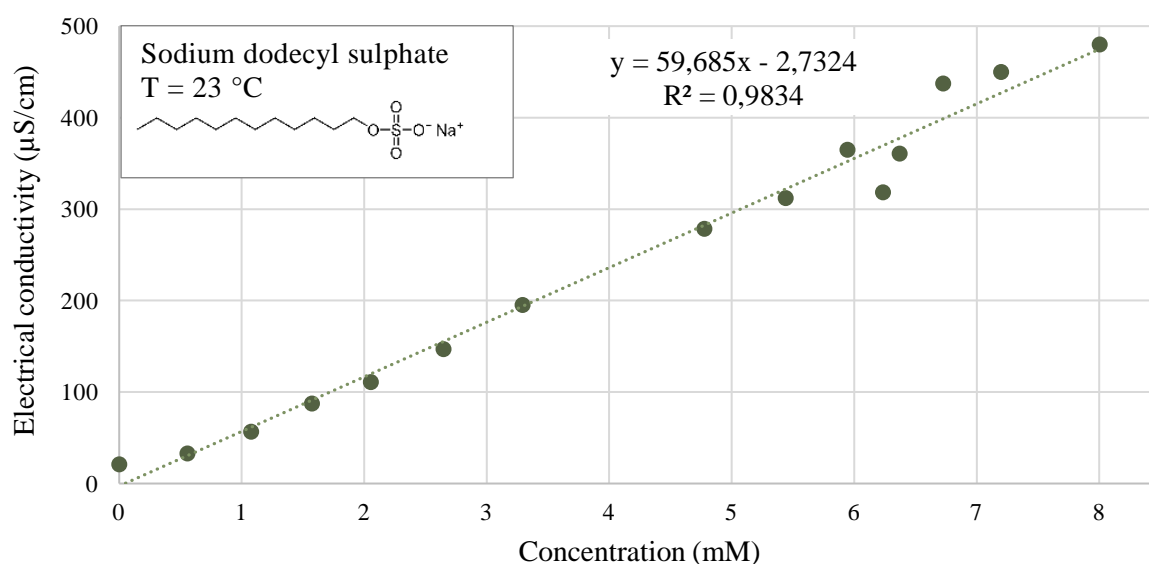


Figure 17 Calibration curve for sodium dodecyl sulphate ($\text{NaC}_{12}\text{H}_{25}\text{SO}_4$). Effect of concentration on the electrical conductivity of the solution.

Then, the solution of SDS was fed to the MD system and the operation was commenced. The test was conducted at conditions which previously indicated high process performance. The temperature was set to $55\text{ }^\circ\text{C}$, and the vacuum was adjusted to 0,78 bar. An E-type anchor was used to secure the complete submerging of the membrane fibres. The permeate was analysed after every increase in the concentration of the feed, and the results are depicted in Figure 18.

Based on the conducted experiment, it can be concluded that a concentration as low as 6 mM of surfactants can drastically change the operational functionality. The wetting needs to be prevented, and in case of happening, the membrane must be cleaned and dried so it can be further used effectively.

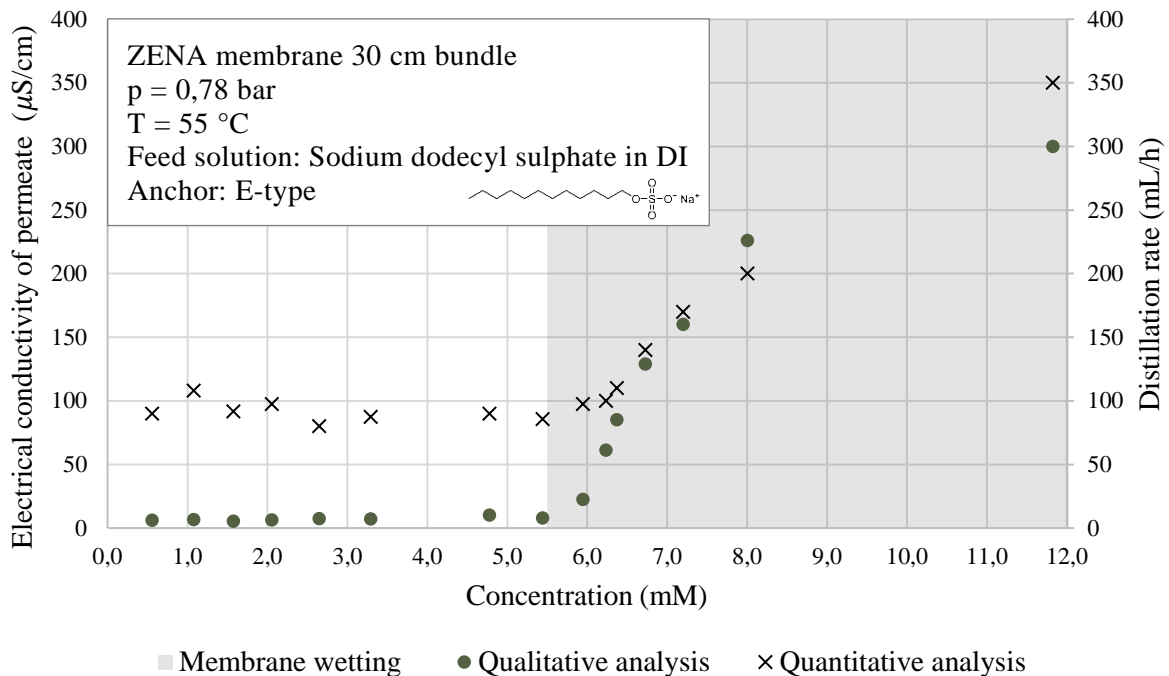


Figure 18 Graphical representation of membrane wetting resistance in the MD experiments using hollow fibres, E-type anchor, SDS and a surfactant; at a temperature of 55 °C and pressure of 0,78 bar

The results show a continuous drop of permeate quality starting at 6 mM. The product started foaming due to the liquid passage of the surfactant solution through the membrane pores. This region is indicated in Figure 18.

The surface tension of a solution at a concentration at which the membrane started to lose effectiveness is 37,13 mN/m (Elworthy & Mysels, 1966). This is the surface tension between the liquid feed and gaseous permeate observable inside a pore (γ_{lg}). The results of the experimental study offered a concentration at which the complete wetting occurs. The contact angle between the feed and the membrane when the membrane is partially wetted (at 6 mM) is close to 0°. The contact angle of the feed solution at a concentration of 0 mM on the surface of the membrane is around 94° (Gryta, 2005). The effect of the decrease of the contact angle by increasing the concentration of the surfactants is depicted in Figure 18.

6 CONCLUSION

This study aimed to optimise the setup of a membrane distillation (MD) unit using a hollow fibre membrane matrix. The results showed that optimising the laboratory unit setup was crucial for successful MD experiments. The MD unit's performance depended on several factors, including the condenser and anchor types, feed solutions, and process conditions. The study investigated these factors and their effects on MD performance. The results demonstrated that the membrane distillation process was effective in reducing the ionic content of the feed solution, and the distillation rate increased exponentially with increasing temperature.

To optimise the laboratory unit setup, four condenser types were examined. The Graham condenser was the most suitable for the study due to its larger contact area and ability to eliminate condensation at the vacuum pump. The study also addressed the issue of membrane floating by proposing and testing five membrane anchor prototypes. The E-type anchor was the most effective in achieving constant submerging and separation in the membrane distillation process, significantly improving the distillation rate.

The study demonstrated that the MD process produced a high-quality permeate efficiently, as evidenced by the significant reduction in ionic content compared to the feed solution. The distillation rate increased exponentially with increasing temperature within the range of experimental conditions. Additionally, the outside-in approach studied in this thesis has demonstrated higher distillation rates and lower energy demand than the inside-out approach, despite operating at higher pressures. Additionally, the outside-in approach mitigates the risk of membrane clogging and ruptures, making it a more efficient and safer option for distillation processes.

Membrane wetting negatively affects the performance of MD, and it can happen due to various reasons, including the presence of surface-active substances dissolved in the feed solution, high transmembrane pressure, membrane degradation, and condensation within the pores. The study found that surfactants, particularly those in wastewater, are problematic for MD. Results show that a model surfactant used in this study, sodium dodecyl sulphate (SDS), negatively affects membrane processes such as reverse osmosis or MD by wetting the membrane. The concentration of surfactants in the feed solution is inversely proportional to the surface tension, and above a specific concentration, the process operation is ineffective.

This thesis introduced, evaluated, and tested the optimal setup, technological parameters and effect of salts and surfactants on the performance of the MD using hollow fibre polypropylene membranes. It reflected on the possible problems, such as wetting and clogging and compared different approaches for this type of MD. Therefore, the study's results have significant implications for water purification and can contribute to ensuring that safe and clean water is accessible to all.

Further research should be conducted to test the effect of membrane roughness, pore size, distribution, and LEP on membrane wetting. Investigating the impact of other significant contaminants on the process can also be a potential area of research.

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8 ABBREVIATIONS

ABBREVIATION	MEANING
AGMD	Air gap membrane distillation
CDI	Capacitive deionisation
CGMD	Conductive gap membrane distillation
CMC	Critical micelle concentration
DCMD	Direct contact membrane distillation
DI	Deionized water
EC	Electrical conductivity
ED	Electrodialysis
FO	Forward osmosis
LEP	Liquid entry pressure
MD	Membrane distillation
MED	Multi-effect distillation
MGMD	Material gap membrane distillation
MSF	Multi-stage flash
PE	Polyethylene
PES	Poly (ether sulfone)
PGMD	Permeate gap membrane distillation
PLA	Polylactic acid
PP	Polypropylene
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
RO	Reverse osmosis
SDS	Sodium dodecyl sulphate/ Sodium lauryl sulphate
SGMD	Sweep gas membrane distillation
TP	Temperature polarization
VMD	Vacuum Membrane distillation
VOCs	Volatile organic compounds
VP	Vacuum pump
WW	Wastewater
WWT	Wastewater treatment