Membrane Distillation in Dairy Processing

By

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Doctor of Philosophy Declaration

I, Angela Hausmann, declare that the PhD thesis entitled Membrane Distillation in Dairy Processing is no more than 100,000 words in length including quotes and exclusive of tables, figures, appendices, bibliography, references and footnotes. This thesis contains no material that has been submitted previously, in whole or in part, for the award of any other academic degree or diploma. Except where otherwise indicated, this thesis is my own work.

Signature   Date

Publications from This Research

- Hausmann, A., Sanciolo, P. Vasiljevic, T., Ponnampalam, E., Quispe-Chavez, N., Weeks, M. and Duke, M. (2011), ‘Direct Contact Membrane Distillation of Dairy Process Streams’, *Membranes* **1**(1), 48-58

- Hausmann, A., Demmer, T. & Duke, M. C. (2012), ‘Principles of Membrane Filtration’ in ‘*Membrane Processing – Dairy and Beverage Applications*’ by Wiley-Blackwell

- Hausmann, A., Sanciolo, P. Vasiljevic, T., Weeks, M. and Duke, M. (2012), ‘Integration of membrane distillation into heat paths of industrial processes’, *Chemical Engineering Journal* **211-212**(0), 378-387

- Hausmann, A., Sanciolo, P. Vasiljevic, T., Weeks, M., Schroën, K., Gray, S. and Duke, M. (2013), ‘Fouling of dairy components on hydrophobic polytetrafluoroethylene (PTFE) membranes for membrane distillation’, *Journal of Membrane Science* **442**, 149-159

- Hausmann, A., Sanciolo, P. Vasiljevic, T., Weeks, M., Schroën, K., Gray, S. and Duke, M. (2013), ‘Fouling mechanisms of dairy streams during membrane distillation’, *Journal of Membrane Science* **441**, 102-111

- Hausmann, A., Sanciolo, P. Vasiljevic, T., Kulozik, U. and Duke, M., ‘Performance Assessment of Membrane Distillation for Skim milk and Whey Processing’, submitted to *Journal of Dairy Science* – under review

Conference presentations

- Hausmann, A., Sanciolo, P. Vasiljevic, T., Ponnampalam, E., and Duke, M. (2010), ‘Fouling of a membrane distillation membrane by whey and skim milk feeds’ presented to *First Membrane Society of Australasia (MSA) Symposium*, Wollongong, Australia

- Hausmann, A. and Duke, M. (2010), ‘Membrane distillation to reduce water consumption in dairy processing', presented to *Postgraduate Research Conference*, Melbourne, Australia

- Hausmann, A., Sanciolo, P. Vasiljevic, T., Ponnampalam, E., Quispe-Chavez, N. and Duke, M. (2010), 'Membrane distillation as an energy and water saving solution for dairy processing', presented to *6th International Membrane Science and Technology Conference*, Sydney, Australia

- Hausmann, A., Sanciolo, P. Vasiljevic, T., Ponnampalam, E., Quispe-Chavez, N. and Duke, M. (2011), 'Investigation on fouling mechanisms of membrane distillation in dairy applications', presented to *Food Science Summer School*, Brisbane, Australia

- Hausmann, A., Sanciolo, P. Vasiljevic, T., Weeks, M. and Duke, M. (2011), 'Membrane distillation in the dairy industry: process integration and membrane performance, presented to *International Workshop on Membrane Distillation and Related Technologies*, Ravello, Italy

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Abstract

Membrane distillation (MD) is a novel membrane process for industry which promises to be a low energy and/or low cost alternative to established separation technologies. The overall objective of this research was the theoretical and experimental investigation of direct contact MD (DCMD) for major dairy processes. Milk and whey were the two major dairy streams explored in this study.

The outcomes are presented in three key parts:

a.) A study of the mechanisms involved in the establishment of the fouling layer and the characterization of the longer term performance of the MD system in the presence of this fouling layer. This was achieved by analysing the initial interactions between the membrane polymer and feed components as well as the final fouling layer compositions, including the distribution of components over the cross-section of fouling layers.

b.) A study of the influence of operating parameters on MD performance with the dairy streams. This included the development of a simple resistance in series model to assess the influence of operating parameters such as temperatures, concentration factor and flow velocity. In this part, the performance of MD was compared to that of reverse osmosis (RO).

c.) A study of the integration of MD in current processing plants by utilization of heat energy currently being exchanged within the manufacturing process. This involved the proposal of an integrated heat exchanger and MD module to facilitate incorporation of MD into existing heat paths of industrial processes. Theoretical modelling as well as experimental tests with a prototype were carried out to determine the operating parameter settings and configurations that led to optimal performance.

In the first part, a detailed fouling study was undertaken and presented in two publications:

- ‘Fouling of dairy components on hydrophobic polytetrafluoroethylene (PTFE) membranes for membrane distillation’ and
- ‘Fouling mechanisms of dairy streams during membrane distillation’.

Membrane fouling of dairy streams is widely explored for filtration processes. Little research has, however, been conducted on membranes used for the more novel MD process requiring hydrophobic membranes. This section not only looked at fouling phenomena occurring during DCMD but at the mechanisms leading up to fouling. Fouling layer compositions were analysed for cations, proteins and lactose, while topology and compositional profiles were visualised by electron microscopy and synchrotron IR micro-spectroscopy. Initial adhesion of single components on a membrane representing PTFE surface was observed *in-situ* utilizing reflectometry. It was found that fouling developed through different stages and a theory for the fouling of whey and skim milk was proposed. The major foulants found for skim milk were proteins. For whey, however, all three components - protein, lactose and minerals - acted together to develop a layer that covered the membrane.

The second part consists of another two publications focussing on different aspects of MD performance with dairy streams:

- 'Direct Contact Membrane Distillation of Dairy Process Streams' and
- 'Performance Assessment of Membrane Distillation for Skim milk and Whey Processing'.

This part explored the influence of the three main factors on membrane performance, namely feed composition, membrane properties and operating parameters (mostly temperature and concentration factor). MD was applied for the concentration of a range of dairy streams with decreasing complexity ranging from whole milk, skim milk, whey and a lactose solution. Major components by which complexity was decreased were the following: fat in the step from whole milk to skim milk, caseins from milk to whey and salts & proteins from whey to lactose. This allowed investigation of the individual and combined influence of these components on membrane performance. Flux was found to be almost independent of processing time (apart from initial start-up) in the case of skim milk, with fluxes quickly stabilising to the same values at any starting concentration. Meanwhile, whey flux showed a time-dependency as flux reduction followed its own trend depending on the starting concentration. Following this work, membrane performance was investigated under various operating conditions. The resistance-in-series model allowed the determination of the conditions that minimize the resistance of the fouling layer and thus improve efficiency and performance. The effect of vapour pressure reduction due to high solid concentrations present at the membrane surface was also discussed as a novel concept which could have an additional bearing on driving force. Optimized conditions were found, yielding fluxes that were comparable to those found with RO. This implied an opportunity to concentrate skim milk or whey at low pressures and with lower electrical energy consumption compared to RO. In addition, the high retention characteristics of MD (>99%) were confirmed for carbon, nitrogen and mineral content. As the energy consumption is the key for MD to be able to compete with current membrane processes, the accessibility of waste heat generated within a dairy plant needed to be addressed and this was the focus in the next (third) part of this thesis.

The third part deals with the integration of membrane distillation into a processing plant to practically evaluate the often stated low cost, low electrical energy aspects of MD, and is presented in a publication entitled:

- 'Integration of Membrane Distillation into Heat Paths of Industrial Processes'.

Large amounts of waste heat are generated within dairy plants due to thermal processing operations. A novel MD design, known as the MD heat exchanger (MDHX) was proposed from this work, which incorporated a heat exchanger and a MD module into a single module. The MDHX is not limited to dairy processing and therefore results were not specifically presented for dairy alone in the paper. The choice of temperatures to optimise performance, however, was made with dairy components in mind. An interesting feature of MDHX is its ability to significantly extend the single pass recovery limit of conventional MD which was typically limited by thermodynamic constraints to less than 10%. The use of MDHX allowed the recycle pumping to be greatly reduced, which in turn reduced electricity required and potentially greenhouse gas emissions. These features were demonstrated using heat and mass transfer modelling and experimental testing of both conventional MD and MDHX. Under some conditions, MDHX was demonstrated experimentally to increase single pass water recovery from 2 % to 14 %, which translates to lower pumping electricity needs of less than 0.01 kWh for every m^3 of water produced. RO on the other hand uses between 1 and 10 kWh for every m^3 of water produced.

This project has provided a detailed insight to the opportunities of MD in the dairy industry, modelled around skim milk and whey. From this work, the following recommendations can be made:

1. MD can be used for pre-concentration before spray drying of fat free dairy streams, yielding fluxes that are comparable to RO with superior separation efficiency and lower electrical energy consumption.
2. Further advancements in membrane material development should focus on protein fouling mitigation to further improve performance.
3. MD can be integrated with heat exchange processes to allow efficient utilization of

the heat energy that is already exchanged within existing processes. The developed MDHX design requires pilot testing to demonstrate the enhancements found by modelling and bench-scale prototype testing from this work.

1

Introduction

The dairy industry is one of the largest utilisers of membrane technology [1]. The integration of this technology has significantly changed the field of dairy processing in many aspects and the number of successful applications is still increasing [2]. The four pressure based membrane filtration processes, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), are commonly employed to concentrate, separate or purify liquid dairy streams. While the main focus is still on product refinement, more recently, RO and NF have also been employed to recover water and recycle chemical cleaning agents [3, 4].

Today, rising energy prices, scarcity of water, rising water quality standards and climate change are emerging as priority issues facing the dairy industry. These issues are exerting increasing pressure on the dairy industry to look at the potential of membrane processes, not only from a product improvement point of view but to explore their energy and water saving potential. In terms of water management, the key challenge for further membrane developments in the dairy industry is recovering reusable water from currently wasted streams. In terms of energy consumption, the key challenges are fouling control and harnessing of alternative energy sources [5]. According to the Australian Dairy Manufacturing Industry Sustainability Report 2007/2008 [6], advances in water recovery and recycling and water treatment have led to a 12 % increase in overall energy consumption. This underlines that water and energy recovery should be achieved in a way that means one is not traded for the other.

RO is a platform technology capable of concentrating dairy streams, without compositional changes, by only removing water from the stream. It produces a water quality that allows reuse within the industry to rinse equipment. The adoption of RO in the field of dairy has led to an increase in water recycling from 15 to 26 % within a period of three years [6]. RO alone, however, is limited by achievable concentrations, often necessitating the use of subsequent evaporation processes, thus significantly increasing the energy demand [7].

Currently employed membrane processes mainly use pressure to drive separation, which in turn uses electricity for high pressure pumps. Meanwhile, electricity creates the highest proportion of the Australian dairy industry's greenhouse gas emissions [6]. Therefore, an alternative technology to perform the same function of RO and/or evaporators, without increasing net energy use is required to address these needs. Membrane distillation bears the potential to achieve this.

Membrane distillation

Membrane distillation (MD) is a novel membrane-based separation process that is driven by the vapour pressure difference across the membrane, rather than a pressure gradient [8]. A usable vapour pressure can be induced in the small vapour space of the membrane using waste sources of low-grade heat (<80°C) from industrial processes or solar energy. Therefore these heat sources can be directed to an MD system to capture purified water using less 'new' energy such as electricity, which in turn produces less greenhouse gas emissions.

The MD process typically relies on a highly hydrophobic micro-porous membrane to maintain a liquid-vapour interface and to only allow water in the vapour state to pass through [9]. Since MD is driven thermally, it is less sensitive to the feed concentration than other pressure driven membrane separation processes which are often limited to a maximum dry-matter content of 12–20 % [7]. Other advantages of MD include a theoretical complete rejection of non-volatile components, low operating pressure, reduced vapour space compared to conventional distillation and evaporation processes, and low operating temperatures of the feed [10].

MD membrane and process development has its origin in desalination for water treatment, and research on its applicability in various industries is progressing rapidly [11-14]. In general, industrial MD applications are always based on one or more of the following three functions:

1. Process stream concentration
2. Water recovery
3. Fractionation of volatiles from a process stream

The primary use of MD has been in the demineralisation of water, however, it has also been tested in the food industry for concentrating different liquid food streams, such as orange juice [15-17], black-current juice [18], grape juice [19], apple juice [20] and raw cane sugar syrup [21]. Additionally, the high vapour pressure of unwanted volatile compounds can be used to reduce them from a feed solution [22]. In the field of dairy processing, however, MD has not been widely tested. Chlubek et al. [23] published a paper on concentrating milk whey by direct contact MD in 1987 and concluded that MD could be a viable process for dairy streams. After this the next paper on dairy applications was published in 2006 by Christensen et al. [24] reporting on the concentration of whey proteins. They achieved a flux of around 1.7 to 0.6 $kg \cdot m^{-2} \cdot h^{-1}$ over a whey protein concentration range of around 7 % to 24 %, respectively, and concluded that a higher flux needs to be achieved for MD to be feasible in this industry. Therefore a performance investigation on state of the art membranes is needed to find optimal operating conditions for MD.

Energy requirement

Due to the energy saving promises of MD, energy efficiency is a focus for MD researchers and commercial developers. Efficiency improvements by controlling process parameters or membrane properties have been stated as one of the major criteria for successful MD application [25]. It already has successfully been coupled with solar energy systems in the form of small capacity desalination plants that require little additional energy input [11]. Solar driven MD has proven technically feasible, but making use of its potential to harness waste heat is still a challenge ahead as waste heat sources are often diffuse and hard to access. Although large amounts of thermal energy are exhausted in many process industries, MD has not yet been implemented in industry.

The ability of MD to utilize waste heat sources has been a great incentive for further research into the technology. Suitable ways of process integration are, however, yet to be explored. From an economic perspective, the estimated cost for MD with heat recovery has been found to be comparable to the cost of water produced by conventional thermal processes such as multiple effect distillation [26]. With the use of waste heat, however, MD can be less expensive than RO, despite its higher total energy demand [27]. Apart from these examples where MD has been considered as a standalone water purification solution, recently it has been proposed as an integrated process in thermal cogeneration plants where the heating is supplied by the district heating supply line, and the cooling is provided by the district heating return line [28].

Membrane fouling in MD

One of the major problems associated with all membrane processes is that of membrane fouling. This often leads to reduced yield and productivity due to lowered permeate flux, increased downtime required for cleaning and decreased membrane life. Therefore, a substantial focus in the research community has been on finding techniques to reduce the severity of the fouling problem for common commercial membrane processes [29-31]. However, little research has been conducted on the fouling of MD membranes in dairy applications. A greater understanding the fouling phenomena during membrane transport will increase the ability to design efficient processes and aid in finding most suitable applications for this novel process. This knowledge could potentially be applied to other industries and areas of common MD membrane use including water treatment and other food processing industries.

Scope of this research

This overview has identified the knowledge gaps that have hindered the application of MD to dairy processing – the required operating conditions, the fouling potential and associated mechanisms, and how to integrate MD into a dairy factory. This study will address each of these knowledge gap areas by:

1. Exploring the fouling phenomena occurring with model dairy solutions on state of the art MD membranes to uncover mechanisms responsible for observed fouling behaviour;
2. Investigating the influence of operating parameters on MD performance in dairy applications. This is supported by a theoretical model of the fouling to isolate its contribution to flux resistance from the membrane's resistance with a view to find optimal operating conditions and compare with the industry state of the art; and
3. Investigating the incorporation of MD into the dairy process. The integrated process will be modelled to explore optimal performance criteria.

2

Scientific Background: Membrane Distillation and Dairy Related Aspects

In order to understand the critical factors affecting MD operation of dairy streams, a review of the current state of knowledge of MD and dairy processing aspects has been carried out. To begin, important aspects of the MD process are presented, followed by the physical and chemical properties of milk and whey leading to membrane fouling. Essential aspects of dairy processing like water requirements and typical heat exhausts are also being assessed as a potential driving force for the thermally driven MD technology.

Membrane Distillation Background

The overall concept of one common MD configuration, direct contact MD (DCMD), is illustrated in Figure 1. The vapour pressure difference across the membrane is created by the direct contacting of a liquid that is cooler than the feed on the permeate side of the membrane. Vapours, consisting mainly of water, with any volatile compounds that may be in the feed, diffuse through the pores to the cooler surface where they condense. This separation process is only mildly influenced by osmotic pressure and can be operated at high feed concentrations. Also, the permeate quality is determined by the volatiles present in the feed and it is less dependent on feed concentration, in contrast to RO where the permeate concentration is always a small percentage of the feed concentration [32].

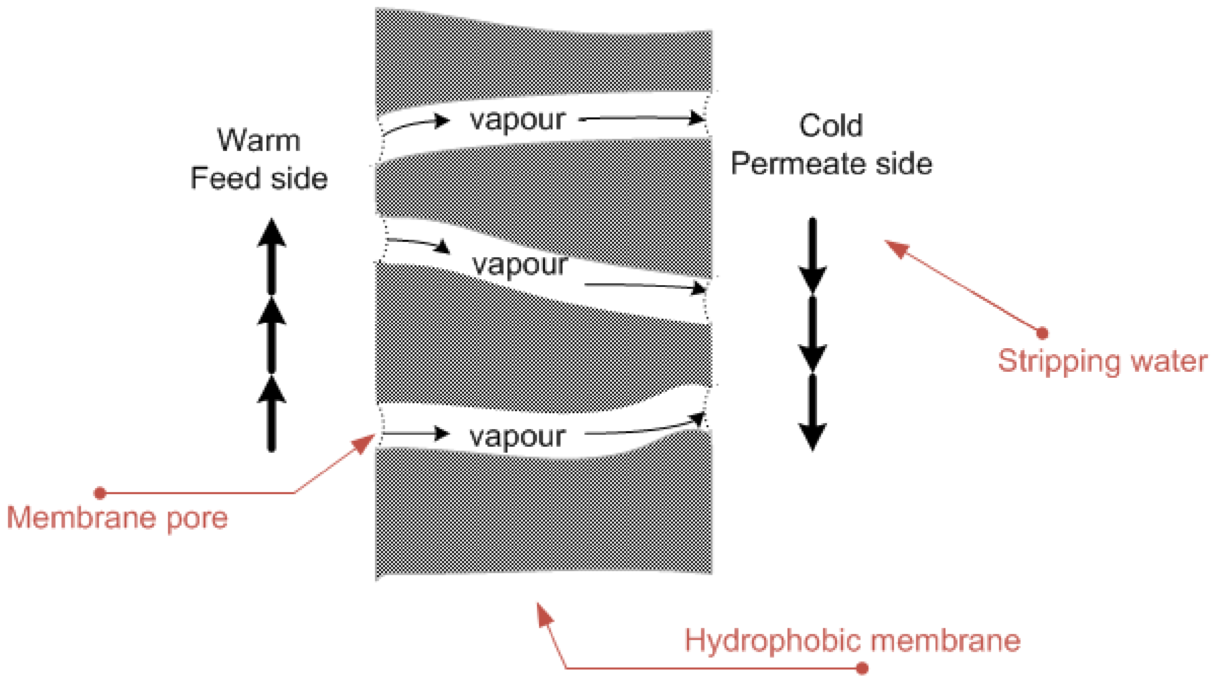

Figure 1: Schematic of DCMD, adapted from Qtaishat et al. [33].

As shown in Figure 2, there are three common MD configurations other than DCMD, which differ in the way the permeate is condensed and/or removed: air gap membrane distillation (AGMD); vacuum membrane distillation (VMD) and sweep gas membrane distillation (SGMD) [8, 34]. They are described as follows:

- In Air Gap Membrane Distillation (AGMD), the permeate is condensed on a cold surface and an air gap is established between the membrane and the condensing surface. The air gap reduces conduction energy losses, however it also adds resistance to the mass transfer, therefore giving low flux values [27].
- In Sweep Gas Membrane Distillation (SGMD), a stripping gas carries the produced vapour which reduces the resistance to mass transfer of the air gap [35]. The condensate must be collected outside the MD module.
- In Vacuum Membrane Distillation (VMD), a vacuum is applied to reduce the vapour pressure on the permeate side. With this configuration the condenser is typically located outside of the membrane module [36].

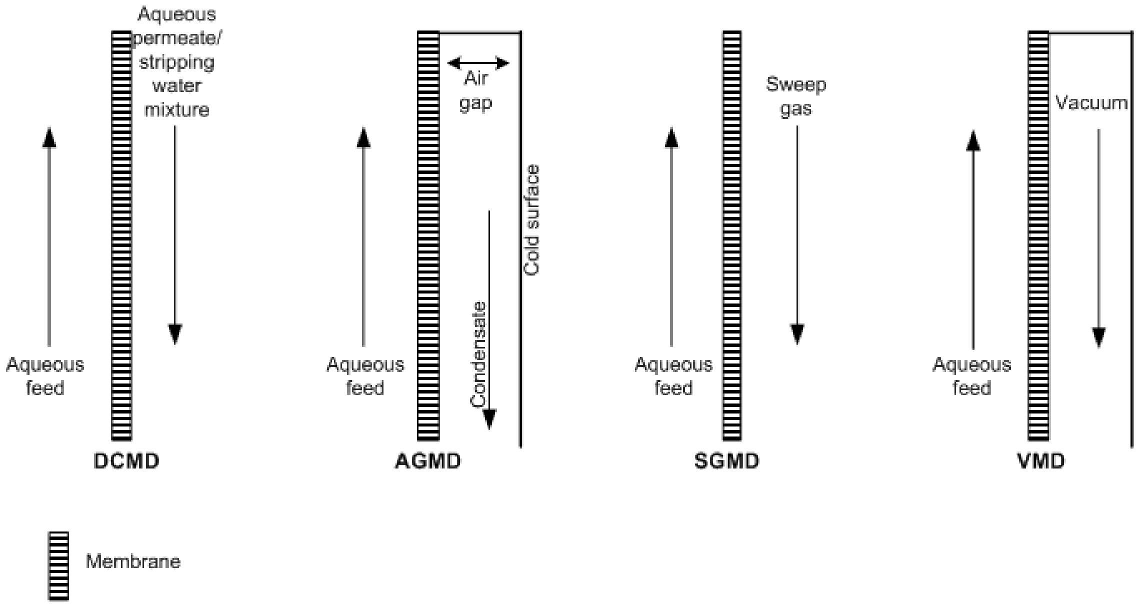

Figure 2: Principles of the four major membrane distillation configurations, adapted from Lawson et al. [37]

DCMD is the first configuration that was developed and is the simplest as it does not require an external condenser or complex module design. As the membrane is the only barrier between both solutions, DCMD can produce higher fluxes than other configurations and is therefore best suited for concentration of aqueous solutions. It is the most common configuration for laboratory scale research [8]. However, it is not the most energy efficient configuration as the small distance between hot and cold side also leads to higher conductive heat losses compared to other MD configurations [27]. For this reason, commercial applications focus more on AGMD [38-40]. For DCMD, the stripping solution on the cold side is usually high purity water as tap water has been found to cause membrane wetting [41]. However, the stripping water is typically replaced over time with the condensed permeate vapour which is of high quality. In some concentration applications a stripping solution of lower vapour pressure can be used to enhance vapour pressure difference as done during osmotic distillation and avoid the need for temperature to impose the vapour pressure drop [42, 43]. Applications that allow for the solution to be heated are simpler as additional chemicals or compounds are needed to control vapour pressure for osmotic distillation.

Typical Arrangements of MD

In a MD process, the function of the membrane is to act as a physical, non-selective barrier between the two phases and sustains the interface where heat and mass are exchanged simultaneously [8]. The membrane does not alter the vapour–liquid equilibrium as it does in pervaporation [44] and therefore is not involved in selective mass transport phenomena.

Key properties of membranes suitable for membrane distillation include their hydrophobicity and thermal conductivity:

Hydrophobicity and non-wetting properties

As outlined in the Introduction, the membrane must be hydrophobic (equivalent to low surface energy), so that surface tension forces withhold liquids from the pores and prevent penetration of the liquids, as well as condensation inside the pores. Penetration of liquid into the pores is a crucial factor impacting MD performance [45]; it is known as 'membrane wetting' and does not occur as long as the hydrostatic pressure is kept below a critical threshold known as the liquid entry pressure (LEP). This can be quantified by the Laplace equation:

$$LEP = \frac{4B\gamma \cos\theta}{d_{pore,\max}} \qquad (1)$$

where $d_{pore,max}$ is the largest pore size of the membrane, γ is the surface tension of the solution, *B* is a pore geometric factor (1 for cylindrical pores) and θ is the contact angle between the solution and the membrane surface [46]. While mass transport (flux) generally increases with increasing pore diameter, Equation 1 shows that with a given hydrophobicity (cos *θ*), the *LEP* of the membrane decreases with increasing pore size. Larger pore membranes, therefore, can allow liquid from the feed side of the membrane to enter the pores at the normal process pressures (<100 kPa), resulting in occlusion of the pores and contamination of the permeate stream with feed solution. However the *LEP* of water for a PTFE membrane of 0.45 µm pore size has been reported to be 288 kPa which is practical for most plant systems [47].

Thermal conductivity

A low thermal conductivity of the membrane is important to minimise unnecessary heat losses through the membrane and reduction of interface temperatures. Thermal conductivity depends on the membrane material used as well as membrane porosity. A high porosity reduces conductive heat loss and simultaneously increases permeability, resulting in increased water vapour transport through the membrane and higher energy efficiency [8]. The mechanical stability of the membrane can, however, be compromised by a highly porous structure, leading to a greater membrane compaction under pressure, which results in loss of performance. Weak membranes can also rupture if not physically capable of withstanding applied pressures and cross flow.

The most common membranes for MD are polymeric micro-porous membranes, usually polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF) or polypropylene (PP) [47, 48]. Ceramic membranes with specific chemical surface treatments are also proposed for DCMD [49-51]. A more recent development is the investigation of membranes with different membrane coatings on the outside surface to reduce fouling for various applications [34, 52, 53].

PTFE membranes of different pore sizes are manufactured by stretching the polymer, so as the membrane gets thinner, the pore size increases. This makes the choice of membrane pore size a matter of adequate membrane thickness, which in turn is a compromise between high flux and low thermal conductivity (thick membrane) [15]. Bigger pores contribute to flux in two ways, it offers effective area for vaporisation and the thinner membrane contributes to membrane permeability as it reduces the path length for vapour transport. Another material characteristic influencing the length of the path the vapour molecules have to pass through is the pore tortuosity, which is a measure between the membrane thickness and the actual pore length. The pore size distribution on the other hand has been found to have a negligible influence on MD performance [54, 55] despite impacting the *LEP* as shown previously.

Suitable Membrane Geometries

The two possible geometries for polymeric membranes used in MD are flat-sheet and hollow-fibre. In general, polymeric flat-sheet membranes are composed of a thin active layer and a porous support layer. This composite structure provides mechanical strength and reduced mass transfer resistance due to the active layer being very thin. Hollow fibre membranes on the other hand are usually self-supporting and therefore thicker and less porous resulting in a lower flux compared to flat-sheet membranes [47]. More recently, hollow fibre membranes with a sponge-like structure and thin walls are being developed [52, 56]. Also, the lower flux of hollow fibre membranes can be offset by the higher packing density and relatively large specific surface area of hollow fibre membranes and modules. However, conductive losses increase with increasing membrane area. Therefore the ratio between energy used for vaporisation and energy lost through conduction is impacted unfavourably. A disadvantage of the tubular module design for hollow fibre membranes is the reduced turbulence between the fibres, which is far more critical in MD compared to pressurised filtration, which is what the current module designs are based on. Module designs with improved mass transfer efficiency have been investigated for MD, such as wavy and curly fibres, as well as inclusion of turbulence enhancers, e.g. knitting fibres around spacers [57-60]. However, these modules often have a lower packing density compared to tubular hollow fibre modules. A practical downside of hollow fibre modules is that broken hollow fibres cannot be replaced when defective. They can, however, be detected [61] and pinned. Despite this, hollow fibre membranes are not common in foods processing including dairy. Flat sheet membranes are either in a plate and frame configuration or spiral wound where the plate and frame is not very common and only used for high viscosity applications. The design of compact flat sheet module configurations such as spiral wound modules is complicated by the nature of the condenser on the permeate side. Nevertheless, large-scale spiral wound modules have been developed for air gap membrane distillation (AGMD) [12] and DCMD [62].

Progress of MD to Date

The earliest MD developments occurred in the late 1960's [63, 64], but at that time high costs of membranes compounded by their inadequate characteristics prevented commercial utilisation of MD. Also, much lower costs for electricity and the development of efficient energy recovery processes have led to better economics of RO. Nowadays, energy costs and the awareness of greenhouse gas emissions associated with electricity production needed for RO have risen. Meanwhile, advancements in membranes used for microfiltration and clothing materials (ie. Gortex type membranes) have resulted in a range of new hydrophobic membranes. These improved membranes have led to increased flux and lower fouling, so that the research into MD started to accelerate again in the 1980s [65-67], but limitations associated with energy efficiency have not been fully addressed by these improvements. MD for commercial applications is still in its early stages and further work is needed to develop commercial systems for various applications. It is supposed that when matured, MD for desalination purpose will be lower in costs compared to RO [27]. Already, the Memstill process which is one of the most advanced MD-process in the air-gap MD configuration, has been improved within three pilot tests from a heat consumption of 2000 MJ/m^3 to 350 MJ/m^3 [38]. Although this is much higher than the energy requirements of RO (11 MJ/m^3 to 61 MJ/m^3 depending on the scale, incoming salinity and use of energy recovery devices [62]), MD's ability to utilise waste heat offers the opportunity for it to outcompete RO as it has low electrical energy requirement (e.g. 2.7–6.3 MJ/m^3 for the Memsys system).

Transport Mechanisms in DCMD

Heat and mass transfer are coupled in MD, resulting in complex performance characteristics that are challenging to optimize [33]. Figure 3 illustrates these processes in DCMD including a built up fouling layer present due to a real operation scenario. Heat is transferred in four steps: (I) transfer from the bulk feed solution (T_{FB}) to the fouling layer surface (T_{FL}); (II) transport across the fouling layer to the feed sided membrane surface (T_{FM}); (III) transport across the membrane as water evaporates and moves from the liquid-vapour interface of the pore entrance and is transported across the membrane. This vapour transfer occurs with convective heat carried by the vapour as well as vaporization energy. Heat conduction also takes place through the membrane matrix and the gas filled pores; (IV) condensation of the water at T_{PM} on the permeate side. The cold flow temperature increases across the permeate sided boundary layer to the permeate bulk temperature (T_{PB}) [8, 15, 33].

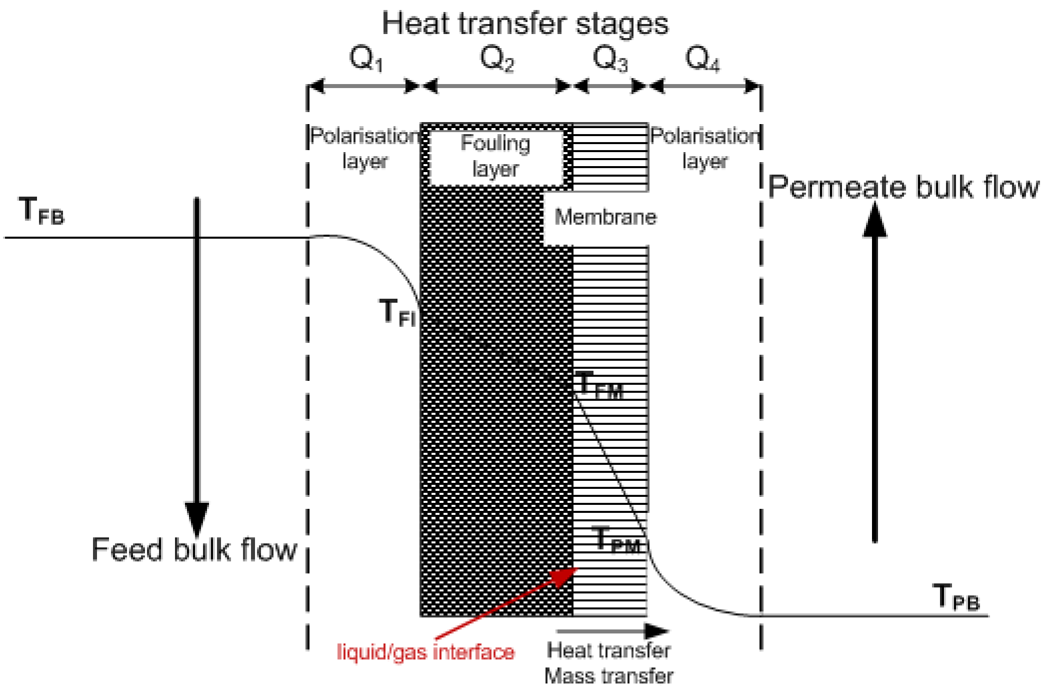

Figure 3: Simultaneous heat and mass transfer during DCMD [8, 15, 33]

The mass transfer in the MD process can also be divided into five steps: (I) transport across the polarisation layer in the feed stream and across the fouling layer; (II) vaporisation of water from the hot feed at the liquid/gas interface; (III) diffusive transport of vapour through the membrane driven by the vapour pressure difference; (IV) condensation into the cold stream on the permeate side and (V) diffusion into the permeate bulk stream. Therefore the two mass transfer controlling factors across the membrane are vapour pressure difference and membrane permeability.

Heat Transfer in DCMD

Although MD is not significantly affected by concentration polarization like pressure driven processes, there is a similar phenomenon, called the temperature polarization effect, which manifests itself as the temperature difference between the bulk solutions and the membrane surface (Figure 3). This temperature difference leads to a decrease from the theoretical driving force, which is defined as the difference between the bulk feed temperature (T_{bf}) and the bulk permeate temperature (T_{bp}). To indicate the actual driving force, the temperature polarization coefficient (*TPC*) is widely used. Values between 0.4 and 0.7 indicate a satisfying design of the system [8]. It is defined as the ratio between the actual driving force and the theoretical driving force [68, 69]:

$$TPC = \frac{T_{FM} - T_{PM}}{T_{FB} - T_{PB}} \quad (2)$$

To estimate the *TPC* for optimising systems, it is impossible to measure the membrane surface temperatures experimentally. Usually these temperatures are evaluated by performing a heat balance that relates them to the bulk temperatures.

The heat transfer between bulk streams and the fouling layer surface is mainly due to convective transport [70] while conduction is negligible:

$$Q_1 = \mathrm{h_{CP}}(\mathrm{T_{FB}} - \mathrm{T_{Fl}}) \quad (3)$$

where h_{CP} is the heat transfer coefficient of the feed polarisation layer and can be estimated using dimensionless numbers [54, 70-76]. The Graetz-Leveque equation is recommended for laminar flow:

$$\mathrm{h_{CP}} = \mathrm{Nu} = 1.86\left(\mathrm{Re}\,\mathrm{Pr}\,\frac{\mathrm{d_h}}{\mathrm{L}}\right)^{0.33} \quad (4)$$

And for turbulent flow it can be estimated by the following dimensionless relationship:

$$\mathrm{Nu} = 0.023\,\mathrm{Re}^{0.8}\,\mathrm{Pr}^{\mathrm{n}} \quad (5)$$

where n equals 0.4 for heating and 0.3 for cooling [75], Nu is the Nusselt number, Re is the Reynolds number, and Pr is the Prandtl number.

The heat transfer coefficient of the feed polarisation layer can be improved effectively in the presence of turbulence promoters, like spacers through reducing thickness of the thermal boundary layer [77, 78].

The second stage of heat transfer is across the fouling layer [70]:

$$Q_2 = h_{Fl}(T_{Fl} - T_{FM}) \quad (6)$$

The actual heat transfer across the membrane consists of latent and sensible heat transfer:

$$Q_3 = J\,H_{latent} + h_M(T_{FM} - T_{PM}) \quad (7)$$

with J the permeate flux, H_{latent} the vaporisation heat and h_m the heat transfer coefficient of the hydrophobic membrane, which can be calculated from the thermal conductivities of the hydrophobic membrane polymer (k_m) and air trapped inside the membrane pores (k_g) [16].

$$h_m = \frac{k_g \cdot \varepsilon + k_m \cdot (1-\varepsilon)}{\delta} \quad (8)$$

where δ and ε are the thickness and porosity of the hydrophobic membrane respectively. Since the thermal conductivity of stagnant air is in general one order of magnitude less than that of the membrane material (i.e. thermal conductivity of PTFE is 0.29 $W \cdot m^{-1} \cdot K^{-1}$ versus 0.03 $W \cdot m^{-1} \cdot K^{-1}$ for air, both at 348 K [76]), a high membrane porosity is desirable to reduce conductive heat loss. This is reflected in a reduced heat transfer coefficient of the membrane (h_m).

At steady state the heat transfer from bulk to membrane surface equals the heat transfer across the membrane:

$$Q_1 = Q_2 = Q_3 = Q_4 \quad (9)$$

From this heat balance, temperatures at the fouling layer surface and membrane surface can be estimated.

Only the latent heat transferred across the membrane is used for mass transport, so heat transferred through conduction is wasted energy. Therefore, the ratio between the heat transferred because of vapour migration through the membrane pores and the total heat transferred through the membrane is defined as the evaporation efficiency, *EE*. Mathematically, the evaporation efficiency is expressed by:

$$EE = \frac{Q_{m,vap}}{Q_{m,vap} + Q_{m,cond}} \quad (10)$$

$$= \frac{J \cdot H_{latent}}{J \cdot H_{latent} + h_m \cdot (T_{FM} - T_{PM})} \quad (11)$$

where $Q_{m,vap}$ is the water vapour migration through the membrane pores and $Q_{m,cond}$ is the conductive heat transfer through the membrane [72]. These equations can be used as a tool to evaluate effects of process changes on the energy efficiency of MD.

Mass Transfer in DCMD

The mass transport across the feed polarisation layer can be estimated from a mass balance across the feed concentration boundary layer as:

$$X_\mathrm{m} = \mathrm{X_b} \exp\left(\frac{J}{\rho K}\right) \tag{22}$$

where X_m is the concentration at the membrane surface, X_b is the concentration in the bulk, K is the feed mass transfer coefficient, and ρ is the density of the feed solution [44].

Mass flux (J) across the membrane is proportional to the water vapour pressure difference from hot to cold side as well as the membrane permeability which can be expressed as:

$$J = c_{global}(p_{Temp,FM} - p_{Temp,PM}) \tag{33}$$

where $p_{Temo,FM}$ and $p_{Temp,PM}$ are the partial pressures of water on the feed and permeate sides and c_{global} the global mass transfer coefficient (or permeability) that depends on the membrane structure and its physical properties, as well as the operating conditions [79].

Equation 13 can be rewritten depending on the model applied, for which there are three basic mechanisms for the mass transport during DCMD; (i) Knudsen-diffusion, (ii) Poiseuille-flow or viscous flow and Molecular-diffusion, or (iii) a combination between these known as the transition mechanism [80, 81]. These models are related to the mass transport mechanism that is active inside the membrane pore, which is dependant primarily on the size of the membrane pores and diffusing molecules. More specifically, the model accounts for whether collisions between molecules, and/or molecules with the membrane are dominant. Knudsen diffusion takes place when molecule-pore wall collisions dominate the mass transfer over molecule-molecule collision [47, 75], e.g. when the pore size is small in comparison to the intermolecular spacing. Molecular diffusion on the other hand takes place when the collision between molecules determines mass transfer. Poiseuille flow (viscous flow) dominates when the gas molecules act as a continuous fluid driven by a pressure gradient. However in DCMD, there is no total pressure difference existing in the pore, so Poiseuille flow can be ignored [80]. Therefore mass transfer in DCMD is limited to Knudsen and molecular diffusion.

In order to understand which model to assume, the Knudsen number (*Kn*) can be used to indicate the dominant mass transfer mechanism in the pores. It is defined as the ratio of the mean free path (*l*) of transported molecules to the membrane pore size (*d*) [82]:

$$Kn = l/d \qquad (44)$$

The average distance travelled by molecules before collisions with other molecules, or the collision distance (*l*), is defined as [83, 84]:

$$l = \frac{k_B T}{\pi((\sigma_w + \sigma_a)/2)^2 P_{pore}} \frac{1}{\sqrt{1+(m_w/m_a)}} \qquad (55)$$

where k_B is the Boltzman constant (1.381×10^{-23} JK^{-1}), σ_w and σ_a the collision diameters for water vapour (2.641×10^{-10} m) and air (3.711×10^{-10} m) [85], T is the mean temperature in the pores, and m_w and m_a are the molecular weights of water and air.

For K_n>1, the membrane pore size is smaller than the mean free path of molecules and Knudsen diffusion dominates the process [47, 75]:

$$C_{\mathrm{Kn}} = \frac{2\,\pi}{3} \frac{1}{RT} \left(\frac{8RT}{\pi M_W}\right)^{1/2} \frac{r^3}{\tau\delta} \qquad (66)$$

where τ the pore tortuosity, r the pore radius, δ the membrane thickness, R the universal gas constant, T the absolute temperature and MW the molecular weight of water vapour.

For K_n<0.01 the molecular diffusion model is used as the collision between molecules determines the mass transfer through the air which exist inside the membrane pores:

$$C_{\mathrm{D}} = \frac{\pi}{\mathrm{RT}} \frac{PD}{P_{air}} \frac{r^2}{\tau\delta} \qquad (77)$$

where P_{air} is the air pressure within the membrane pore, D the diffusion coefficient, and P the total pressure inside the pore which equals the sum of partial pressure of air and water vapour [47].

For 0.01<*Kn*<1 the mass transfer takes place by both mechanisms, Knudsen and molecular diffusion. Although pore sizes vary over the membrane area, the majority of the membrane area will be governed by this transition region [54]. In this case the Knudsen-molecular diffusion transition model must be employed [47, 75]:

$$C_{\mathrm{C}} = \frac{\pi}{\mathrm{RT}} \frac{1}{\tau\delta} \left[\left(\frac{2}{3} \left(\frac{8RT}{\pi M_W}\right)^{\frac{1}{2}} r^3 \right)^{-1} + \left(\frac{PD}{P_{air}} r^2 \right)^{-1} \right]^{-1} \qquad (88)$$

These equations show the complex nature of mass transfer in MD and the main influencing factors. Reviewing the theoretical description of the heat and mass transfer in MD is essential for understanding the performance testing outcomes to be measured in this study.

Advantages of MD over Current Technologies

As outlined before, MD has not yet reached a level of maturity that would allow widespread commercial installations. However, DCMD provides many potential advantages over common separation processes, such as [8, 33, 48]:

- It can be driven at relatively low temperatures (30 to 100 °C) and therefore can utilize low grade heat (solar or industrial waste heat);
- It requires low operating pressure compared to pressure-driven membrane filtration processes;
- It is gentle on temperature and/or shear sensitive products;
- It has a lower capital cost due to the lower pressure requirement;
- It produces a high quality permeate - typically >99% free of non-volatile suspended and dissolved solids;
- It uses readily available, inert membrane materials;
- It is less affected by concentration polarization phenomena compared to pressure-driven membrane processes; and
- It is not subject to flux decline due to osmotic pressure increases.

Despite these advantages, for MD to become a widely available commercial process, its energy consumption needs to be competitive with alternative processes. RO is a much more mature technology and only needs around 15 - 30 MJ/m^3 but uses electrical energy to drive the separation, but it cannot use waste heat [86, 87]. It has been shown that MD can be cheaper than RO if waste heat instead of fossil fuel derived energy is used [27, 88]. Therefore, the economic viability of MD depends greatly on availability of waste heat sources of compatible energy value to make use of its potential to harness waste heat. The use of cooling devices on the permeate side to increase flux is also critical in terms of energy if the reduced temperature cannot be achieved via waste streams. Often, heat recovery from the permeate leaving the system to the feed entering into the module is realized to increase efficiency [89-91]. Another often stated advantage of MD is the possibility of using cheaper materials like plastic for the module, pumps, piping and fittings as high pressure housings are not necessary [32]. However this would not be possible in the dairy industry where high microbiological risks demand for easy to clean materials like stainless steel. In terms of environmental impact is has however been shown that energy demand and source are the main impacting factors and environmental impact related to chemicals and materials is of minor relevance for both, MD and RO [92].

Advantages of MD over evaporation include the smaller vapour space of MD, which means that MD can offer a much larger area for evaporation with a given footprint compared to conventional evaporators [32, 45]. In addition, the fully contained evaporation surface means that any liquid velocities can be sustained without lost surface control or liquid crossover [93]. Also, in normal evaporation processes, the vapour may carry small droplets of water that contain contaminants [32]. MD on the other hand can reduce contaminants cross-over as no droplets can pass through the membrane with typical pore sizes between 0.1 µm and 0.6 µm [9, 47].

Applications of MD in Food Processing

In the last decade, waste heat and solar driven MD has gained substantial interest, especially for the production of fresh water from saline water (e.g. seawater) [12-14, 94, 95]. For desalination or water treatment applications the focus lies on the permeate quality and energy efficiency. The other application is primarily within the food industry, where MD is tested for concentrating different liquid food streams, like orange juice [15-17], black-current juice [18], grape juice [19], apple juice [20] and raw cane sugar syrup [21]. In most cases some form of pre-clarification has been applied before feeding to the MD module to address the issue of increasing viscosity with increasing concentration and resulting lower turbulence. For food applications it needs to be considered that many flavour substances are volatile and operation temperature needs to be kept below their saturation vapour pressure to avoid loss of flavour [17]. The high vapour pressure of unwanted compounds, like alcohol in some cases can be used to reduce alcohol from a feed solution [22]. A practical application is the removal of inhibiting ethanol during fermentation that is a by-product of the fermentation process [96].

Dairy Opportunities for MD

For dairy applications, there is very limited literature available regarding MD. Chlubek et al. [23] published a paper on concentrating milk whey by DCMD in 1987. They pre-treated whey by precipitating proteins so that mainly lactose and minerals were left in the feed stream. This stream was tested on a Teflon flat sheet membrane and they concluded that MD could be a viable process for dairy streams. However, research in dairy applications did not continue until a more recent paper was published by Christensen et al. [24] in 2006. They tested a polypropylene membrane tube in a DCMD configuration to concentrate a whey protein concentrate up to 34 % TS. The motivation of their testing was to improve product quality by using a more gentle temperature compared to standard evaporation (55°C vs 70°C) which reduces partial denaturation of whey proteins. They conclude that DCMD is a possibility for industrial application if higher fluxes can to be achieved. Also, the lower temperature is readily available in dairy waste streams and serves as a potential source of energy to drive MD.

Research Drivers in Dairy Processing

In 2008, Dairy Australia flagged water availability and energy efficiency as the two key environmental issues for manufacturers [6]. Generally, more and more countries have started to promote energy savings and energy programs in the dairy processing sector [97]. The following section identifies the major heat exhausts that could be used to run an MD process, and the dairy streams that can be processed by MD to reclaim process water.

Energy Consumption

Large amounts of thermal energy are used in the dairy industry. One reason is the requirement of pasteurisation of the incoming raw milk for food safety in most countries [98, 99]. However, nowadays heat recovery systems with recovery rates up to 90% and 94% have been widely implemented for pasteurisation processes [7]. For example, a dairy plant that processes 6 ML of raw milk daily often uses the cheese whey to pre-heat the incoming milk before pasteurisation. Typically, the whey is cooled from 45 ºC to around 30ºC by a heat exchanger coupled to the incoming raw milk stream which heats this stream up from 6 ºC to about 27 ºC. In this example, the heat transferred is about 2300 kW which could be a source of energy for an MD system. This is one example of several heat exchange operations within a dairy plant.

Also, cleaning-in-place processes consume a lot of heat energy as these are carried out on a daily bases and typically require temperatures around 65-75 ˚C [7]. On the other hand, the most energy-intense sector in the dairy industry is milk powder production, accounting for 72% of the total energy used in the dairy manufacturing sector [6, 7, 99]. Powder production often involves pre-concentration via membrane processes and evaporation followed by spray drying. Spray drying is by far the most energy intense of these operations as shown in Table 1 which is the main reason to pre-concentrate before spray drying.

Table 1: Energy consumption of unit operations during powder production [7].

Operation	Energy in MJ/kg water removed
Membrane processes	0.014–0.036
Evaporation	0.8
Spray drying	3-5

Generally evaporation involves a significant energy consumption and as stated by some authors in other applications such as sugar crystallisation, an upstream MD process to increase solids concentration in the feeds to evaporators can improve energy efficiency by partly replacing multistage evaporation [8, 21]. Another reason to pre-concentrate as much as possible before spray drying is that that unlike evaporators, no method exists to recover the latent heat carried by the vapour in spray dryers, which further adds to its low energy efficiency [7]. Despite the higher energy efficiency, pre-concentration via RO membranes is limited by the maximum pressure that can be applied to the membrane/module. In seawater desalination to 70,000 mg/L of dissolved solids, pressure of up to 70 bar are used, being the upper limit of RO technology and in dairy applications sanitary design requirements limit high pressure pumps to around 40 bar.

Water Consumption

Water consumption is another environmental challenge for the dairy industry. Typically, washing and cleaning operations of a dairy plant use around 2±5 litres of water per litre of milk processed [100]. Water recovery is of increasing significance for this industry as the quantity of effluents discharged is high, but contains a high proportion of biodegradable organics thus limiting reusability in its present form [100]. The motivation for process water treatment can be to meet increasingly stricter restriction for discharge [101], water reuse, and wastewater constituent recovery [102].

Pressure driven membrane processes in the dairy industry are mainly used for product refinement through separation of all major and minor dairy constituents. They are also increasingly used for water treatment. For dairy waste water reduction, Vourch et al. [103] found that it is possible to recover 89 % of the feed water volume and reduce the conductivity to 9 µS/cm and the total organic carbon to 3.3 ppm from starting conductivity of 700 µS/cm and total organic carbon of 3100 ppm, by using an integrated NF/RO treatment process.

Another possible source for water is milk itself, which consists of around 87 % water. The production of dairy products usually involves some form of concentration leaving behind a diluted stream. This water needs to be made available and emerging membrane processes increasingly fulfil this aim. MD could be of benefit for such an industry where large volumes of water are consumed and simultaneously many concentration processes take place that could be used to produce water. The MD process has much in common with heat exchangers in terms of heat transfer but allows mass transfer at the same time. A simple application of MD uses the temperature of waste streams, utilising this temperature loss to drive the membrane process to transfer distilled water through the membrane. The end result is either a reduced volume of concentrated waste or potentially a higher value of the concentrated stream depending on the application. At the same time treated water is gained for external use or better yet is the offsetting of fresh water consumption by onsite reuse of the high quality treated permeate water.

Dairy Streams and Fouling Potential

This section focuses on the compounds within typical dairy streams and their role in membrane fouling. Fouling is the deposition and accumulation of feed components on the membrane surface and/or within the pores [104, 105], therefore reducing mass transfer across the membrane. In the case of MD, thermal transfer resistance in the fouling layer is linked to a flux loss (Figure 3). It significantly decreases efficiency of membrane processes and renders chemical cleaning necessary, which, in turn, can reduce membrane lifetime, leading to increased membrane replacement costs. Further, the spent cleaning chemicals become a waste issue, so reducing the chemical use by understanding and controlling fouling is clearly advantageous. Due to the transport of materials towards the membrane surface and selective removal of water, the formation of a cake layer by the retained components on the membrane surface is the most common type of fouling. However, another common fouling mechanism is surface pore blockage, where a fouling layer develops on the membrane surface and blocks pores. Unlike a cake layer, this layer is not necessarily made up of components that are rejected due to steric effects, but is often due to salt precipitation [106]. In MD, the hydrophilicity and microporous nature of a fouling layer can have an additional effect on driving force via curvature effects on the vapour pressure [107].

In dairy processing, there are many components that cause membrane fouling, and the severity of this fouling depends on the type of membrane plant and the specific operation. Operating parameters like temperature, cross flow velocity, concentration, etc. greatly influence fouling and need to be optimized for every membrane application separately. The general influence of operating conditions on membrane performance has been addressed in the following sections of this thesis. The chemistry of dairy components needs to be understood when optimizing the MD process for such streams. The following section therefore looks at the chemistry of the two major dairy streams, skim milk and whey.

Milk Proteins

There are two main categories of milk proteins, caseins and whey proteins. Additionally, nitrogenous compounds like urea, amino acids, ammonia and creatine form the non-protein nitrogen (NPN) fraction [108, 109]. During cheese making the caseins are precipitated enzymatically using rennet or by lowering pH down to their isoelectric point (IEP). The caseins form a protein network incorporating other milk components. The liquid that is left behind after acid or rennet coagulation of the casein and manual concentration of this curd, is called whey. Due to the retention of milk components in the cheese structure, whey is a dilute stream consisting predominantly of lactose and salts and the soluble protein category, called whey proteins. The typical concentration ranges of the components in skim milk and whey are presented in Table 2.

Table 2: Typical composition and concentration ranges for skim milk and whey [108, 110, 111].

Component	Skim milk Avg Concentration (% w/w)	Whey Concentration (% w/w)
Lactose	4.6	4.6
Casein	2.6	0.13
Whey protein	0.63	0.43
NPN	0.03	0.05
Fat	0.07	0.06
Minerals	0.65	0.52
Total solids	9.5	6.7

Proteins are a known major membrane foulant due to their multiplicity in functional groups that allows a protein to interact with other feed components and the membrane itself. Furthermore, protein properties are affected by various factors, such as pH and ionic strength [112]. Some properties of the milk proteins are listed in Table 3.

Table 3: Some properties of milk proteins [108].

Protein	Content (%)	MW (g/mol)	Average residue surface energy (kJ/res)
Casein (80% of milk proteins)	2.6		
α_{s1}-casein	1	23,614	4.9
α_{s2}-casein	0.26	25,230	4.7
β-casein	0.93	23,983	5.6
κ-casein	0.33	19,023	5.1
Whey protein (20% of proteins)	0.63		
α-lactalbumin	0.12	14,176	4.7
β-lactoglobulin	0.32	18,363	5.1
BSA	0.04	66,267	4.3
Immunoglobulins	0.07		

Hydrophobicity of the components is an important parameter in the context of membrane fouling especially when using hydrophobic membranes. The average energy per residue data shown in Table 3 indicates hydrophobicity of the single caseins. However, despite the high value for κ-casein, out of the four caseins, κ-casein is the one that has a dual hydrophilic/hydrophobic character while the α-casein and β-casein are largely hydrophobic in character. The protein hydrophobicity makes it intrinsically susceptible to adsorption onto hydrophobic membrane surfaces [113, 114]. The precise mechanism of fouling by adsorption is complex and apart from hydrophobic interactions several other adsorptive mechanisms have been proposed like hydrogen bonding and π -π stacking [115, 116]. In addition to these parameters, the adsorption process can also be affected by the protein structure, concentration, pH and ionic strength [117].

Caseins form colloidal aggregates called micelles in milk thereby staying in solution. Micelles are composed of all of the four casein types with α-casein and β-casein forming the inner core of the micelle, while κ-casein is located on the surface and stabilises the structure by forming an interface between the aqueous environment outside the micelle and the hydrophobic caseins within [111]. The hydrophilic region of this protein protrudes from the micelle surface and forms a 5-10nm 'hairy' layer [109]. Colloidal calcium phosphate is part of the casein micelle and helps stabilising the micelle by forming bridges between the caseins. This protein-mineral interaction also buffers the surrounding supersaturated solution against precipitation induced through changed conditions, e.g. temperature or pH.

The two major whey proteins, β-lactoglobulin (β-Lg) and α-lactalbumin (α-La), most often exist as dimers [118]. β-Lg is a globular protein and represents ~50% of the whey proteins while α-La is a small, spherical protein [109]. β-Lg has been reported to contribute more to membrane fouling which has been attributed to its ability to form protein sheets on the membrane surface [119].

Milk Minerals

All of the twenty-two minerals that are considered essential for human nutrition are present in milk [111]. The salts in milk can be divided into two families. One is the family of monovalent minerals that exist almost entirely as free ions in milk (Na, K, Cl). The second is the family of colloidal salts like calcium, magnesium, phosphorus and citrate [111]. The mineral distribution between the aqueous phase and colloidal minerals is shown in Table 4 for milk and whey. It can be seen that approximately 30% of total minerals are associated with proteins, while 70% are available in a soluble form [118]. Colloidal calcium is associated with casein micelles, either as colloidal calcium phosphate (CCP) or as calcium ions bound to phosphoserine residues [118]. The ratio between calcium in the colloidal and soluble phase is highly dependent on the temperature and pH of the dairy solution and changes in temperature and pH will affect both the concentration of soluble calcium in milk as well as the structure of the casein micelle. The aqueous phase of milk is supersaturated with respect to a number of calcium salts therefore caseins have a buffering role against precipitation. Consequently, when caseins are absent, such as is the case of whey, there is a greater likelihood of calcium phosphate precipitation [120, 121]. However, whey proteins have also been found to interact with calcium, but only at pH values above the protein isoelectric point where the protein carries a negative charge [122]. Also, denatured whey proteins have an increased ability to bind calcium phosphate due to the exposure of free carboxyl groups on the unfolded denatured protein and therefore buffer against salt precipitation [123, 124].

Table 4: Mineral concentrations in milk; distribution between serum and casein micelles [108, 110, 111].

Component	Milk Avg. Conc. (mg/L)	Milk Soluble % (w/w)	Milk Colloidal % (w/w)
Calcium	1000-1400	33.5	66.5
Magnesium	100-150	67	33
Sodium	350-600	92	8
Potassium	1350-1550	92	8
Phosphorus (total)	750-1100	43	57
Chloride	800-1400	100	0
Citrate (as citric acid)	1750	94	6

Calcium phosphate scaling

Calcium phosphate is a general concern for dairy processing due to its supersaturation in the aqueous phase of milk leading to scale fouling. Several ways to reduce its effect on membrane performance have been proposed. It can be removed from the dairy feed by addition of calcium chelating components like citrate, which ties up calcium ions more strongly than phosphate therefore preventing crystal formation [118]. Another option is to precipitate calcium phosphate prior to membrane operation by increasing temperature and pH of the dairy feed. Due to the reverse solubility of calcium phosphate with temperature and its susceptibility to high pH, bulk calcium phosphate crystals form under these conditions, hence preventing their precipitation inside the membrane module during operation [125-127].

Therefore, operating conditions that prevent calcium phosphate scale fouling are low temperature and low pH [128, 129].

Lactose

The milk sugar, lactose, is a disaccharide consisting of the monomers glucose and galactose. It has a molecular weight of 342 g/mol and its concentration in milk is around 4.6 %. There are two anomers, α- and β-lactose, their difference in steric configuration leads to varying optical rotation and solubility [108]. The solubility of lactose in water is a function of the temperature (T) as well as the equilibrium between α- and β-lactose which exists according to [111]:

$$\frac{[\beta]}{[\alpha]} = 1.64 - 0.0027\mathrm{T} \qquad (19)$$

If lactose crystallizes below 93.5 °C usually α-lactose is formed and at higher temperatures β-lactose is formed. Nucleation is slow which implies that few crystals are formed and these become large [108]. Lactose has not been reported to be a major contributor in membrane fouling. It can, however, form complexes with calcium salts [110, 130] which can prevent crystallization and thus suspend formation of a fouling layer. Lactose has also been found to protect against protein unfolding [131] and therefore can indirectly influence the fouling characteristics of the dairy solution. This phenomenon has been related to increased hydrophobic protein interactions in the presence of lactose due to reduced interactions of water and proteins [132, 133]. Marti et al. [131] report on the flow behaviour of milk protein solutions in the presence of lactose and found that for concentrated milk protein dispersions the presence of lactose increased viscosity to a higher extent than calculated for a system without interaction between solvent and dispersed protein molecules. They conclude that increased protein-protein interactions in the presence of added lactose could be responsible. These interactions are also likely to occur at the membrane surface due to the high component concentration.

Conclusions from the Literature Review

Apart from this literature review, further elements reviewing current knowledge are covered within following published chapters. Based on the literature review presented here, MD has been identified as a well studied process in water treatment, but not well applied in dairy where major energy and water opportunities are emerging. Due to its low electrical energy consumption, ability to harness waste heat and its low sensitivity towards osmotic pressure, MD appears well placed for energy and water innovations in the field of dairy processing. For this, scientific detail is required that involves dairy-membrane interaction chemistry (i.e. membrane fouling), process integration and performance with dairy streams. The chemistry of dairy components is complex, but well defined enough to form a good basis for understanding fouling, and enabling process optimization. However, efforts to optimize MD performance with dairy streams and to understand interaction chemistry during MD of dairy streams have not been reported in the current literature. The present thesis aims at gaining greater understanding of how dairy feed components and MD operating parameters influence the MD process. This will address the gaps in science and engineering needed to design an energy efficient MD process for concentration of dairy streams and water recovery. Ways to integrate MD into dairy processing through harnessing the heat energy amounts transferred within a dairy plant must be studied in tandem to fouling and performance for successful implementation of MD in the dairy industry. Based on these conclusions from present literature, the three pillars forming the basis of the present thesis are (i) fouling investigation, (ii) performance assessment and (iii) process integration.

3

Principles of Membrane Filtration

Introduction

The aim of this work was to review existing literature on current commercial membrane processes employed in dairy processing and focussing on the transport mechanisms and putting MD in relation to these widespread membrane processes. The chapter deals with the influence of the three main factors on membrane performance, namely feed characteristics, membrane properties and operating parameters. These three factors are also valid for MD.

Notes from the examination process of this PhD thesis:

- On page 27 it is stated that osmotic pressure influences MF and UF performance less than NF and RO performance. It should be noted that in cases where small molecular weight compounds are retained by a MF/UF membrane the influence of osmotic pressure increases. However, in practice, it is not common to account for osmotic pressure drops in low pressure MF/UF operation.

The book chapter titled ‘Principles of Membrane Filtration’ by Angela Hausmann, Mikel Duke and Thomas Demmer was published in book, *‘Membrane Processing - Dairy and Beverage Applications'* by Wiley-Blackwell.

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PART B:

DECLARATION OF CO-AUTHORSHIP AND CO-CONTRIBUTION: PAPERS INCORPORATED IN THESIS BY PUBLICATION

This declaration is to be completed for each conjointly authored publication and placed at the beginning of the thesis chapter in which the publication appears.

Declaration by [candidate name]: Angela Hausmann

Signature: [redacted]

Date: 03/05/2013

Paper Title:
Principles of Membrane Filtration

In the case of the above publication, the following authors contributed to the work as follows:

Name	Contribution %	Nature of Contribution
Angela Hausmann	85	Literature review Preparation of Manuscript
Mikel Duke	10	Revision of manuscript
Thomas Demmer	5	Revision of manuscript

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DECLARATION BY CO-AUTHORS

The undersigned certify that:

1. They meet criteria for authorship in that they have participated in the conception, execution or interpretation of at least that part of the publication in their field of expertise;
2. They take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
3. There are no other authors of the publication according to these criteria;
4. Potential conflicts of interest have been disclosed to a) granting bodies, b) the editor or publisher of journals or other publications, and c) the head of the responsible academic unit; and
5. The original data is stored at the following location(s):

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and will be held for at least five years from the date indicated below:

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Signature 2		6/5/2013
Signature 3		7/5/2013
Signature 4		

4

Fouling of Dairy Components on Hydrophobic Polytetrafluoroethylene (PTFE) Membranes for Membrane Distillation

Introduction

The aim of this work was to look at fouling phenomena occurring during DCMD. Membrane fouling of dairy streams is widely explored for filtration processes, however little research has been conducted on membranes used for the more novel MD process requiring hydrophobic membranes. This study investigates performance of a small scale MD system for two model dairy feeds, skim milk and whey, and their major single components. While this chapter focuses on the component interactions leading to deposition, further analysis of flux decline mechanisms will be provided in subsequent chapters 5 and 7.

Notes from the examination process of this PhD thesis:

- It should be noted that diamond-pattern flow spacers (commonly used as brine spacers in RO membrane elements) were used in all experiments on the feed and permeate side of the membrane.

The paper titled ‘Fouling of dairy components on hydrophobic polytetrafluoroethylene (PTFE) membranes for membrane distillation’ by Angela Hausmann, Peter Sanciolo, Todor

Vasiljevic, Mike Weeks, Karin Schroën, Stephen Gray and Mikel Duke was published in the peer review journal, *Journal of Membrane Science,* 442(0): p. 149-159, Article first published online: 10 APRIL 2013

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Declaration by (candidate name):	Signature:	Date:
Angela Hausmann	[redacted]	03/05/2013

Paper Title:

Fouling of dairy components on hydrophobic polytetrafluoroethylene (PTFE) membranes for membrane distillation

In the case of the above publication, the following authors contributed to the work as follows:

	Name	Contribution %	Nature of Contribution
1	Angela Hausmann	80	Experimental planning and execution Interpretation of Data Preparation of Manuscript
2	Peter Sanciolo	3	Support and Technical Expertise Revision of manuscript
3	Todor Vasiljevic	3	Support and Technical Expertise Revision of manuscript
4	Mike Weeks	3	Support and Technical Expertise Revision of manuscript
5	Karin Schroën	3	Support and Technical Expertise Revision of manuscript
6.	Stephen Gray	3	Support and Technical Expertise Revision of manuscript
7	Mikel Duke	5	"

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The undersigned certify that:

1. They meet criteria for authorship in that they have participated in the conception, execution or interpretation of at least that part of the publication in their field of expertise;
2. They take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
3. There are no other authors of the publication according to these criteria;
4. Potential conflicts of interest have been disclosed to a) granting bodies, b) the editor or publisher of journals or other publications, and c) the head of the responsible academic unit; and
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Signature 4		30/5/2013
5		22/5/2013.
6 —		6/5/2013
7 —		6/5/2013

5

Fouling Mechanisms of Dairy Streams during Membrane Distillation

Introduction

The aim of this work was to investigate mechanisms leading up to fouling phenomena observed in the previous chapter now focussing on complete skim milk and whey solutions instead of single components and combinations thereof. For this, fouling development over time was investigated as well as performing a structural and compositional analysis of the established fouling layer.

Notes from the examination process of this PhD thesis:

- It should be noted that diamond-pattern flow spacers (commonly used as brine spacers in RO membrane elements) were used in all experiments on the feed and permeate side of the membrane.
- The observation of fouling components entering the membrane pores during MD of whey is also reflected in an increase of permeate conductivity as presented in Table 1 of chapter 6.

The paper titled 'Fouling mechanisms of dairy streams during membrane distillation' by Angela Hausmann, Peter Sanciolo, Todor Vasiljevic, Mike Weeks, Karin Schroën, Stephen

Gray and Mikel Duke was published in the peer review journal, *Journal of Membrane Science,* 441(0): p. 102-111, Article first published online: 06 APRIL 2013

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Declaration by [candidate name]:	Signature:	Date:
Angela Hausmann	[redacted]	03/05/2013

Paper Title:

Fouling mechanisms of dairy streams during membrane distillation

In the case of the above publication, the following authors contributed to the work as follows:

	Name	Contribution %	Nature of Contribution
1	Angela Hausmann	80	Experimental planning and execution Interpretation of Data Preparation of Manuscript
2	Peter Sanciolo	3	Support and Technical Expertise Revision of manuscript
3	Todor Vasiljevic	3	Support and Technical Expertise Revision of manuscript
4	Mike Weeks	3	Support and Technical Expertise Revision of manuscript
5	Karin Schroën	3	Support and Technical Expertise Revision of manuscript
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7	Mikel Duke.	5	""

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6 -	[redacted]	6/5/2013
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6

Direct Contact Membrane Distillation of Dairy Process Streams

Introduction

The aim of this work was to investigate general performance of MD with dairy solutions. MD was applied for the concentration of a range of dairy streams, such as whole milk, skim milk, whey and a lactose solution. In this series of streams one major component after the other was removed: fat in the step from whole milk to skim milk, caseins from milk to whey and salts & proteins from whey to lactose. This allowed investigation of the influence of these components on membrane performance.

Notes from the examination process of this PhD thesis:

- It should be noted that diamond-pattern flow spacers (commonly used as brine spacers in RO membrane elements) were used in all experiments on the feed and permeate side of the membrane.
- To prevent microbial growth, 0.2 $g \cdot L^{-1}$ of sodium azide (Sigma-Aldrich, St Louis, USA) was added to the feed solution for every experiment, however due to the extended runtime pH did drop by a maximum of 0.2 which is not likely to influence performance.

The paper titled ‘Direct contact membrane distillation of dairy process streams‘ by Angela Hausmann, Peter Sanciolo, Todor Vasiljevic, Elankovan Ponnampalam, Nohemí Quispe-Chávez, Mike Weeks, Mikel Duke was published in the peer review journal, *Membranes,* 1(1): p. 48-58, Article first published online: 04 JAN 2011

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7

Performance Assessment of Membrane Distillation for Skim milk and Whey Processing

Introduction

The aim of this work was to determine most efficient hydrodynamic conditions for MD operation of skim milk and whey. To assess influence on performance, the resistance in series model as well as the concept of critical and sustainable flux described in chapter 3 were applied to MD.

Notes from the examination process of this PhD thesis:

- It should be noted that diamond-pattern flow spacers (commonly used as brine spacers in RO membrane elements) were used in all experiments on the feed and permeate side of the membrane.

The paper titled ‘Performance Assessment of Membrane Distillation for Skim milk and Whey Processing’ by Angela Hausmann, Peter Sanciolo, Todor Vasiljevic, Ulrich Kulozik and Mikel Duke has been submitted for publication to *Journal of Dairy Science*.

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5.	[redacted]	4/6/2013

8

Integration of Membrane Distillation into Heat Paths of Industrial Processes

Introduction

The aim of this work was to find a way to harness the vast energy amounts typically being transferred within a dairy processing plant for MD. A novel MD design, known as the MD heat exchanger (MDHX) was proposed which incorporates a heat exchanger and a MD module into a single module to facilitate the addition and removal of heat into the MD hot and cold channels respectively. The advantages of such MDHX are not limited to dairy processing.

The paper titled 'Integration of Membrane Distillation into Heat Paths of Industrial Processes' by Angela Hausmann, Peter Sanciolo, Todor Vasiljevic, Mike Weeks and Mikel Duke was published in the peer review journal, *Chemical Engineering Journal*, 211-212: p. 378-387, Article first published online: 03 OCT 2012

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9

Conclusions and Recommendations

The objectives for this work on membrane distillation of major dairy process streams were to:

1. obtain a greater understanding of the DCMD membrane process by examining the fouling and separation behaviour during operation of skim milk and whey,
2. develop an understanding of how mass transfer and energy efficiency are affected by operating parameters, and
3. explore ways to efficiently integrate MD into dairy processes harnessing the large amount of heat that is transferred within processes.

For the first objective, a fouling study including compositional analyses of the established fouling layers and investigation of the initial adhesion as well as performance of single components and combinations thereof was performed. The results of this study allowed the proposal of fouling mechanisms for skim milk and for whey. For skim milk, the caseins, due to their complex nature as part hydrophobic/part hydrophilic compounds, form a coating layer on the hydrophobic membrane with the hydrophilic parts of the protein facing the bulk feed solution. Intact and hydrophilic casein micelles passing within the bulk stream adhere to these ‘membrane - attached’ micelles, but only form a layer due to charge interactions between the micelles in the presence of salts. In the case where salts are not present, the micelles in the bulk feed do not adhere to the layer formed on the membrane due to the electrostatic repulsion resulting from a same charge and formation of a gel-like layer is thus prevented. For whey, the whey protein interaction with the membrane polymer is weaker than for caseins due to their lower hydrophobicity, resulting in less whey protein deposition on the membrane. It is proposed that, for whey, fouling is dominated by whey protein–lactose–calcium interactions, and when together, lead to a thicker fouling layer. The role of each of the three components in this interaction is not clear. Lactose can lower water activity, which may make water-protein interactions less effective resulting in lactose interacting with proteins directly via hydrogen bonds. The extent of the lactose interaction with the whey protein component was also found to depend on the presence of salts. In the absence of salts, lactose addition to whey protein had no influence on deposition. Lactose was found not to be able to interact with the membrane directly but through other associations and interactions with other components, possibly due to the formation of crystals within the feed stream once an anchor point to the membrane is established by other components. Caseins were found to adsorb onto the membrane polymer very quickly and compete for area. The whey proteins on the other hand were found to adsorb much slower and appeared to require all types of whey proteins being present to establish a thick layer. Due to the stronger interaction between caseins and the membrane surface, skim milk forms a homogeneous layer that grows in thickness. The rapid nature of this interaction gives rise to a rapid flux reduction with this dairy stream. Once established, however, the casein coating renders the membrane hydrophilic preventing other components from being exposed to the hydrophobic membrane thus preventing further growth of the fouling layer and reduction of flux over time. Skim milk fouling therefore starts with the deposition of proteins and salts while lactose joins at a later fouling stages. Whey interactions, on the other hand, are weaker and therefore whey flux remains reversible for much longer time periods compared to skim milk. Once whey deposition starts, salt and protein deposit first and the layer continually grows thereafter from patches and spreads across the membrane area, forming a thicker, and less dense, layer than skim milk due to the more open inorganic crystalline nature of the salt controlled fouling layer of whey. The layer develops over time at a consistent composition only increasing in total deposition. Some minerals and proteinaceous material from whey were found to penetrate into the membrane fibres. These findings have shed light on the science of membrane fouling with specific example to MD and dairy streams. The techniques used to analyse fouling layer included synchrotron IR microscopy and reflectometry, which are novel to membrane science. The knowledge generated in this work is therefore more widely applicable to membrane scientists and industry, where common properties like membrane hydrophobicity and chemistry of the components are now topic of discussion amongst experts. The knowledge gained here has given some insight into the potential surface functionalities that could be explored to reduce fouling, which will be discussed in the future work section.

For the second objective, the performance of PTFE membranes for MD was initially observed as a function of dry-matter concentration for dairy streams with decreasing complexity from whole milk to pure lactose. Fats, in the case of whole milk, appeared to create a stronger interaction, leading to membrane wetting. The focus was, therefore, turned towards mostly fat-free streams - skim milk and whey. Membrane wetting during MD of skim milk, whey or components thereof, even after prolonged runtimes of around 20 hours, did not occur. An investigation of the influence of process parameters on process performance at constant dry-matter concentration and operating conditions revealed that varying conditions of flow and temperature could be utilised to boost MD flux to values that are comparable to RO. The highest fluxes were achieved at higher cross flow velocities. The observed improvement in flux, however, was found to be greater for skim milk than for whey. For whey, increasing cross flow velocity only increased total flux but not relative flux measured as percentage of the pure water flux. Generally, higher cross flow velocities in MD are known to improve temperature profile along the membrane for any stream which is the reason for the increase of total flux for whey. This different response to variation in flow conditions confirmed earlier findings which indicate a different fouling mechanism is operating for the two streams. For skim milk, the fouling layer is composed of the casein micelles which are discrete larger particles than whey proteins and therefore not very cohesive compared to a networked whey fouling layer. Therefore, the more discreet particulates in skim milk can be broken up by high shear, while for whey there is no benefit in increasing shear. A reduced feed temperature (from 55 °C down to 35 °C) led to a more sustainable flux for whey and slightly increased normalized skim milk flux due to reduced hydrophobic effects between particles/molecules and the hydrophobic surface at lower temperatures. Permeate temperature impacted performance of both dairy streams in a similar way, resulting in a slightly higher flux at higher permeate temperature despite the lower driving force. Fouling at the reduced temperature difference across the membrane was instead greatly reduced. Further investigation of this potentially useful effect would require a detailed investigation of the relative interactions of all components on the membrane. In general, not the membrane itself but the formation of the fouling layer during these studies was found to control the process and a reduced vapour pressure of the solution due to fouling could be an explanation for the reduced performance in high fouling instances.

The knowledge developed under this objective indicates that at a flow velocity of 0.141 $m \cdot s^{-1}$ and 54 °C feed temperature and 25 °C permeate temperature the MD performance for skim milk at 20 % solids can compete with that of RO while consuming less electrical energy. For whey, a reduced feed temperature of 45 °C is preferred for flux to remain constant over time. A potentially interesting application for MD in the dairy industry is to pre-concentrate streams before spray drying which is currently done via RO and/or evaporation. Advantages of MD over evaporation include a cleaner permeate and a more efficient module design. In terms of module design, MD allows for much smaller unit sizes due to the short distance between the place of evaporation and condensation which allows efficient removal of exhausted heat. This research has also found that retention during the MD process is independent of component composition and was always above 99 %. Such high retention values are also superior to those found in RO, and since flux was found to be comparable to RO under certain conditions, and electrical energy requirements are low for MD, the available source and temperature of thermal energy determines whether MD can compete with RO at the current development level of this technology. The issue of availability and accessibility of abundant thermal energy is looked at under the next objective.

The third objective is focused on the energy efficiency of membrane distillation by integrating a membrane distillation unit into existing heat paths of a dairy factory. For this, a new module design was developed which integrates a membrane distillation unit with a heat exchange process. Heat and mass transfer modelling and experimental studies were performed for this novel MD design, known as the MD heat exchanger (MDHX). This work has shown that MD may be a promising process to recover high quality water without substantially increasing electricity consumption by using a process heat exchange. The integration of MD and HX into a single unit resulted in an improved temperature profile along the MD membrane. It has been shown that the concept of transferring heat along the membrane can be applied when integrating heat exchange into the MD process, but it is only mostly needed for the hot channel thus potentially simplifying a module design. At the chosen experimental conditions, the MDHX process was demonstrated experimentally to increase single pass water recovery from 2 % to 14 %. This promises to reduce the electrical pumping costs to less than 0.01 kWh for every m^3 of water produced. Much higher recoveries are theoretically possible but subject to further investigations. Apart from reducing electrical energy consumption, this module design allows access to valuable process heat without generating waste heat. The heat exchanger integration also bears practical advantages as this design allows for stainless steel modules which are required for hygienic reasons when processing dairy streams.

Future research directions

This research has focused on an experimental study of membrane performance in DCMD of two major dairy streams, skim milk and whey. Protein fouling was found to limit performance for both dairy streams investigated. The development of new membrane materials that are less susceptible to protein fouling could greatly increase applicability of MD in dairy processing. A thin layer of hydrophilic material acting as a barrier for the underlying hydrophobic membrane, or a dual hydrophobic/oleophobic material could potentially reduce protein adhesion and consequent fouling layer establishment. Such membranes are now available, but research is just emerging in this space. More recently, inorganic membrane materials such as ceramic membranes are being made available for the MD process. These materials are used for membrane processes in filtration mode in the dairy industry with great success. The emergence of such materials for membrane distillation could greatly further improve attractiveness of this process in the investigated applications.

Future studies should be directed to longer term investigations with repeated cleaning cycles to confirm membrane wetting does not occur with the studied dairy streams after repeated cleaning and fouling. The most appropriate cleaning regimes for the given membrane material and cake layer composition also needs to be investigated.

Furthermore, the membrane fouling study presented in the current work would benefit from further investigation into the composition and structure of fouling layers at different fouling conditions. Currently, a fouled membrane analysis has only been performed in detail on a membrane after fouling at standardised conditions. This has given great insight into which components have a bearing on membrane performance. A more extensive analysis of different fouling layers is needed to more completely validate the mechanisms proposed using the results obtained in this study.

MD is an energy intensive process, relying on thermal energy to drive the separation. The proposed membrane distillation heat exchanger (MDHX) has greatly improved pumping (electrical) energy efficiency by increasing single pass recovery. However recovery of latent heat, which accounts for the majority of energy transferred through the membrane, should be addressed in future work. Further developments of this concept should also include an up-scaled multi-layered design. Also, pilot scale studies incorporating the MDHX into actual heat paths are still needed, and can be in many other industries besides dairy. In addition, the most energy efficient way to operate such MDHX module is at low flow rates while for dairy streams it has been found that MD flux is only competitive to RO fluxes at high flow velocities. Meanwhile MDHX now isolates the separate functions of cross flow, which achieve both increased recovery and fouling control, such that they can be independently controlled to separately achieve the best performance. Lower flow rates would be expected to result in higher energy efficiency but increase overall module size and membrane area. All these possibilities need further research to prove the feasibility of MD in dairy processing and industry process integration.

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