2
Membrane Processes for Dairy Fractionation

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2.1
Introduction

Traditionally, milk has been separated in order to produce a wide range of dairy products. In some cases, separation is minimal, such as in regular full-fat milk, which is standardized in order to have the correct amount of fat. But for semi-skim milk and skim milk, separation needs to be done more rigorously because a large amount of the milk fat or even all of it needs to be removed in order to obtain the desired fat percentage in the product. When considering complex dairy products, such as cheese, it is clear that not the entire milk is used but only partly, and valuable by-products are generated (see Table 2.1). From the milk, the cream and casein fraction (main component of cheese) are separated, after which a certain amount of fat is added back according to specifications for the type of cheese that is to be prepared. For Gouda cheese production, rennet, $CaCl_2$, and starter culture are added, after which a gel is formed by the casein, which is subsequently cut to small pieces (curd) to remove the so-called whey. The curd particles are subsequently pressed into cheese shape, brined, and stored. The whey contains the so-called whey proteins, and these are of considerable value, since they are easily digestible, and are added to, for example, sport drinks.

For the separation of fat from milk, mostly centrifuges are used, but membranes could be an interesting alternative, which is explained in Section 2.2.1. Besides separation of milk fat, also all other milk components are in a range in which membranes are effective (for a summary see Table 2.2). In Figure 2.1, a general comparison is made between the size of the dairy components and the pore size of membranes.

In some fields, membranes have established their value such as processing of whey and they are gaining popularity in other dairy applications as described in Daufin *et al.* [1]; for a recent review paper see Brans *et al.* [2]. However, separation of milk in many different fractions has not been described in the literature; mostly papers focus on a single stage. Some successful examples are the separation and fractionation of fat globules, the reduction of bacteria and spores in skim milk, concentration of casein micelles (for cheese manufacturing), and purification of serum proteins, and

Membrane Technology, Volume 3: Membranes for Food Applications.
Edited by Klaus-Viktor Peinemann, Suzana Pereira Nunes, and Lidietta Giorno

ISBN: 978-3-527-31482-9

Table 2.1 General overview of processing steps required in Gouda cheese preparation including some by-products (reprinted from Brans *et al.* [2] with permission from Elsevier).

Processing step/Separation	Product	"By-product"
Separation of cream from rest and standardization fat content	Cheese milk	Cream or skim milk depending on fat content
Curding through addition of rennet, $CaCl_2$, and starter	Gelled milk	
Cutting of curd	Curd	Whey
Pressing of curd particles	Shaped cheese	
Brining	Salted cheese	Brine with cheese components
Ripening	Mature cheese	

these will be discussed in the next section. In general, it can be mentioned that the various membrane processes that are discussed in the literature for dairy applications have a number of aspects in common related to flux decline and fouling, and related to that selectivity. Logically, many papers deal with strategies to prevent flux and selectivity reduction, for example, the uniform transmembrane pressure is developed to have similar conditions over the entire length of the membrane, and these strategies will be discussed in Section 2.3. Since flux and selectivity loss also originate from the membrane specifications; a pore-size distribution is expected to influence the sharpness of the separation, we will also discuss membranes with more uniform pore sizes such as asymmetric ceramic membranes, track-etched membranes [3], silicon microsieves [4], and metal microfilters [5].

Table 2.2 Average composition of cow milk: concentration and size distribution (reprinted from Brans *et al.* [2] with permission from Elsevier).

	Concentration in whole milk (g/l)	Size range and average (at weight average)
Water	87.1	
Fat globules	4.0	0.1–15 μm, average 3.4 μm
Casein (in micelles)	2.6	20–300 nm, average 110 nm
Serum proteins	0.7	3–6 nm
α-lactalbumin	0.12	14 kD
β-lactoglobulin	0.32	18 kD
BSA	0.04	66 kD
Proteose-pepton	0.08	4–40 kD
Immunoglobulins	0.08	150–900 kD
Lactoferrin	0.01	86 kD
Transferrin	0.01	76 kD
Others	0.04	
Lactose	4.6	0.35 kD
Mineral substances	0.7	
Organic acids	0.17	
Other	0.15	

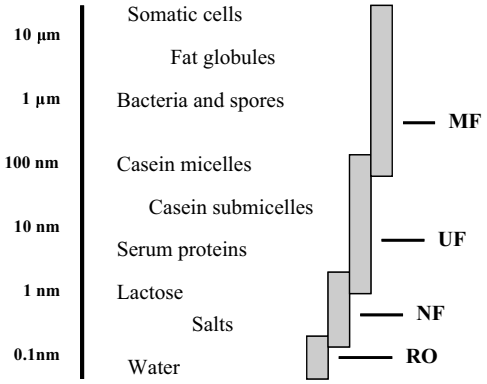

Figure 2.1 Comparison of size of components in milk and pore size of membranes. MF: microfiltration; UF: ultrafiltration; NF: nanofiltration; RO: reverse osmosis (reprinted from Brans *et al.* [2] with permission from Elsevier).

2.2
Membrane Separation of Components

2.2.1
Removal of Milk Fat from Whole Milk

As mentioned previously, mostly centrifugation is used for separation of milk fat from milk, although membrane separation is technically possible, as indicated in a patent by Alfa-Laval [6]. An advantage of using membranes instead of centrifuges could be that the fat globules are less damaged, which is expected to enhance cream stability, and sensory perception. Milk-fat droplets range in size from 0.1 to 15 μm, with an average around 3.4 μm. At room temperature, the fat is mostly solid, and in order to avoid clumping the liquid needs to be heated up to 50 °C. Goudedranche *et al.* [7] who were mainly interested in consumer perception of cream, describe the fractionation of milk-fat globules with a 2-μm ceramic membrane, but unfortunately did not report the size distribution of the two fractions. The consumers preferred the small fat globules that gave products with finer texture, to the larger fat globules and a standard cream. Clearly, fractionation of fat particles can lead to products that are more appreciated by consumers, and this should drive further development if only for the cream in milk.

2.2.2
Removal of Bacteria and Spores from Skim Milk (Cold Pasteurization)

The main advantage of using microfiltration for the reduction of bacteria and spores from milk is that the taste of the milk is not affected because no heat treatment is required. Besides, the reduction that can be achieved is higher than for centrifugation [8], and as a result, the shelf life of milk is extended. Further, microfiltration has

Table 2.3 Comparison of cold sterilization results from various sources.

Membrane type and flux	Process conditions cross-flow/pressure, UTP, backpulsing	Log reduction	Source
Ceramic 1.4 μm; 1.4×10^{-4} m/s	50 kPa, 7.2 m/s UTP	above 3.5	Saboya and Maubois [10]
Reversed asymmetric 0.87 μm; 1.4×10^{-4} m/s	0.5–1 m/s; backpulsing 0.2–1 s^{-1}	between 4 and 5	Guerra *et al.* [11]
Microsieve 0.5 μm	dead-end filtration of spiked SMUF	6.6	van Rijn and Kromkamp [12]
Bactocatch: ceramic membranes	6 to 8 m/s		Holm *et al.* [13]

been described in patent literature as a pretreatment method for skim milk to be used in the production of raw milk cheeses [9].

Various authors have worked on this topic, and they have used rather different methods, and operational conditions. In Table 2.3, the details are summarized, and it is clear that various membranes and conditions have been used, although not all information is displayed in patent literature. In general, the log reductions that can be obtained (10 000 fold reduction or more) are very interesting, and this makes microfiltration an interesting option for cold sterilization, albeit the log reduction is not as high as obtained by regular heat treatment. The highest log reduction (6.6: higher than for regular pasteurization) was claimed for microsieves, which are silicon plates with very accurately manufactured pores using laser interference lithography. Although the bacterial reduction was measured for dead-end filtration of SMUF (simulated ultrafiltrate) spiked with *Bacillus subtilis*, over a 0.5-μm microsieve, we believe that the high reduction obtained with this model system for milk is a result of the extremely narrow pore-size distribution of the microsieve. In Figure 2.2, micrographs of a ceramic membrane and a microsieve are shown.

2.2.3
Concentration of Casein Micelles in Skim Milk

As mentioned in the introduction, in cheese production, various waste streams are created, and especially whey is a big waste stream; from 10 l of milk, 1 kg cheese is produced, and therewith also 9 l of whey. Because of these huge volumes that are involved, it is an interesting notion to start cheese making with a concentrated casein solution, and to remove whey proteins and other low molecular weight components. Although casein is only 2.6% weight percentage of milk, it contains a lot of water and is very voluminous. Typical diameters of casein are between 20–300 nm, with an average of 110 nm [14].

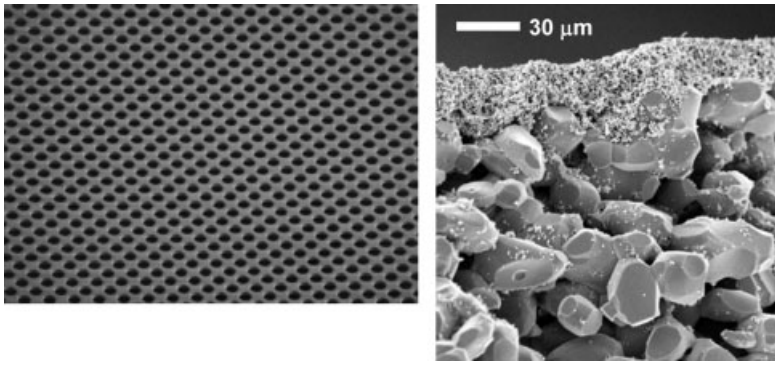

Figure 2.2 Micrographs of a microsieve (image courtesy of Aquamarijn) and ceramic membrane.

This topic has attracted the attention of various authors, who used various process conditions and membranes; an overview is given in Table 2.4. Although the studied conditions were rather different, the results were not, maybe with the exception of the work of Krstic *et al.* [15], who used turbulence promoters. For concentration of casein micelles, control of the membrane flux through control of fouling seems most important, and the fact that some whey protein may end up with the casein and vice versa, is not such an issue. Casein concentration through microfiltration is a better option compared to the use of traditional ultrafiltration as pretreatment for cheese (which concentrates both casein and whey protein), since this leads to less whey protein in the cheese process. When comparing casein concentration to cold sterilization, it is immediately clear that separation of bacteria needs to be and remain sharp, and therefore, this separation needs to meet higher demands regarding selectivity than casein concentration, although the economics of the process are affected by the selectivity of the process [16].

Table 2.4 Comparison of casein concentration from various sources.

Membrane type and flux	Process conditions cross-flow/pressure	Concentration factor	Source
Ceraflo 0.22 μm; 2.5×10^{-5} m/s	6.9 m/s; 190 kPa	3	Pouliot *et al.* [17]
Membralox 0.2 μm 1.9×10^{-5} m/s	7.2 m/s; 193 kPa	2	Vadi and Rizvi [18]
1.3×10^{-5} m/s		10	
Ceramem asymmetric 0.05 μm; 3.1×10^{-5} m/s	5.4 m/s; 138 kPa	2	Punidadas and Rizvi [19]
Membralox 0.1 μm; 9.7×10^{-5} m/s	0.45 m/s; 34 kPa turbulence promoters	1	Krstic *et al.* [15]
2.5×10^{-4} m/s	12.5 m/s; 65 kPa (+ TP)		

2.2.4
Recovery of Serum Proteins from Cheese Whey

Traditionally, whey was considered a waste product of cheese making, but nowadays, whey proteins are a considerable source of income for dairy companies. Not surprisingly, separation technology, including membrane separation was developed to capture these valuable components. Whey is mostly high in salt, and therefore, demineralization is needed, and for this electrodialysis or ion-exchange resins are used [20], but also nanofiltration has been proposed by van der Horst and coworkers [21]. An added benefit of nanofiltration is that it reduces energy consumption, and the partially demineralization product can be spray dried and used in food or feed applications. In the work of Doyen and coworkers [22], various membranes were compared among which were polymeric (PSF/PVP), ceramic (ZrO_2) and organomineral (ZrO_2/PSf) membranes, and they found that the plateau fluxes were comparable; the fouling layer was the limiting factor in whey protein concentration and not the permeability of the membrane. Since all proteins are retained, prevention of gel formation is critical for process operation.

Various proteins are present is whey, which are all of considerable economic worth, such as α-lactalbumin, β-lactoglobulin, bovine serum albumin, immunoglobulins, lactoferrin, transferrin, and some minor proteins and peptides (see also Table 2.2). For example, β-lactoglobulin can be used in emulsification, foaming and gelling [23], and for lactoferrin and α-lactalbumin there are pharmaceutical applications [1, 24]. Further, there is an increasing interest in bioactive hydrolysates from serum proteins [25]. The reported separation methods for these proteins include thermal aggregation of α-lactalbumin [26], ion-exchange chromatography, precipitation, ultrafiltration or a combination of these methods [27–31]. Besides, it was shown to be possible to enhance the selectivity of an ultrafiltration process by adjusting pH and salt to influence electrostatic and steric interaction [23, 32].

From the previous sections, it is clear that various separations such as fat separation, cold sterilization, casein concentration, and whey-protein isolation, have been carried out successfully using membranes. However, one factor limits milk fractionation and this is flux decrease related to fouling. Design parameters that can be used to control this are discussed in the next section.

2.3
Methods to Enhance Membrane Separation

As mentioned in the previous section, the accumulated layer or fouling layer determines membrane behavior in many dairy separations. It is generally accepted that it is not the membrane but (the rate of) accumulation that is the limiting factor for membrane filtration of milk [33], although different authors point to different aspects of the accumulated layer as being most relevant [34, 35]. This is also due to the various methods that have been used to access the fouling layer such as SEM (e.g., [34]), AFM (e.g., [35]), ATR–FTIR and EDX [36], streaming-potential measurements [37], and

flux measurement, in combination with retention measurement as is regularly used (e.g., [38]). An overview of the various methods used to assess membrane fouling can be found in a recent review by Le-Clech *et al.* [39], and the relation between membrane surface morphology and membrane performance is described comprehensively by Khulbe *et al.* [40].

For simplicity reasons, in this section we will use the term flux decrease for any effect that causes this instead of fouling. Flux decrease may thus be linked to concentration polarization, cake filtration, adsorption, depth fouling, pore blocking, or any other effect that reduces the flux. In spite of the different interpretations of membrane fouling/accumulation of components, a number of concepts have been developed to keep the flux at acceptable levels, and these will be discussed first. To limit ourselves, we will discuss methods that act on short-term flux decrease, and will not discuss cleaning methods, which are needed to mediate long-term flux decrease, and codetermines the lifetime of a membrane. In section 2.5, we will discuss particle and component behavior in more detail, in relation to specific aspects of flux decrease, and show how this can be used to design separation processes.

2.3.1
Critical Flux Concept

In the critical flux concept proposed by Field and coworkers [41, 42] and recently reviewed by Pollice [43] for membrane bioreactors, three regions are distinguished, as schematically indicated in Figure 2.3. In region I, the transmembrane pressure is below the critical pressure and the flux is linearly dependent on the applied pressure. This dependency can be determined by the clean-water flux as stated in the hard form or lower than the clean-water flux, which is the weak form of the critical flux criterion. Filtration in this region is also known as subcritical flux operation and is advised to obtain optimal selectivity, since accumulation is minimal, due to the low applied

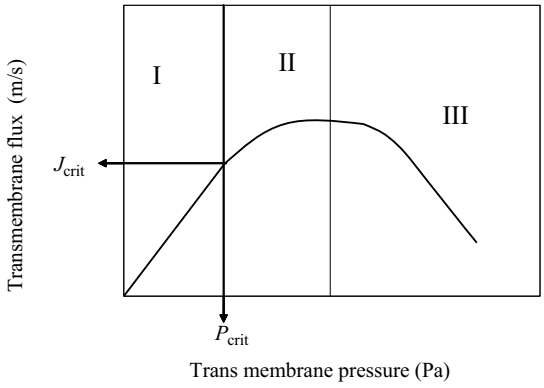

Figure 2.3 Schematic representation of the critical flux concept. In region I, the flux is linearly dependent on pressure until at a critical pressure (P_{crit}) the critical flux (J_{crit}) is reached. The flux levels of as a function of pressure in region II, and even decreases in region III when the pressure is increased further (reprinted from Brans *et al.* [77] with permission from Elsevier).

pressures. Because of the low pressure, the flux values are low and the required membrane area necessarily high. In region II, the flux is no longer linearly dependent on the transmembrane pressure, and the flux may be determined by the accumulated layer. The value of the flux can be estimated with gel filtration model and/or backtransport models (e.g., [44]). Although selectivity of the membranes may be influenced in this region, it is still often chosen because it allows best use of the installed surface area when considering only volumetric productivity, regardless of selectivity. In region III, the applied pressure it too high to maintain an acceptable flux, and mostly this is related to cake formation and compaction. If a membrane process is to be operated in region III, it is necessary to remove the deposited layer at short intervals, for example, through frequent backpulsing.

When considering the dairy processes presented in the previous section, in relation to the critical flux concept, it should be mentioned that reduction of bacteria and spores, and concentration of casein micelles is carried out near the critical pressure. Concentration of whey protein is carried out in region II in order to minimize the membrane area, while isolation of whey proteins has to take place in region I for selectivity reasons. In all regions, adsorption of components to the membrane surface can take place, and this can lead to flux loss, and related to this loss of selectivity. In order to prevent this, membrane modification may be needed, and this will be presented in a later section, first we focus on other processing methods that help keep the flux at acceptable levels.

2.3.2
Uniform Low Transmembrane Pressure Concept (UTP)

In order to increase turbulence in membrane modules, increasing cross-flow velocity is a straightforward option. However, this also results in a pressure gradient across the membrane module, leading to different filtration conditions along the length of the membrane. Since this will inevitably influence local selectivity, a new concept was proposed, the so-called uniform low transmembrane pressure concept (UTP), which allows a constant pressure drop over the length of the membrane module, for example, through applying a cross-flow on the permeate side [10]. Obviously, this extra cross-flow increases the amount of energy needed during operation but in spite of this, UTP is currently the most popular strategy against flux decrease during the filtration of skim milk to retain bacteria and the concentration of casein micelles. Instead of a cross-flow on the permeate side, membranes can also be adjusted as is the case in Isoflux and Gradient Porosity membranes [10]. These membranes have a decreasing membrane resistance over the length of the tube, which has the same effect as UTP, but without the need of a cross-flow on the permeate side.

2.3.3
Turbulence Promotion

In the literature, various options to promote turbulence have been proposed such as vibrating modules [45], rotating-disk modules [46, 47], static mixing inserts [15],

spacers, turbulence promoters, and inserts, and the use of Dean vortices or microturbulences [48]. Some methods prevent particle deposition through increased shear rates close to the membrane surface, by either vibration, or rotation. Although interesting effects can be realized through vibration, in general it is difficult to use these equipments on a large scale. Regarding rotation, sealing of the equipment to prevent microbial contamination is an issue, and this may make large-scale installation impossible. The static mixing elements have been shown to increase fluxes (see Table 2.4), and are effective turbulence enhancers, although there are some doubts regarding their cleanability, and the creation of so-called dead areas, which are a source for recontamination by microorganisms. Creation of flow instabilities, such as Dean vortices, is an elegant method to locally increase mass transfer, but may not be suited for many membrane configurations.

2.3.4
Backpulsing and Flow Reversal

Although turbulence promotion may be one of the side effects of backpulsing and flux reversal, we have decided to dedicate a separate section to them given their relevance for membrane separation (i.e., prevention of flux decrease) in practice. Various terms are in use for the temporary reversal of flow through the membrane, such as backpulsing, backwashing, backflushing, and backshocking [49, 50], and in all these cases permeate is pressed back into the feed stream. Through this type of reversal of flow, the deposited components are carried away from the membrane and ideally taken away by the cross-flow. The frequency at which flow is reversed can be high (0.2–1.0 s^{-1}) as reported by Guerra and coworkers [11]. These authors reported good results for the reduction of bacteria in skim milk with a combination of UTP and backpulsing (see Table 2.3).

Besides reversal of flow through the membrane, the feed flow as such can also be used to improve filtration performance, be it through pulsating flow, or even reversal of flow. In this case, rapid velocity changes occur in the cross-flow channel [51, 52]. Pulsating flow is difficult to use at large scale, because the effect of the pulses is dampened. Of the methods mentioned in this section, in general, high-frequency backpulsing is the method of choice in industrial applications possibly in combination with UTP application.

2.3.5
Other Methods

Many other process options that may aid membrane filtration are known from the literature and they are listed in Table 2.5 in order to make this overview complete; as mentioned previously, (chemical) cleaning as such is not taken into account. Air slugs have been used to locally enhance turbulence [53, 54], but unfortunately, they also induce foaming and protein denaturation in dairy applications. Scouring particles have been used for the same purpose, but they are notoriously hard to reuse and cause damage to the membrane and installation [55]. Acoustic waves and

Table 2.5 Other methods to enhance membrane performance.

Method	Advantages/disadvantages	Source
Air slugs	Hard to control in large membrane systems; foam formation; protein denaturation	Cui and Wright [53] Cui and Taha [54]
Scouring particles	Hard to control in large membrane systems; reuse of particles; damage to system	Noordman *et al.* [55]
Acoustic or ultrasonic waves and sonication	Protein denaturation; expensive to scale up	Wakeman and Tarleton [56] Duriyabunleng *et al.* [57] Villamiel and de Jong [58]
Constant or pulsed electric fields	Suitable for isolation of whey proteins	Visvanathan and Ben Aim [59] Wakeman [60]

sonication cause vibrations and cavitations, which facilitates transport of particles, but at the same time, they induce denaturation of protein [56–58]. Due to these specific disadvantages, none of these techniques seems to be promising for application in dairy processing. Electric fields, either constant or pulsed, have been successfully applied in the separation of whey proteins [59, 60], but because pH adjustment is needed this is not expected to be a viable process for separation of other milk components.

2.4 Use of Models for Membrane Separation

Although it is tempting to use an experimental approach to investigate membrane separation, models can in principle facilitate the design of membrane processes more than any experiment can, although we strongly feel that experimentation and validation are always required. Many models are available in the literature for ultrafiltration and microfiltration, predicting various aspects of filtration on different scales, but many are related to the behavior of "particles", which are idealized components. Some examples of these models can be found in [61–68]. Most probably, the review papers of Belfort and coworkers [44], and Bowen and Jenner [69] are good starting points for those that are not so familiar with models for membrane filtration. Besides, various descriptive models are proposed, but mostly these models are limited to the specific apparatus, membrane, and liquids/components for which they were derived, and therefore are of limited use.

When testing models against experimental data, there is always the challenge to match the idealized situation of the model, which mimics the physical aspects very well, with the not so ideal situation during filtration. For example, numerous components may be present, the membrane may have a pore-size distribution,

which influences the separation, and interactions with the membrane may play a role. It is not always necessary to consider all these aspects, but even selection of the most relevant ones may be a difficult task, although some success stories are also known from the literature.

For concentration of casein from skim milk, Samuelsson and coworkers [70] used models with different backtransport mechanisms, and they found that shear-induced diffusion described the observed behavior best. Clearly, basic understanding of particle and component behavior contributes to understanding of the relevant phenomena during separation and the separation characteristics (see next section for another example). Further, computer models were found to be very useful to investigate various aspects of module design such as the liquid flow in relation to cake formation [71], but also the effect of inserts and spacers have been evaluated through CFD [72, 73]. When considering what is done in the field of modeling, many aspects have been described well, for example, CFD can be used very well in the design of flow-through modules, however, a link between particle behavior, and separation on the module scale is hard to achieve, also because of the completely different scales at which effects take place. Some interesting studies have recently become available in the literature [74], in which particle behavior is linked to behavior during filtration. Concentration polarization and cake layer build-up on microsieves was investigated for particles that are not able to pass the pores at a fixed cross-flow velocity of $0.32\ m\ s^{-1}$. Illustrative examples of CFD simulation results are shown in Figure 2.4a. At longer filtration times the layer becomes thicker, and eventually the layer becomes this concentrated that cake layer formation takes place. In Figures 2.4b and c, the pressure dependency of the flux is shown. The CFD simulations have generated very detailed information on the local composition in relation to membrane fluxes, and have proven to be of great value in understanding filtration behavior as well as determining those conditions at which selectivity is expected to be least affected, that is, the critical flux/pressure value can be derived from Figure 2.4. Although the situation in the simulation cannot be translated one on one to milk-filtration experiments because of computational limitations, we still learned valuable lessons that guided us in choosing better process conditions.

2.5
How to Get from Separation to Fractionation

In the previous sections, various aspects have been discussed and some of these we find extremely relevant to move from separation to fractionation. More specifically, we will discuss membranes with uniform pore size, extensive computer simulations on particle behavior, and membrane modification here, since they may hold the key to fractionation. First, if the pore size is uniform, the selectivity of the separation is expected to be very sharp (although other options are also available as will be explained in the outlook section). Secondly, modeling of particle behavior is essential to obtain a better understanding of backtransport mechanisms, which in turn will determine the selectivity of a separation in relation to process conditions. Since

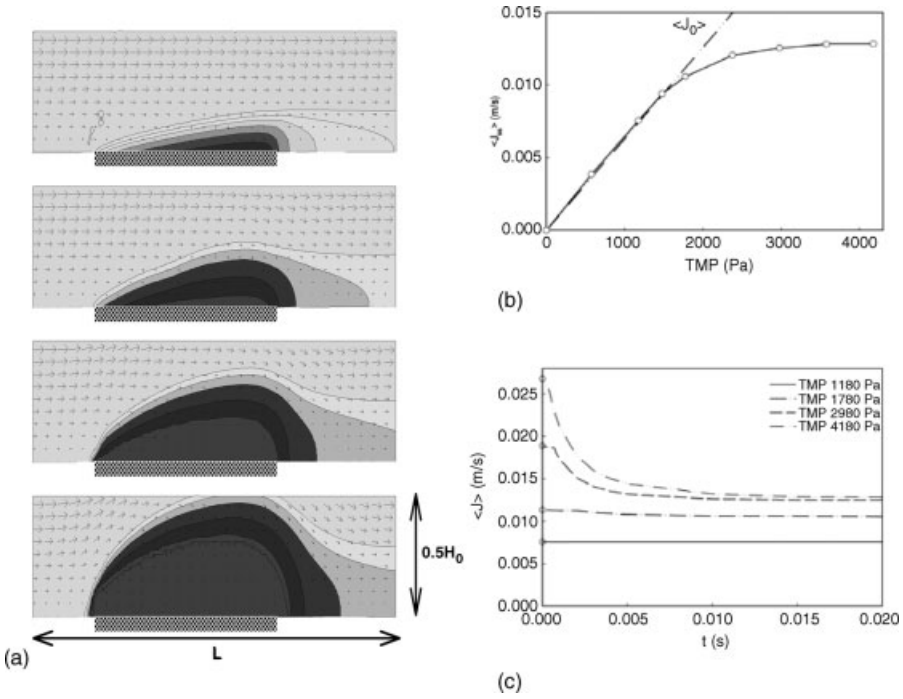

Figure 2.4 Illustration of a CFD simulation on concentration polarization and cake-layer formation during microsieve filtration. (a) the effect of transmembrane pressure on layer build-up; (b) the steady-state flux as a function of transmembrane pressure; and (c) the flux as a function of time (reprinted from [74] with permission from Elsevier).

components will contact a membrane eventually, membrane modification targeted at prevention of adsorption or other initial contacts is also expected to be one of the keys to get to fractionation.

2.5.1 Membranes with Uniform Pore Size

Various membranes are known for their uniform pore size, such as Nuclepore membranes that date as far back as 1962 [75], silicon-based microsieves [12], polymeric microsieves [76], but also metal sieves [77]. Aside from the fact that these membranes are ideal candidates for highly selective separation, they are also an ideal research tool, since pore-size distribution does not play a role.

Because microsieves can be made with different pore sizes and geometries, they allow investigation of parameters that otherwise would not have been possible. For example, particle release from various pore geometries was investigated through

computer modeling, and it was found that particles were released most easily from triangular pores, although from a fractionation point of view this design may not be the ideal choice because the pore is only partially blocked. For fractionation, a round pore is the best choice [78] since it is either blocked and does not contribute to the flux, or is fully selective. In another paper, Brans and coworkers [78] showed the importance of the substructure of the microsieve, which limits the operating flux considerably, but can be resolved through a small change in design.

2.5.2
Simulation of Particle Behavior

Component behavior during filtration is very complex, and this is even enhanced by the size distribution of the components. Based on their size, they may or may not be retained by the membrane, or by the accumulating layer, and size will determine which backtransport mechanisms they will be subjected to. In a classic study by Belfort *et al*. [44], backtransport mechanisms were linked to permeate fluxes and sizes of the components. In general, Brownian diffusion is the dominating transport mechanism for "particles" below 0.1 μm and inertial lift is the main mechanism for "particles" above 10 μm. For "particles" with intermediate size, which are abundantly available in milk, shear-induced diffusion is the main mechanism of backtransport. It is obvious that for a relevant model, information on the resulting diffusion coefficients is needed in order to come to realistic representations for membrane filtration.

Especially, for particles of intermediate size, simulation of their behavior is far from trivial, because the interactions between particles and liquid need to be fully resolved; and this is possible in the Lattice-Boltzmann method [79, 80]. For casein micelles and fat globules, there are indications that they can be treated as hard spheres [81], and this facilitates modeling. Kromkamp [82] has used this approach to investigate the shear-induced diffusion behavior of monodisperse and bidisperse suspension, and the resulting diffusion coefficients can be implemented in filtration models such as described in Section 2.4 for microsieve filtration (see Figure 2.4).

2.5.3
Membrane Modification

As indicated in the previous sections, in milk many components are present (notably proteins) that will interact with membrane surfaces, and mostly will do so in an irreversible way unless subjected to rigorous cleaning. Since any irreversible accumulation influences the selectivity of the separation, prevention of these interactions is a good way to keep selectivity in place, and this is even more relevant for the previously mentioned microsieves with uniform pore size. For these specific membranes, we have developed the chemistry to modify them at will [83, 84], including protein repellence through covalent attachment of EO_6-containing

components that reduce the adsorbed amount of BSA and fibrinogen below the detection limit [85, 86].

2.6 Outlook

Although uniform pores, modeling, and modification are relevant to mature dairy fractionation, we have to stay open for other opportunities, as is nicely illustrated in the work of Kromkamp *et al.* [87]. In this case, particle segregation and migration was found to play an overruling role in a specific dairy separation. Milk-fat globules (sizes ranging from 1 to 10 μm), were to be fractionated with a tubular, ceramic MF membrane with 5.0 μm average pore size, and the transmembrane pressure over the membrane was varied, to keep the permeate flux constant without allowing particle accumulation. In Figure 2.5, the particles size and the relative fat content of the permeate are shown as a function of the applied pressure. For the highest cross-flow velocities, at which particle migration is promoted most, the particle size and fat content are relatively constant, but much lower than in the feed. For the lower cross-flow velocity, at which particle migration is less pronounced, the particle size and fat content clearly increase with higher flux, while the particle size and fat content almost reach the value in the feed solution at the highest flux measured. Note that these effects cannot be a result of components accumulation since that was excluded in the measurement. This has lead to the conclusion that inside the feed stream segregation (particle migration) has taken place with the larger particles located in the middle of the feed channel, as is depicted schematically in Figure 2.6, and this implies that there is a completely new angle on fractionation, namely through control of the applied

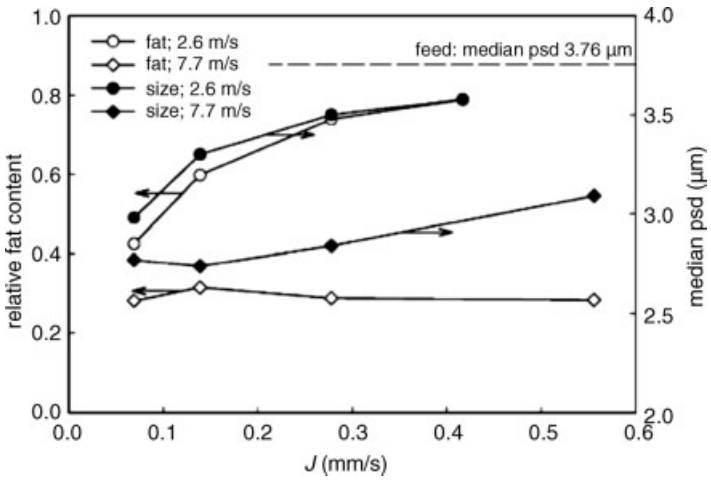

Figure 2.5 Relative fat content and particle size of milk fat globules as a function of the applied transmembrane flux, and cross-flow velocity (reprinted from [87] with permission from Elsevier).

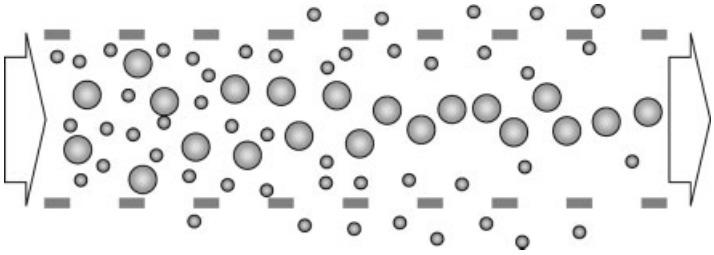

Figure 2.6 Schematic representation of migration effects that facilitate membrane fractionation [88].

flux. In this case, the pore size of the membrane is no longer relevant, but simulations of particle behavior and membrane modification are still very relevant to make best use of this finding.

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