The principle of ultrafiltration (UF) is filtration of solutions or suspensions under pressure through a semipermeable membrane. The membrane has pores that allow the solvent and small molecules to pass through and the larger molecules to be retained. Ultrafiltration may therefore be considered as both a concentration and a fractionation process according to the particular components of interest.

Ultrafiltration is often associated with reverse osmosis (RO), sometimes called hyperfiltration, and UF and RO are known as membrane processes. The association exists because both are pressure-driven processes, the apparatus and plants for each look very similar, and originally cellulose acetate was the base material of the membranes for both processes. But RO membranes do not have pores and are permeable only to water, so that RO is purely a concentration process. The principle of RO is quite different from that of UF. Water passes through an RO membrane by a solution/diffusion process and is opposed by the osmotic pressure of the solution being concentrated so that far higher pressures are used for RO than for UF.

Ultrafiltration has been used for a long time in the laboratory. For example, a most readable review of UF on this scale was
produced by Ferry in 1936 (1). More recently Glover et al. (2) have reviewed membrane processing with particular reference to milk and whey. The current interest in membrane processing arose from the discovery (3) just before 1960 of the technique of making cellulose acetate membranes on a large scale for commercial use. Reverse osmosis received the initial impetus from the American desalination program. This was then followed by developments in UF when it was realized that UF has a much wider application and that better membranes could be made from other materials.

THE FILTER RANGE

Ultrafiltration serves to concentrate molecules in the size range 1 \( \mu m \) down to \( 10^{-3} \mu m \), filtering out molecules below this level. This is the range of colloidal particles and macromolecules, including, for example, the casein micelle with a diameter of \( 10^{-1} \mu m \). The filter range is shown in Fig. 1 together with the sizes of the components of milk. This puts UF into perspective with other types of filtration.

THE ULTRAFILTRATION PROCESS

The simplest form of UF in the laboratory employs a sheet of membrane supported on a grid near the bottom of a closed beaker in which pressure can be maintained in the region of 200 to 500

<table>
<thead>
<tr>
<th>( 10^{-4} )</th>
<th>( 10^{-3} )</th>
<th>( 10^{-2} )</th>
<th>( 10^{-1} )</th>
<th>1</th>
<th>10</th>
<th>( 10^2 )</th>
<th>( 10^3 )</th>
<th>( 10^4 ) (( \mu m ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultrafiltration</td>
<td>Reverse osmosis</td>
<td>Microfilters</td>
<td>Fiber filters</td>
<td>Solution ions</td>
<td>Colloidal macromolecules</td>
<td>Suspension particles</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lactose</td>
<td>Whey</td>
<td>Casein</td>
<td></td>
<td>Salts</td>
<td>proteins</td>
<td></td>
<td></td>
<td>Water</td>
</tr>
</tbody>
</table>

**FIG. 1.** The filter range.
kPa (2–5 bar). A magnetic stirrer must be operated in the solution, and the arrangement is known as the stirred cell. A more sophisticated laboratory approach uses membranes in tubular or plate-and-frame assemblies and a peristaltic pump to provide a flow of the feed over the membrane. On the industrial scale, the same principle is scaled up to various levels of engineering sophistication incorporating pressure, flow, and temperature monitoring and automatic control. Plants are rated in terms of their membrane areas, which can be 100s or 1,000s of square meters.

The performance of the membrane is described by its retention of the large molecules and its rate of filtration, the permeate flux. If \( C_f \) is the concentration of a component of the feed, and \( C_p \) is the concentration of that component in the permeate, then retention \( R \) is given by

\[
R = \left[ \frac{C_f - C_p}{C_f} \right] \times 100
\]

In the ideal ultrafiltration of milk, \( R \) is 100% for casein and 0% for lactose.

Permeate flux is measured in liters per hour per square meter of membrane and quoted under standard conditions of operating pressure and temperature. Fluxes occur in the region of 150 liters m\(^{-2}\) hr\(^{-1}\) at 25°C for water, and 50 liters m\(^{-2}\) hr\(^{-1}\) at 50°C for milk at normal (\( \times 1 \)) concentration.

The most important aspects of an understanding of the principle of UF are the mass transfer through the membrane and the consequences of that transfer on the feed side of the membrane, where filtration is to proceed. Consider Fig. 2, representing a feed (milk) entering a tubular membrane from the left, having a permeate containing lactose, salts, and water removed by ultrafiltration and leaving on the right a product concentrated in fat and protein. The properties of the membrane that will affect its permeability are its pore size, its thickness, and its hydrophilic nature. The properties of the permeate that will affect its rate of flow will be the molecular sizes and shapes of its components, its viscosity, and its temperature, insofar as temperature will affect viscosity. Since the process is driven by pressure, the flux will be directly proportional to the
pressure difference across the membrane, but some of the applied pressure will be dissipated by the opposing viscous forces as the feed flows along the membrane tube. Hence, the pressure available for ultrafiltration will decrease as the feed moves along the tube.

At the membrane surface (the site of filtration), the retained molecules will collect and be concentrated as the permeate is extracted. Unless they are dispersed, they will hinder further filtration, and the permeate flux will fall. To ensure that the process continues, high rates of shear or large degrees of turbulence must be employed to move the solids away from the membrane and assist them to diffuse back into the main stream of the flow. Nevertheless, by the nature of the process, there will always be a higher concentration of solids near the membrane than in the main body of the feed. This increase of concentration in the direction towards the membrane is termed concentration polarization. Concentration polarization can never be eliminated; it can only be minimized. Equilibrium is set up between the rate at which solids are left at the membrane by the removal of permeate and the rate of their assisted diffusion back into the main flow of the feed. The level of concentration polarization will increase as the concentration factor of the

FIG. 2. Concentration polarization.
feed increases; hence, the permeate flux declines as concentration proceeds. In Fig. 2, concentration is proceeding as the feed moves to the right; hence, concentration polarization is more serious the longer the membrane tube. The polarized layer forms within seconds of the start of filtration, causing a rapid initial decline in flux. Flux can be increased by higher flow rates of the feed, but a compromise with energy expended in pumping must be accepted. In practice, flow velocities over the membrane in the region of 5 m/sec are used.

As concentration polarization increases, solids are deposited on the surface of the membrane and in the pores. To some extent deposition occurs after any ultrafiltration of milk, as demonstrated by measuring a pure water flux immediately afterwards and finding that it is considerably reduced from the level obtainable from a cleaned membrane. This deposit acts as a secondary membrane, greatly influencing the rate of filtration. Table 1 gives examples of thicknesses of deposits recovered from membranes that have ultrafiltered aqueous protein solutions at the concentrations listed.

Since the fluxes obtained from skimmed milk are only a little higher than those from whole milk, it is evident that fat is not the main hindrance to the process. Deposits consist mainly of protein: in the case of cow’s milk, β-lactoglobulin is responsible for the greatest decline in flux because of its ability to form layers of material (5).

<table>
<thead>
<tr>
<th>Protein (%)</th>
<th>Deposit thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1–0.3</td>
</tr>
<tr>
<td>4</td>
<td>0.7–2</td>
</tr>
<tr>
<td>12.8</td>
<td>6–12</td>
</tr>
</tbody>
</table>

*From ref. 4.
Following this description of the process, the factors governing the rate of ultrafiltration may be appreciated in summary:

1. area of membrane;
2. length of membrane;
3. pressure difference across the membrane;
4. rate of shear at the membrane surface or degree of turbulence in the flow stream;
5. concentration of the feed;
6. viscosity of the concentrate;
7. viscosity of the permeate;
8. hydrodynamic resistance of the membrane; and
9. hydrodynamic resistance of the deposited layer.

DIAFILTRATION

Since the small molecules and water pass through the membrane together, the concentrations of these components in the water phase in both the concentrate and the permeate will be the same. Thus, in the ultrafiltration of milk in which the concentration of lactose is initially about 4.8%, provided the retention of lactose during ultrafiltration is zero, the concentration of lactose in the permeate will also be about 4.8%, since both milk and permeate are approximately dilute aqueous solutions. If milk is diluted with water and ultrafiltration is continued, lactose will be removed with the permeate, producing a low-lactose milk. At the same time, the salts content will be similarly reduced. This combined process of dilution and ultrafiltration to wash out the permeating components is known as diafiltration. The usual method is to add water at the same rate as the permeate is being removed. Levels of the retained components may be adjusted as required by the appropriate amount of ultrafiltration.

If milk is taken as an example, a low-lactose milk of required composition may be prepared as follows (6): If
\[ V = \frac{m_w}{1 - R} \cdot \ln \frac{l_1}{l_2} \]

**MEMBRANE COMPOSITION AND STRUCTURE**

The first membranes were made of cellulose acetate. The cellulose molecule consists of two glucose units, each with three hydroxyl groups. Replacement of an average of 2.5 of these hydroxyl groups by acetyl groups produces the base for an ultrafiltration membrane. The breakthrough in membrane technology came with the discovery that it was possible to make a membrane with a very thin surface layer—the layer that is effectively the filter—supported on a much thicker and much more porous sublayer, which gives strength to the whole structure. These are the so-called asymmetric membranes now in general use. The thickness of the whole membrane is of the order of 100 μm, most of which is the sponge-like sublayer supporting the filtering layer, which is \(\sim 0.25\) μm thick. This structure is illustrated in Fig. 3.

The early membranes were made by dissolving cellulose acetate in acetone and adding a small quantity of magnesium perchlorate to serve as a swelling agent. This formed a gel from which the perchlorate could be leached out to leave a system of interconnecting pores. Heating the surface of this gel produced the tight skin, the thin ultrafiltration layer. Different porosities could be made by varying the time/temperature relationship of the heat treatment. The permeability of the layer is chosen as a compromise between a desirable permeate flux and a permissible loss of components from the concentrate.

Cellulose acetate as a material for membranes has some limitations, particularly for use on biological systems. Since it is an ester
and a polysaccharide, it is subject to hydrolysis, which limits its use to a pH range of 3 to 7 and an upper temperature limit of 35°C. It can also be affected by alcohols, some organic acids, and some bacteria. All of these impose limitations on the use and cleaning and sterilization of cellulose acetate membranes.

For these reasons they have now been superseded, first by polyamide and later by polysulfone membranes. The polysulfones are much more tolerant to temperature and pH, withstanding temperatures up to 80°C and pH values from 2 to 12. They also have better resistance to chlorine, compaction under pressure, and electrochemical action. The polysulfone membranes are now, in turn, being challenged by inorganic membranes of zirconium oxide made integral with their graphite supports. These are unaffected by temperatures up to 400°C, by pH values over the whole range 0 to 14, and by pressures up to 4 MPa (40 bar) and have great mechanical strength.
MEMBRANE CUT-OFF LEVELS

Membranes are made with stated molecular weight cut-off levels covering a very wide range, from 1,000 to 100,000. However, such specifications must be regarded as a guide rather than an expectation of performance. The size and shape of molecules more than their weight will govern their passage through a membrane, and the size distribution of pores in the membrane is more likely to be diffuse than sharp. Furthermore, in practice, deposits on the membrane will greatly modify the permeability of the system. Membranes used in milk processing have cut-off levels in the 5,000 to 20,000 molecular weight region.

MEMBRANE GEOMETRY

Membranes may be flat or tubular. They are attached to a supporting porous backing, which in turn is further supported by an outer perforated plate or tube. The most characteristic dimension of an assembly is the width of the flow channel between adjacent membranes, i.e., the space between the flat sheets or the internal diameter of the tubular forms. Flow channels between flat sheets are 0.5 mm to 2.5 mm wide; tube diameters range from 6 mm to 25 mm. Variations on these two configurations exist in flat membranes rolled into spirals and in tubular forms being reduced to 1 to 2 mm internal diameter, then known as hollow fibers.

The unit in membrane assemblies is called the module. This is either a pile of plates, a bundle of fibers or tubes, or a spirally wound assembly. Sizes of modules are quoted in areas of membrane that range from a few hundredths of a square meter for the laboratory to about 50 m² per module on the industrial scale.

ULTRAFILTRATION PLANT AND OPERATION

Apart from the membrane module assembly, the components of an ultrafiltration plant are normal centrifugal pumps, valves, pressure gauges, heat exchangers, all constructed in stainless steel to required hygienic standards if milk or whey is to be processed. Entrance and exit pressures for the membrane section are usually
about 5 bar and 2 bar; flow rates are in the region of 500 liters min\(^{-1}\); and the operating temperature is 50°C, safely below the temperature at which the whey proteins start to denature and away from the temperature most favorable to bacterial growth at 37°C. To reach any appreciable concentration, the milk must pass over the membrane many times. Operation can be either in a batch system, whereby after each pass the milk is returned to the starting tank, or in a continuous system, in which the milk is circulated over the membrane in a closed loop. A little of the concentrate is bled off continuously, and more feed is introduced at the entrance of the loop to keep the volume constant. In this latter method, the average retention time of the milk in the plant is reduced to a few minutes, which restrains bacterial growth. When this system is used industrially, during each 24-hr period the plant is run for 20 hr and is cleaned for 4 hr. Cleaning is with detergent to remove the fat, sodium hypochlorite or enzyme to break down the protein, and nitric acid to remove the minerals. Under these conditions, the life of a membrane is guaranteed for 1 year.

**MILK PROPERTIES RELEVANT TO ULTRAFILTRATION**

The composition of cow's milk is given in Table 2, and the corresponding molecular sizes are shown in Table 3. It can be seen from Tables 2 and 3 how appropriate ultrafiltration is for the separation of proteins from the lactose and salts in milk. Between α-

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (%)</th>
<th>Chemical nature</th>
<th>Physical state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fat</td>
<td>3.8</td>
<td>Triglycerides</td>
<td>Emulsion</td>
</tr>
<tr>
<td>Protein</td>
<td>3.2</td>
<td>Caseins; whey proteins</td>
<td>Colloidal solution</td>
</tr>
<tr>
<td>Lactose</td>
<td>4.8</td>
<td>Calcium phosphate</td>
<td>Solution</td>
</tr>
<tr>
<td>Minerals</td>
<td>0.7</td>
<td>Citrates</td>
<td>Bound and free</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Na and K chlorides</td>
<td>Solution</td>
</tr>
</tbody>
</table>
**TABLE 3. Molecular sizes of milk components**

<table>
<thead>
<tr>
<th>Component</th>
<th>Molecular weight</th>
<th>Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fat globule</td>
<td>—</td>
<td>4,000</td>
</tr>
<tr>
<td>Casein micelle</td>
<td>$10^7-10^9$</td>
<td>100</td>
</tr>
<tr>
<td>Blood serum albumin</td>
<td>69,000</td>
<td>5</td>
</tr>
<tr>
<td>β-Lactoglobulin</td>
<td>36,000</td>
<td>4</td>
</tr>
<tr>
<td>α-Lactalbumin</td>
<td>14,500</td>
<td>3</td>
</tr>
<tr>
<td>Lactose</td>
<td>342</td>
<td>0.8</td>
</tr>
<tr>
<td>Ca⁺⁺</td>
<td>40</td>
<td>0.4</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>35</td>
<td>0.4</td>
</tr>
<tr>
<td>Water</td>
<td>18</td>
<td>0.3</td>
</tr>
</tbody>
</table>

*From ref. 8.

Lactalbumin and lactose there is a very convenient large size interval at a level to suit the pore size of easily made UF membranes. The tables also illustrate that for filtration purposes it is much more realistic to think in terms of molecular dimensions than molecular weights, which could give misleading impressions of size.

Milk is by no means a commodity of constant composition. It varies with

- individuality of the cow,
- breed,
- feed,
- age of the cow,
- stage of lactation,
- season, and
- milking procedure.

However, on the industrial scale, large quantities of milk are bulked together, smoothing out these variations.

Viscosity is the most important physical property of milk relevant to ultrafiltration. Casein makes the largest single contribution to the viscosity of milk, rather more than the fat and considerably more than the whey proteins, the lactose, and the salts. Since casein
ULTRAFILTRATION OF COW'S MILK

plays such a major role, factors affecting the stability of casein, such as acidity, salt balance, and heat treatment, will all influence viscosity. As concentration by ultrafiltration proceeds, the viscosity of milk increases markedly. For example, the viscosity of skimmed milk, which is \(~1.5\) cP at 25°C at its normal solids concentration of 8.5%, increases sevenfold as ultrafiltration increases the solids content to 30%.

THE RATE OF ULTRAFILTRATION OF MILK

If whole milk is concentrated by ultrafiltration as a batch process, the permeate flux declines with the increase in concentration, as in Fig. 4. The concentration factor is the ratio in which the starting volume of the milk is reduced, which will also be the factor by which the concentrations of the fat and protein are increased if the retentions of these components are 100%, as is usually the case.

It will be seen that the practical limit of concentration is about four- to fivefold. Taking the composition of the starting milk from Table 2, the approximate composition of the concentrate is given in Table 4. In practice, it is found that the retention of lactose may be up to 10%.

![Graph](image)

**FIG. 4.** Ultrafiltration of milk. Decline of flux as concentration increases.
TABLE 4. Composition of the concentrate

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fat</td>
<td>15.2</td>
</tr>
<tr>
<td>Protein</td>
<td>12.8</td>
</tr>
<tr>
<td>Lactose</td>
<td>3.7</td>
</tr>
<tr>
<td>Minerals</td>
<td>0.6</td>
</tr>
<tr>
<td>Water</td>
<td>67.8</td>
</tr>
</tbody>
</table>

*Calculated on the basis of zero lactose retention.

If ultrafiltration is carried out on a feed and bleed principle, the average concentration factor in the membrane loop will be close to the final level. Hence, the flux curve will decline initially as in Fig. 4 and then continue horizontally near the required concentration for the main processing time.

For the concentration of skimmed milk, the flux curve will be a few, (=5) liters per square meter per hour above that for whole milk. Since the rate of filtration is controlled by the protein content of the feed, the flux from whey will be still higher and decline less rapidly with increase in concentration factor than the flux from skimmed milk. However, at comparable protein levels in whole milk, skimmed milk, and whey, the permeate fluxes are similar. The protein concentration in a 25-fold whey concentrate is about the same as in a fourfold milk concentrate. It is therefore possible to concentrate whey up to 20- to 30-fold.

APPLICATIONS OF ULTRAFILTRATION IN DAIRYING

The main application is for the manufacture of soft cheese, to incorporate the whey proteins and so increase the yield of cheese (9).

Whey is the liquid drained from cheese curd during cheesemaking. From 10 kg of milk, the yield of hard cheese is approximately 1 kg and 9 kg of whey is discharged, taking with it 50% of the
solids in the original milk. The composition of rennet whey from cheddar cheesemaking is given in Table 5. Milk ultrafiltrate consists of water, lactose, and salts; whey consists of water, protein, lactose, and salts. If for making cheese, milk is first concentrated by UF to a point at which there will be no further liquid to drain after the coagulation stage, i.e., no whey, the whey proteins will be retained in the cheese. This process is now established in industry with the advantage of an improved yield of cheese of about 15%. It is applicable only to the manufacture of soft cheeses, which have high water contents (in excess of 60%) that can be reached in the ultrafiltration stage. Milk is first concentrated up to fivefold, forming a "precheese." Starter and rennet are added, and the precheese is put directly into molds where coagulation takes place. Several types of soft cheese are now being made in this way, the largest production being in feta cheese, for which an increased yield of 21% above yields by traditional methods is claimed.

The same technique cannot be applied directly to the making of hard cheese, since milk cannot be concentrated to the level of the total solids in hard cheese, ≈62%. Development is in progress using a combination of UF and evaporation for making the harder cheeses (10).

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lactose</td>
<td>4.9</td>
</tr>
<tr>
<td>Protein</td>
<td>0.5</td>
</tr>
<tr>
<td>Nonprotein nitrogen</td>
<td>0.4</td>
</tr>
<tr>
<td>Fat</td>
<td>0.3</td>
</tr>
<tr>
<td>Ash</td>
<td>0.6</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>0.2</td>
</tr>
<tr>
<td>Water</td>
<td>93</td>
</tr>
<tr>
<td>Whey proteins</td>
<td></td>
</tr>
<tr>
<td>β-Lactoglobulin</td>
<td></td>
</tr>
<tr>
<td>α-Lactalbumin</td>
<td></td>
</tr>
<tr>
<td>Blood serum albumin</td>
<td></td>
</tr>
<tr>
<td>Immunoglobulins</td>
<td></td>
</tr>
<tr>
<td>Lactoferrin</td>
<td></td>
</tr>
</tbody>
</table>
Ultrafiltration of whey is practiced primarily to combat the problem of disposal of the large volumes of a liquid with very high biological oxygen demand (BOD) values and, secondly, to make better use of valuable nutrients than has been done hitherto. By a combination of UF to concentrate the protein, diafiltration to remove the lactose, and, finally, drying, a whey protein concentrate is being produced. It contains approximately 75% protein in dry matter and is used in the meat and bakery industries where its good functional properties make it an excellent substitute for egg white.

Extraction of the protein from whey does not solve the pollution problem, since the BOD resides in the permeate, which is mainly a lactose solution. Lactose is not of great nutritional value, but if it is hydrolyzed into its two component monosaccharides, glucose and galactose, a sweet syrup is produced. This can be done with mineral acids, ion-exchange resins, or by enzyme action. A process has been developed in which the permeate is passed through a column of silica beads holding the enzyme β-galactosidase (11). Over 90% of the lactose is hydrolyzed, and the product is used in the bakery, confectionery, and ice cream trades.

Alternatively, the lactose in the permeate can be fermented to produce alcohol. The process is already in commercial operation (12).

RECENT DEVELOPMENTS IN ULTRAFILTRATION

With improvements in membrane technology, the pore size distribution is becoming better defined. As an extension of the above separation of whole protein, there is now promise of fractionating individual whey proteins (13). There is a proposal for using ultrafiltration to produce an α-lactalbumin-enriched fraction from whey. Such a product would be of great interest in the medical field in the humanizing of cows' milk, since α-lactalbumin is the main protein in human milk. If whey is ultrafiltered over a membrane having a cut-off level of 20,000 molecular weight, the β-lactoglobulin will be retained, and the α-lactalbumin will pass into the permeate. A second stage of ultrafiltration using a membrane with
a 2,000 molecular weight cut-off for this permeate will retain and
concentrate the α-lactalbumin.

The enzymatic membrane reactor technique is suggesting new
uses. If an enzyme reaction is conducted in a container lined with
an appropriate UF membrane, the breakdown products of the action
will be passed through the membrane and can be collected, and the
enzyme can be retained for further use. In this way, the initial steps
of human digestion can be carried out in vitro, enabling predigested
proteins to be collected in the permeate (13). Such a product would
be helpful to those suffering digestive disorders, and indeed it is
known that a demand for predigested proteins exists.

Ultrafiltration on a laboratory or industrial scale offers the pos-
sibility of selectively concentrating the components of cow’s milk.
This is an important development for the bovine dairy industry and
provides a valuable model for those interested in the fractionation
of milk.

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