

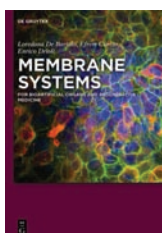
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**Integrated Membrane Operations**

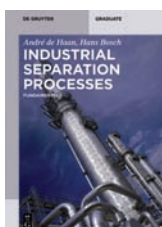
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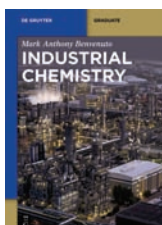
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# **Integrated Membrane Operations in the Food Production**



Edited by  
Alfredo Cassano, Enrico Drioli

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# Preface

Process intensification and membranes will play an important role to match the future challenges of agro-food production processes. One of the techniques to intensify processes by target enhancement is the integration of membranes into processing in order to exploit the interesting specific membrane operation properties.

This book aims to provide some relevant examples of integrated membrane operations in agro-food productions, highlighting their contribution for an industrial sustainable growth in this area in terms of energy consumption, reduction of environmental impact and product quality.

Each chapter reports successful examples of integrated membrane processes in different agro-food sectors, including selected information on basic principles of membrane unit operations, commercial applications and an overview of current research and development.

The first chapter (Cuperus and Franken) focuses on ongoing development works based on the use of membrane technology for the production of green products, better and/or natural products.

In Chapter 2 (Lutz and Gani) the integration of membrane processes in agro-food production is analyzed according to the process intensification strategy.

Integrated membrane operations are reviewed and discussed in different agro-food areas such as fruit juice processing (Chapter 3 – Cassano, Conidi and Drioli), citrus processing (Chapter 4 – Cassano and Jiao), milk processing (Chapter 5 – Mucchetti), whey processing (Chapter 6 – Gésan-Guiziou), winemaking (Chapter 7 – El Rayess and Mietton-Peuchot), brewing and sugar production (Chapter 8 – Lipnizki and Ruby-Figueroa), stevioside purification (Chapter 9 – Mondal and De) and purification of soy extract (Chapter 10 – Mondor).

The concentration of polyphenols (Chapter 11 – Tsibranska and Tylkowski) and the recovery of bioactive compounds (Chapter 12 – Brazinha and Crepsio) from food processing streams through membrane-based operations are also analyzed.

Chapter 13 (Giorno, Mazzei and Piacentini) and Chapter 14 (Charcosset) focus on emerging membrane processes, such as biocatalytic membrane reactors and membrane emulsification, in integrated processes for the production of nutraceuticals and innovative food formulations.

Basic aspects of electrodialysis, as well as its application in integrated processes for food applications, are discussed in detail in the concluding chapter (Chapter 15 – Roux-de Balmann).

The editors would like to take also this opportunity to thank all the authors for their expert contribution to this volume.

Enrico Drioli  
Alfredo Cassano



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*Chapter 11*

# 1 Membrane applications in agro-industry

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## 1.1 Introduction

Membrane technology is an important part of the engineer’s toolbox. This is especially true for industries that process food and other products with their primary source from nature. However, in many applications these membranes are typically used as end-of-pipe technology, e.g., membranes being used to handle or recycle waste water. In other applications, membranes are used to facilitate production or to improve the products. For example, surface water is purified to grow stainless red tomatoes. Many such applications have been previously described in literature and patent applications. For reference, some of these applications are shown in Table 1.1.

This chapter is focused on ongoing development work using membranes. The work is related to agro-business and is driven by the demand for green products, better products and/or natural products. Specifically, this is exemplified by a range of development work on extracting plant compounds for food, cosmetics and wellbeing products. On the other hand, in the more classical “total crop approach”, membranes are thought to have an important role in the future. Very often, the term “biorefinery” is used for all types of cascade that are used for stripping a typical crop-related material. Furthermore, examples of biofuels, especially second and third generation fuels, keep popping up.

We will also discuss some research related to vegetable oils and fat processing. These involve new directions for oils such as canola and rapeseed as well as some tropical oils.

## 1.2 Membranes in biorefinery

### 1.2.1 What is biorefinery?

The American National Renewable Energy Laboratory (NREL) defines a biorefinery as “a facility that integrates biomass conversion processes and equipment

**Table 1.1:** Examples of applications of membrane technology related to agro-food processing

Application	Main action/product	Reference
Greenhouses	Softened water provides better products (e.g., stainless tomatoes)	[1]
Apple juice fabrication	RO to concentrate, UF to clarify juice	[2, 3]
Whey processing	Various	[4, 5]
Winery	Decolorization of red wine	[6, 7]
Potato industry	Waste water treatment	[8]

to produce fuels, power and chemicals from biomass. The biorefinery concept is analogous to today's petroleum refineries that produce multiple fuels and products from petroleum" [9].

Biorefineries stimulated the use of biomass, but because of the oversupply of raw materials in our food chains in the past, there was no strong driver to improve the efficiency in using biomass. However, the increased request in food and non-food applications calls for a change in attitude in the interaction between food and non-food chains.

In this section, some processes will be described that enable both further processing of food products as well as the use of the remaining non-food products (waste).

### 1.2.2 Mild extraction techniques

In many cases, spent biomass in the Netherlands is either burned or composted. However, biomass can also be used for biorefinery because it contains a score of useful components. In biorefinery the biomass is separated into different components that can be used after further processing and separation. To separate the biomass (from plant, field crop, wood, algae, etc.) in different components, the biomass needs to be pretreated in such a way that the functionality of the constituents is not lost. Using destructive processes (such as pyrolysis or thermo-chemical treatment) the constituents are broken down in such a way that they are no longer fit for high-quality applications. Using mild pretreatment processes, the desired components are extracted and remain intact for further processing. Waste streams are minimized in this setup and the yield of the biomass process is maximized.

The present state of the art mild extraction techniques for biomass mostly consist of grinding of the biomass to pulp. In this way, the cell structure is ruptured and the cell content is released. This processing method is effective with respect to the release of the desired components from the cells, but it also has the disadvantage that the cellulose-like plant material is reduced and will be present as suspended solids in the solution. These suspended solids cause all sorts of problems in further downstream processing.

Another approach to pretreat biomass streams is to consider the extraction and separation processes as one. The pretreatment process consists of a mild extraction step followed by a mild separation technique. In this case, it is of the utmost importance that the extraction and separation steps are geared to one another.

From the point of view of the separation techniques, it is important that the extraction techniques are chosen in such a way that the separation can be "simplified". For example, an extraction technique that minimizes the amount of suspended solids will make the membrane process easier and more effective. In the case of "waste streams" this approach is particularly important.

Mild extraction techniques that meet the above criterion, amongst others, are: cold aqueous acid extraction, enzymatic extraction, ultrasound, pulsed electric field (PEF) and extraction using CO<sub>2</sub>. Any technique that does not alter the properties of the desired products can qualify as a mild separation technique. As such, membrane techniques and chromatography are typical mild separation processes.

Using this mild extraction and separation process, specialty and/or fine chemicals (e.g., omega-fatty acids, antioxidants, dyes and other bioactive compounds) can be isolated for use in chemistry, pharmacy and the human food industry. The rest stream can be used in application with a lower value, such as animal feed stock and/or biofuel.

Techniques for mild extraction are, among others:

1. Milling and pressing. This is the oldest and most used of the mild extraction techniques. The technique in its most basic form is simple, and consists of chopping up the biomaterials and milling it down to a pulp. In a combined step the material is pressed to gather liquid juice from the plant material. As a result, a concentrated solution is obtained that contains the contents of the plant cells; but cell debris and chlorophyll will be also present in this solution.

Although this technique does not fit the criterion that the amount of suspended solids is minimized, the fact that desired materials such as proteins are not denatured means that this process is often referred to as “mild”. In this chapter the technique is listed for comparison reasons.

2. Enzymatic extraction/treatment. Enzymatic treatment of the biomaterial is often used as a pretreatment to aid a further extraction step. In most cases, either an enzyme is added or naturally occurring enzymes are used to weaken the cell structure in order to facilitate the extraction process. This step is often used in combination with milling and pressing.
3. Cold aqueous acid (lactic acid) extraction [10]. In this process a slurry is prepared by dispersing the biomass comprising the naturally occurring microorganisms in an aqueous liquid. In this slurry the conditions have to be chosen in such a way that an aerobic digestion by the microorganisms can take place, in which the naturally occurring microorganisms are capable of converting saccharides into lactic acid. As a result of these conditions, the cells structure is weakened and (part of) the cell content is dissolved into the liquid phase of the slurry.

Using this method (part of) the cell content is released into the slurry in a controlled manner, leading to only a clear solution with no or hardly any cell debris. This method is only one of several used for removal of minerals from road-side grass (see section 1.2.4).

4. Ultrasound. Under intense sonication, enzymes or proteins can be released from cells or subcellular organelles as a result of cell disintegration. In order to extract the desired components, the cell membrane must be destructed. Cell disruption is a sensitive process and good control of this is required to avoid an unhindered

release of all intracellular products, including cell debris and nucleic acids. In addition, product denaturation should be avoided. Ultrasound achieves greater penetration of a solvent into a plant tissue and improves the mass transfer. Ultrasonic waves generating cavitation disrupt cell walls and facilitate the release of matrix components [11, 12].

5. Pulsed electric field (PEF). PEF is a technology that causes biological cells to be ripped open and perforated. During the process, the biological cells are subjected to an electric field with high field strength, allowing plant and animal cells to be opened up. At higher power settings, microbial inactivation will follow. The high electric field perforates the cell membranes of bacteria and thereby causes their inactivation. By making use of intense but short high-frequency pulses, there is only slight heating of the product itself while the bacterial inactivation effect remains. In order to generate the PEF, both a source and a treatment chamber are required. The treatment chamber consists of at least two electrodes, with an insulating region in between, where the treatment of the product takes place [13].

The PEF process holds promise as a more efficient way of getting useful products out of cell membranes. PEF is particularly well-suited to processing fruit and vegetable juices because the enlargement of the cell pores makes juice extraction easier. PEF may be useful in extracting sugar from sugarbeets and oils from oil bearing plants. PEF may have a use in the developing field of extraction of oil and other products from microorganisms such as algae [14].

6. Supercritical CO<sub>2</sub>. Supercritical fluid extraction (SFE) can be used to either remove unwanted material from a product (e.g., decaffeination) or collect a desired product from a solid matrix (e.g., essential oils from herbs). The process relies on the solubility of the extracted compound in supercritical CO<sub>2</sub>. Process parameters such as pressure and temperature can be altered, allowing for selective extraction. For example, volatile oils can be extracted from plant material at low pressures and both oils and lipids can be extracted using higher pressure [15].

Little is known about the use of supercritical CO<sub>2</sub> in extracting valuable components from biomass. Feyecon has carried out successful tests on the extraction of oils from algae, but first cost calculations showed that the process is not viable for large-scale harvesting applications, at least at this moment [16].

### 1.2.3 Use of membranes in biorefinery

The use of membrane technology in downstream processing strongly depends on the way the products are extracted. The traditional way is milling and pressing of biomass, either pretreated or “green”. In both cases, a considerable amount of suspended solids is generated, mainly caused by the cell debris in the solution.

In this case the membrane technology must be suited to handle a considerable amount of fouling. This means that the used equipment must be able to generate a considerable shear to minimize the fouling and concentration polarization effects.

### 1.2.3.1 Crossflow

Crossflow is one of the oldest methods to avoid membrane fouling. For detailed descriptions of the crossflow principle, the reader is referred to the many textbooks on membrane technology [17–19]. This principle of operation is applied to the difficult filtration of solutions and suspensions, where high shear and good mass transport are necessary to avoid the build-up of particles or macromolecules at the membrane surface. The most common method to realize the high shear is by pumping the feed solution at high speed in relation to a stagnant membrane (module).

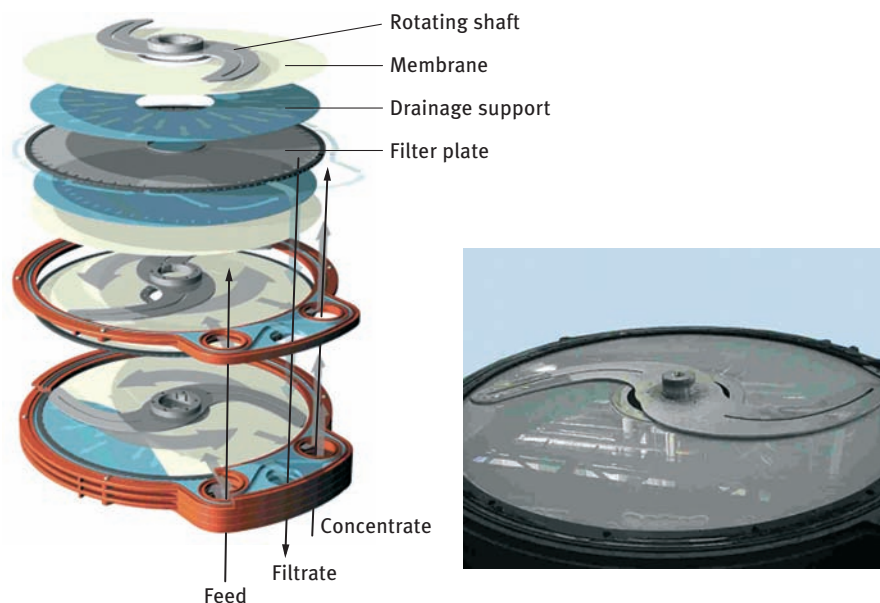
One of the biggest drawbacks of crossflow membrane filtration, especially when the high shear is realized by pumping the feed around, is the energy consumption. The relation between flow going into the membrane module (thus feed-flow + recirculation flow) and permeate flow can be as high as 50. This means that a large proportion of the energy is not used for filtration, but for moving the feed along the membrane. In contrast, (semi) dead-end operations or reverse osmosis (RO) are operated in a single pass, meaning that all the pumping energy is effectively used for filtration.

Several investigations have been conducted to reduce the energy consumption in the filtration process while maintaining a high mass transfer coefficient and to lower the membrane resistance. Some of these methods are as follows:

- Module design. Improvements to module design to stimulate the mass transfer involve constructions such as the use of flow diverters or sectioning of the (large) modules in order to get a better flow distribution and avoid channeling. Flow diverters can be used in any type of membrane.
- Cross-rotation filtration in which a rotating shaft between the membrane plates is used to create a high crossflow velocity.
- The other method of rotation in membrane system is by using rotating discs.
- Vibration-enhanced membrane separation, which is the last method to be discussed in this section.

### 1.2.3.2 Cross-rotation (CR) filtration

The principle of CR filtration is shown in Figure 1.1. In a CR filtration system, plates, support layers, membranes and rotors are assembled in a vertical sandwich form. An outer frame and two massive plates at the bottom and the top, along with the plate and rotor stack, comprise a compact unit. A rotating shaft in the middle of the plate stack moves the rotors, creating a velocity  $>10$  m/s over the membrane surface [20].



**Figure 1.1:** (A) The principle of cross-rotation filtration and (B) view onto an open plate stack [20]

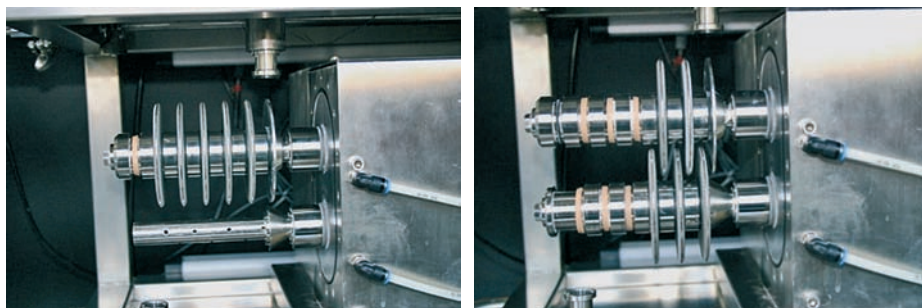
CR filters are developed for use in “open” ultrafiltration (UF) and microfiltration (MF) applications. Compared to conventional membrane systems, this design allows higher specific filtrate flow rates to be achieved. Pressure drop within the CR filter is minimized because feed and flow over the membranes are independent of one another. Concentration polarization and cake-layer formation on the membrane surface is suppressed by high crossflow conditions. This system is specifically used when a high concentration of the feed is present or required. Typical applications are fermentation broths, pulp bleaching solutions, sludge and polymer solutions [20].

### 1.2.3.3 Rotating membranes

Improvement of the mass transfer can also be achieved by rotation of the membranes. Membrane systems that use a stack of rotating membranes in different configurations have been developed in various configurations. In contrast to the system of CR filtration as described above, here the membrane stack is rotating. Very often, membrane stacks using ceramic disks are used as they provide the necessary stiffness for the membrane stack. In these systems the following module types are used:

1. Single shaft disk filter system (see Figure 1.2 left). In this system, one stack of rotating membranes is used. In most cases a stagnant flow diverter is used inbetween the rotating stack for an improved shear at the membrane surface. Also, the method of supplying the feed to the system influences the shear forces at the membrane surface.





**Figure 1.2:** (A) Single shaft disk separator and (B) double shaft disk separator

2. Double shaft disk filter system (see Figure 1.2, right). In this system two stacks of rotating membranes are used. It is preferable that the two shafts rotate counter-current to create the maximum shear forces at the membrane surface. This membrane overlapping can increase the permeate flux considerably (the magnitude depends very strongly on the type of feed and the crossflow conditions) [21].

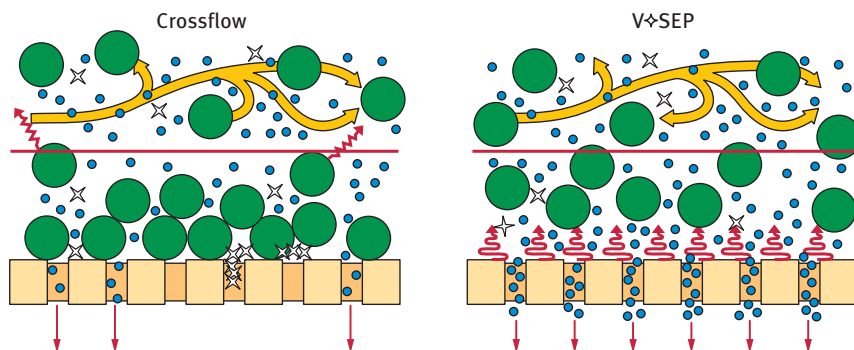
For an overview of dynamic shear-enhanced membrane filtration (a review of rotating disks, rotating membranes and vibrating systems) the reader is referred to the paper by Jaffrin [22]. This paper reviews various systems of dynamic filtration, also called “shear-enhanced filtration”, which consists of creating the membrane shear rate necessary to maintain the filtration by a rotating disk, or by rotating or vibrating the membranes. This mode of operation permits very high shear rates, of the order of  $(1\text{--}3) \times 10^5/\text{s}$  and to increase both permeate flux and membrane selectivity [21, 22].

#### 1.2.3.4 Vibrational membranes

The traditional method of reducing the effect of fouling in membrane systems is to operate with crossflow of the feed over the membrane. The economical limit to crossflow velocity (mainly caused by limits in module design and energy costs) is given by a shear rate of typically 10,000–15,000/s. As such, the membranes in crossflow operations will still be subject to fouling, because the flow cannot remove solids and particulate retained within the turbulent boundary layer [23].

An alternative method of creating increased shear rates at the membrane surface is to move the membrane itself. The principle of vibratory membrane filtration has been known for more than 20 years. Pall introduced the Pallsep vibrating membrane filter (VMF) that uses an oscillating disc filter stack vibrating at approximately 50 Hz about a vertical axis. With such a system, shear rates in the order of 100,000–150,000/s are generated at the membrane surface (see Figure 1.3 for a comparison of crossflow and vibratory membrane filtration) [23].

The shear developed at the membrane surface is independent of the feed-flow rate. This allows independent control of system pressure and shear rate. This



**Figure 1.3:** Boundary layer resistance in crossflow (left) and V-SEP (right) [22]

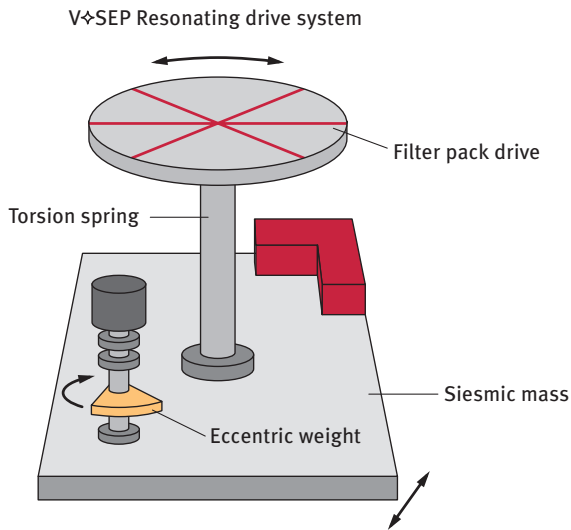
operational feature makes a vibratory system well-adapted to handle high viscosity fluids. It also permits operation with high recoveries (high permeate to feed ratio) such as 0.95 vs. less than 0.1 for most crossflow operations [23]. The main use of the Pallsep VMF system is in biotechnological applications (e.g., microfiltration of fermentation broths).

An industrial version of the Pall system is developed by New Logic. They introduced the V-SEP (vibratory shear-enhanced processing) [23]. Like the Pall system, V-SEP moves the membrane (leaf) elements in a vibratory motion tangential to the face of the membrane. The feed slurry moves at a low velocity between the parallel membrane leaf elements. The shear waves induced by vibration of the membranes repel solids and foulants from the surface, giving free access for liquid to the membrane pores.

A V-SEP system has only two moving parts: the torsion spring (on which the membrane module is mounted) and the bearings. The vibration is induced using a motor with an eccentric weight that is mounted on a metal plate (the seismic mass) supported by a rubber mount. The induced vibration frequency (typically 50 to 60 Hz) is transferred to the membrane module using the torsion spring [23]. The V-SEP resonating drive system is shown in Figure 1.4.

The stack of discs is moved at high speed in a torsional oscillation with an amplitude of up to 1.5 inch at 50–60 Hz, thus creating a shear rate of around 150,000/s, which is more than 10 times higher than the maximum shear in crossflow operation [23]. Unlike crossflow filtration, nearly 99% of the total energy utilized is converted to shear at the membrane surface.

It should be noted that the magnitude of the flux increase as compared to conventional crossflow strongly depends on the type of membrane process and the type of application. For example, in particle filtration using micro- or ultrafiltration membranes, a flux of more than five times can be achieved. In this case, the increased shear not only lifts the particles but also allows the process to be carried out at increased



**Figure 1.4:** V-SEP resonating drive system [22]

pressure without the adverse effect of cake-layer formation. The filtration efficiency of typical strong fouling processes like broth filtration is increased by a factor of five to ten.

In addition to a better filtration efficiency, another advantage of this process is that it has the ability to concentrate solid content to a much higher end, and also that the slurry can become viscous without blocking the modules.

As might be expected, the effect of relative flux increase is less pronounced with processes such as nanofiltration (NF) or RO. In these processes the stagnant boundary layer is less pronounced. However, the other advantages – high concentration and possible high viscosity – remain. If a V-SEP module is compared to spiral-wound elements, it has the advantage that feeds with high viscosity and/or fouling potential can be used without the fear of plugging the feed spacer.

Although all the technical equipment shown above is quite impressive, it must be noted that the cost of this equipment and the membrane modules is a manifold of the “standard” capillary or spiral-wound membrane module.

Of course, if extraction techniques are used that do not generate large amounts of suspended solids, the process can be simplified considerably. In these cases a “standard” capillary or spiral-wound membrane module can be used. Furthermore, the fluxes and separation properties of the latter systems will be better: not because of the module or system design, but simply because foulants (i.e., suspended solids) are absent.

In the next section an application is presented that does not require expensive membrane equipment, because a mild extraction technique is used.

**Table 1.2:** Relative costs of different membrane processes

Process	Equipment costs	Operational costs	Typical use
Dead-end	Low	Low	Only low fouling aqueous streams
Crossflow	Medium	Very high	Fouling streams
Cross-rotation	High	Medium	High fouling streams
Rotating membranes	Very high	Low	High fouling streams
V-SEP	High	Low	High fouling and viscosity streams

#### 1.2.4 Removing minerals from road-side grass

Biomass of plant origin may be combusted, directly yielding energy in the form of heat, or it may be converted into convenient energy carriers, for example combustible liquids such as hydrocarbons or alcohols, and combustible gases such as methane.

The handling and conversion of biomass of plant origin, however, is difficult because of its physical characteristics, in particular morphology, and because the biomass comprises components that disturb or are harmful in combustion or conversion processes.

Undesirable components of biomass of plant origin comprise of carbohydrates, chlorides, alkali metal and alkaline earth metal salts, calcium and magnesium salts, ammonium salts, proteins, ash precursors and water. Unpleasant odors may affect the environment, in particular when drying or when combusting the biomass.

Many attempts have been made to treat biomass in order to bring it into a form suitable for the production of energy or energy carriers. Such treatments included the following steps:

- Grinding, cutting, milling, or other mechanical treatment aiming at particle size reduction.
- Extrusion, pressing or heat treatment aiming at destruction or opening of the biomass cell structure, or removal of water.
- Extensive heating or roasting, aiming at melting or pyrolysis, yielding fuels, such as charcoal, tar or gas.
- Treatment with strong acid or strong base, or oxidising agents, aimed at conversion of the biomass lignocellulosic components and making them digestible by enzymes.

All these methods result in a slurry that on one hand has not reduced the contents of the undesirable components to a level required for combusting the biomass, and on the other hand creates a liquid phase with a large amount of suspended solids.

The presence of the suspended solids would then require an expensive separation technique, making the process not economically viable.

Danvos has described an alternative process for the conversion of biomass into a biomass product that is suitable for use as a fuel [10]. The biomass is of plant origin and comprises microorganisms naturally occurring in the biomass. The process comprises of the following steps: (i) preparing a slurry by dispersing the biomass, including the naturally occurring microorganisms in an aqueous liquid; (ii) maintaining the slurry at conditions suitable for aerobic digestion by the microorganisms to obtain a slurry comprising the biomass product as a dispersed solid phase; and (iii) recovering the biomass product. The recovering process comprises of washing and drying the biomass product. The recovered biomass product can be used in a combustion process after pressing and drying [10].

The resulting liquid phase does not contain any suspended solids. In this way, water can be recycled using the same spiral-wound membranes for nanofiltration and RO as used in water treatment. The concentrate of both steps can be used in bio-conversion processes (concentrate of NF) and as inorganic fertilizer (concentrate of reverse RO).

### 1.2.5 Biofuel including microalgae

In the last 10–15 years there has been an increasing interest in the production of chemicals and fuels from renewable resources [24]. Reasons for this trend include growing concerns about global warming and climatic change, volatility of oil supply, increasing instability of crude oil price and existing legislations restricting the use of nonrenewable energy sources. As mentioned previously, several scenarios have been proposed for using new and existing agricultural crops and activities into valid products, but nowadays they are merely included in biorefinery concepts [25–27]. The “first generation biofuels” mainly involve production of carburants from sugar and oil sources – i.e., ethanol and biodiesel – that also could be used for food purposes. To avoid this unhealthy competition, much effort has been put into the “second generation biofuels” that are based on indigestible parts of the food chain or on typical sources that are considered to be waste. These include large parts of sugarbeet and waste from agricultural crops, but also grass, straw etc. Via a combination of processes, liquid or gaseous biocarburant is generated: typically bioalcohol and biogas. “Third generation biofuels”, e.g., from oil algae, are made via alternative “agricultural production schemes” that do not conflict with regular food-oriented agricultural activities. The exploitation of these sources is mainly lab-scale and larger pilot-scale experiments are oriented at learning probable production schemes. It is expected that algae can produce oil and some bioalcohol. There are many types of algae studied and they typically produce a range of products. This is biorefinery at its best, and at this

moment it is difficult to say which method will come up with winning combinations [28, 29].

However, first generation biofuels are hardly biorefinery products, as the sources are specially grown for making fuels and waste is considered to be just waste. In second generation biofuels, production is aimed towards zero-waste, at least during the generation of fuels, because waste still could be an unwanted by-product. In spite of this, for the main liquid biofuels (bioalcohols) and either first or second generation biofuels, production processes are fairly analogous and basic steps include hydrolysis, fermentation and alcohol refining. Therefore, technical and economic bottlenecks in first and second generation biofuel processing lay in their upstream and downstream processing, with some small differences.

One of the main bottlenecks of bioalcohol production is the refinery to almost pure alcohols that can be used as fuel or as fuel additive. The main three biofuels based on alcohols: butanol, ethanol or acetone-butanol-ethanol (ABE) are all produced at low percentages in fermentation (typically <5 wt%) and have to be rectified. These processes were devised in the 1900–1910s, as excellently reviewed by Garcia [25], but their development has been discontinued by the use of petrochemical oil. Membranes are envisioned to be used in the low-alcohol end (5–40%) by organophilic pervaporation and in overcoming the azeotrope at the high alcohol percentage. The latter can be achieved by either pervaporation or vapor permeation. Overcoming the azeotrope by vapor permeation is now well-practiced in many first generation fuel processes in the US that use corn as carbohydrate source. Vapor permeation (VP) is preferred over pervaporation as it integrates more easily with distillation and the fouling problem is hardly an issue. The latter is easily understandable as most severe membrane foulants are non-volatiles and they are not present in a vapor. Usually in these processes the VP unit is integrated with the distillation column that performs the trajectory from the low-end alcohol directly from the fermentor. By clever engineering, the energy costs of the operation are significantly reduced compared to classical processes. Interestingly, typical membranes used in this area can be polymeric (PVA-PAN membranes) as well as ceramic membranes (zeolite membranes) [25].

In the downstream part coupled to the fermentation, a lot of research is still being undertaken. This is partly because extraction of the alcohols at low levels keeps the bioproduction at a good level. Also, on many agricultural sites there is no rest-heat to accommodate the first parts of the distillation easily. Moreover, one can understand that if a type of (semi-) continuous fermentation is envisioned, alcohol recovery at low temperature is desired. Using typical organophilic membranes, e.g., poly-di-methyl-siloxane (PDMS) membranes, the principles of such setups have been shown. However, there remain problems that are frequently caused by too-low selectivity or long-term fouling. Typically, organophilic PDMS yield a selectivity ( $\alpha$ ) of 7 for ethanol and somewhat higher for butanol. Many researchers have screened materials for a more selective membrane. Interesting selectivities have been found using zeolite-filled PDMS ( $\alpha$  EtOH~40), PVTMSP ( $\alpha$  EtOH~26) and PEBA ( $\alpha$  EtOH~25).

However, in the long-term selectivities tend to lower towards uneconomic values. This is mostly attributed to minor components (butyric acid as one prominent) from the fermentation broth, which are assumed to cause fouling. Using an extra filtration step (NF) to prevent fouling results in too high costs. Using a cleaner substrate helps, but as components as butyric acid are generated in fermentation their presence seems unavoidable [27].

From the third generation fuel production methods the use of microalgae seems the most prominent. In principle, one may regard microalgae systems as sunlight harvesting devices. Using nutrients and sunlight, algae can be pushed to produce carbohydrates or oils but also a number of other compounds that are thought to be useful in cosmetics or healthcare. These include special proteins, PUFAs carbohydrate building blocks [28, 30]. The outcome of a certain process depends on the algae system that is cultivated and the environment during the production. The production of algae oil is often regarded as third generation biodiesel. In its simplest process form it only requires drying and pressing to make biofuel (however, drying can already be costly if not done in sunlight only). Today it is questionable whether microalgae can be economically viable with biofuel income as the only return on investment, hence much research is devoted to the reclaim of more precious components.

Worldwide, the interest in microalgae is enormous. In the USA alone more than 500 MUS\$ has been raised by different companies to work on algae processing, tackle engineering problems and launch new products. Microalgae were originally grown in water basins but today a large array of vertically hanging polymer bags is considered to be the most effective method. During photosynthesis, the algae absorb  $\text{CO}_2$  and nutrients and generate carbohydrates. Fully-grown microalgae have to be separated from water and further processed. MF and UF systems [31] were considered to have a role here, but the energy requirements are a major concern. Currently, suction mode UF or MF seems to be the most promising technique [26]. After harvesting the algae, they have to be opened up and extracted to yield their interesting products. Here, membrane filtration is also considered for different routes. In particular, in upstream processes membranes are envisioned, but as these can hardly be seen as real production systems we do not go into detail in this book. Some of these also produce little amounts of ethanol that are also thought to be recovered. To this end, again pervaporation is explored.

Of course, in an ideal scheme the microalgae would excrete their beneficial products. This requires microalgae and cultivation routes other than those fostered so far. In an alternative method the mild extraction technologies presented in section 2.2 could help to harvest the oil from the microalgae. For example, OriginOil's algae single step oil extraction process harvests, concentrates and extracts oil from algae, and separates oil, water and biomass in one step. The process does not use chemicals or heavy machinery and no initial dewatering is required; and it separates the oil, water and biomass in less than 1 hour. The company's Quantum Fracturing technology combines with electromagnetic pulses and pH modification to break down cell





**Figure 1.5:** Pilot plant for recovery of ABE from fermentation using pervaporation (courtesy of Pervatech.com). The same type units may be used for bioethanol and aroma recovery

walls and release oil from the algae cells [32]. Although no details are disclosed, it looks like acid conditions are used to weaken the cell structure, and electromagnetic pulses (PEF) are used to perforate the cell walls. The oil is then released into the aqueous system and is separated by gravity. In particular, the fact that no suspended solids are present improves the separation efficiency. Again it proves that mild extraction is beneficiary in further downstream processing.

## 1.3 Membranes in vegetable oils and fats

### 1.3.1 Membrane technology applied to vegetable oils

Research in the use of membrane technology for oils and fats has been mostly directed at solvent recovery, processing of the miscellae, degumming, bleaching deacidification, hydrolysis of triglycerides and esterification to obtained structured lipids. The most recent focus is on processing of minority components that could have added-value in specialty food, wellbeing products or pharmaceutical-oriented products [24].

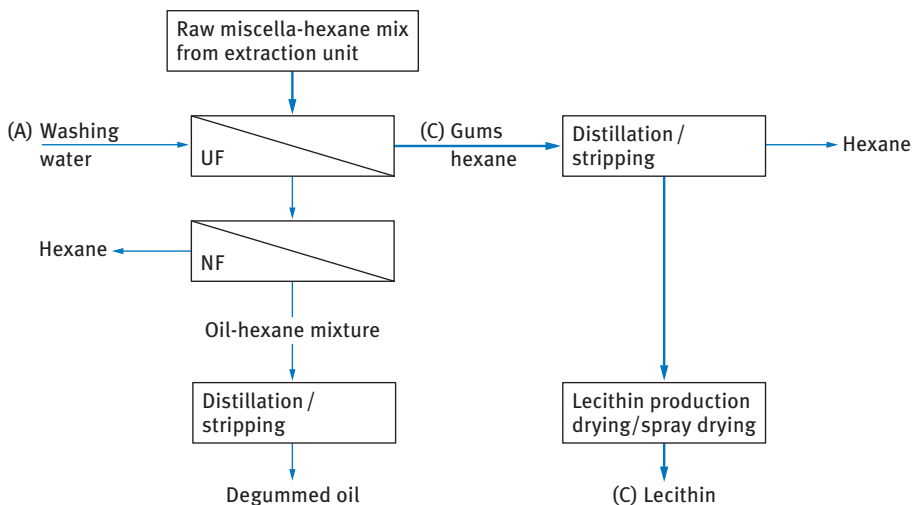
Historically, a lot of developmental work has been dedicated to degumming, for various reasons. The first work was dedicated to replace water degumming and partial deacidification [33]. One of the main ideas behind this was that fewer chemicals would be needed and it would yield a product quality improvement and less waste. The process originates from the 1980s and from then on many variations have been described. However, even though considerable scaling-up has been done, in one



way or another these efforts never materialized into economic viable process alternatives. One of the main reasons for that is a lack of fouling control as well as the overall costs of the process [34]. Moreover, in a number of production processes, e.g., hexane recycling, considerable lower energy costs were forecasted for the use on membranes. However, as the heat balances of large-scale processes in oil and fat extraction are very much coupled, such energy costs are already low and this hardly improves with the advent of membranes. In addition, process economy of the traditional processes has been improved, and other alternatives have been developed. Hence, less driving force remained for further developments [35–41].

The area where membrane degumming remains interesting is the niche application of fabrication of high-quality lecithin. Using a membrane process reduces heat input – although some hexane still has to be evaporated – and less heat yields a better product. In principle, such a process can be used for various seed oils like rapeseed, sunflower and canola. As the oil and phospholipid concentration may be quite high in such applications, concentration polarization and fouling are important factors. Moreover, for oils like sunflower the plugging of pores by waxes can considerably attribute to flux decline [42, 43]. Several procedures have been tried to counteract such phenomena, but literature hardly mentions the solutions that may have been found.

Many concepts of seed oil refining using membrane technology are inspired by the work of Unilever in the 1980s [33]. Many variants of this concept have been published [44, 45]. The setup shown in Figure 1.6 illustrates degumming using water and UF, thus largely avoiding chemicals. The gums (phospholipid) concentrate (B) now will also include free fatty acids and some non-triglycerides. In another embodiment,



**Figure 1.6:** Degumming using membrane technology. Many variants have been proposed, and a major aim is to operate with the minimum of chemicals

water is not added to (A), and (B) largely consists of phospholipids and hexane that is purer than in the first option. The latter setup is mainly aimed at production of “natural lecithin”, hence without the interference of chemicals. Such a process is mainly focused on high-quality lecithin and is therefore destined to be at a relatively small scale. The NF step pictured in Figure 1.6 for the recovery of hexane after extraction is optional. For the current large-scale seed oil extraction processes, it is forecast that NF is not economically viable. From the first processing steps (seed pretreatment and mechanical pre-pressing) so much heat can be recovered that the heat for hexane evaporation is easily provided for.

From the work done in the advent of this process (in the 1980s) it is suggested that the type of membrane was not very critical for the final result. As long as it was “tight UF” it worked. However, work after that showed that long-term stability could be an important factor. In addition, tightness of the membrane sometimes seems to have an influence on the final product that is generated. Apart from the fact that the membrane should retain phospholipids, a tighter membrane may also (partially) reject other components such as phytosterols, and /or natural antioxidants like tocopherols [34, 37]. These components have a beneficiary influence on the lecithin produced. Such effects could also be obtained by securing low but not zero water levels in the feed of the membrane. Logically, this is related to the “colloidal” behavior of the feed stream. Water promotes miscellea formation and these in turn can capture several components in their vicinity. It seems also clear that water content has an influence on fouling and concentration polarization in the membrane process, so care has to be taken.

### 1.3.2 Solvent recovery and reuse

The recovery of extracting solvent in vegetable oil has been studied by many researchers. One of the main ideas was that by using membrane, lots of energy could be saved. At first glance, in large-scale application this seems to be the case. However, for many seed oils the desolventizing action is coupled to “toasting” (a process to inactivate enzymes and facilitate oil exit from the seeds). This process inevitably yields rest-heat that can easily be used in the process for solvent recovery. Especially in the case of hexane, this process on a large scale is almost unbeatable as energy is recovered very efficiently. During the 1990s the use of hexane in oil extraction was discussed for health and environmental reasons. Later on the effect on health was proven irrelevant because it is hardly detectable in the refined oil.

Nevertheless, these discussions triggered research in to other solvents, such as ethanol, IPA and heptane. Such solvents would require alternative energy house-keeping in large extraction plants and membranes were considered to be a viable tool. Thus, know-how was generated to use other solvents and applied in niche applications in the oil and fats industry.

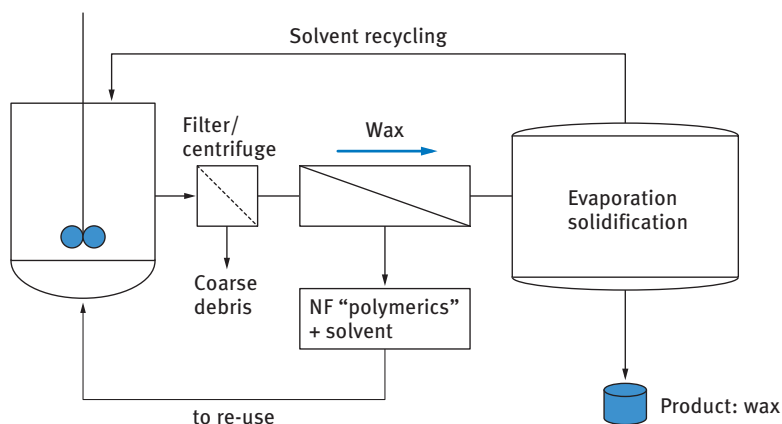
Another solvent used in oil and fats is acetone. In wet fractionation acetone is of particular importance. It has been shown that membranes are easily capable of

separation of the acetone and triglycerides. A high rejection of oil is possible and removal of acetone works until a relatively high concentration, notwithstanding some osmotic pressure that might occur. The last step still remains a thermal treatment to make the oil acetone free.

### 1.3.3 Wax removal and/or recovery

Wax removal or dewaxing is an issue in many vegetable oils, but especially in sunflower and olive oils [43]. The dewaxing process for oils, vegetable as well as diesel oil, is also known as “winterisation”. Traditionally, the process involves cooling of oil until it is 0–10°C and then settling the oil. Moreover, the onset of crystal formation may also take a long time, and the cleaner the oil the longer it takes. As the viscosity of the oils is fairly high, settling takes a long time. Of course, this can be speeded up by using centrifuges, especially when de-saponification is combined with this process. The use of straightforward filtration has been used for a long time and was followed by using MF and UF in the 1980s. By using membrane filters, the settling process is merely superfluous. These involve filtration of pure oil, hence viscous media, and MF and UF can handle that reasonably well. The use of NF may also be used for wax recovery from low molecular oil. A typical example of this can be found in the recovery of wax from citrus waste [46]. A same process may be used for the winning of waxes from vegetables (and waste). In such cases, (dry) peels or leaves are typically extracted with an organic solvent like ethanol or hexane. A typical process that involves a membrane to recycle solvent is shown in Figure 1.7.

These solvents extract oils, including the wax that is either dissolved in the oil or is present on leaves or peel. The typical wax has a C40–C60 backbone and has a small molar mass. Because the amount of wax can be very low (<2 wt% peel), there



**Figure 1.7:** Removing wax and recycling solvent from citrus peel oil extraction

is an urge to reduce the amount of extractant and waste as well as the energy needed for the recovery of the solvent.

Here the wax and solvent plus a whole range of different components (cellulosic fragments, some oil, etc.) is extracted and coarsely separated by a centrifuge, a filter or both. Typically waxes are fed to an NF filter together with solvent and some small fragments. This may be partly recycled to the extractor for reuse. The dissolved carbohydrates are largely separated from the solvent and wax that permeate the NF membrane. In the final strip, the solvent is largely evaporated and the wax is separated and solidifies after cooling.

#### 1.3.4 Goodies in oil

A number of studies are devoted to upgrading minority compounds of oil. The typical compounds depend on the oil but include tocopherol, carotenoids, phytosterols and many others.

The beneficial effects of these “goodies” are often not medically proven and sometimes are only suggested on the basis of history or alternative “pharma belief”. Omega fatty acids – one of the components of, e.g., fish oil that has proven health effects – originates mainly from fish and related marine source. It is currently not processed via membrane technology and thus it is not discussed here.

Most of the components regarded as “goodies” presumably have an antioxidant role in the plant or oil. There has been a time that many of these components were just removed from the oils as they cause yellow color or turbidity. In the traditional chemical refining the components were just washed out as soap or adsorbed to bleach earth. Thus, in general, to acquire a concentrated stream

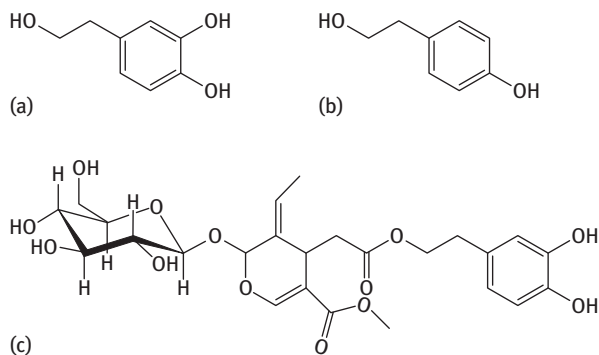
**Table 1.3:** Minority compounds in oils and their benefits

Compound	In oil/plants	“Chemical” action	Presumed health benefit
Tocopherols	Many, especially soy, peanut, rape	Antioxidant	Vitamin E related
Tocotrienols	Many, esp. soy, peanut, rape	Antioxidant	Vitamin E related
Carotenoids	Many, pumpkin, mustard, rape, palm, fruit, vegetable	Antioxidant	Vitamin A related
Phytosterols	Rape seed, pine tree, nuts	Antioxidant	Cholesterol control
Oryzanol	Rice bran	Antioxidant	Vitamin related
Phospholipids	All vegetable oils	Cell-wall	Vitamin B/cholesterol control
Polyphenols	Many oils and plants, wine, olive	Antioxidant	“Anti-cancer”
Omega FFA	Fish oil	“Anti-ageing”	Brain

of “goodies” one must work with unrefined oils. Quite a body of research agrees that concentrated potions can be made by straightforward NF of oil in a solvent. There are several membranes that have retention for the desired compounds. Interestingly, in the most common solvent for seed oil processing (hexane), retentions are not very high. Using specific solvents such as ethanol or acetone makes manipulation easier, as does the combination with treatments that convert species in more soluble blocks. This is especially true for compounds bonded to cell membranes.

In a number of cases pure oils have also been subjected to treatment with membranes. In a number of cases negative retention (–30 to –50%) of tocopherols have been found. However, in these systems permeability of the system is quite low, and even lowered by the negative retention – as the driving force decreases rapidly. The negative retentions are also found when hexane is used as a solvent. Permeabilities are somewhat higher, but would require considerable optimization before becoming a practical reality.

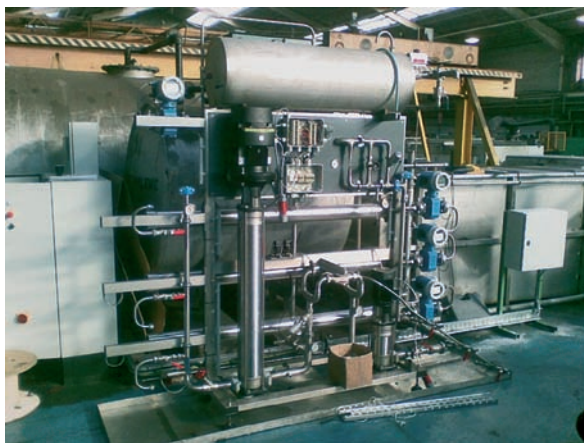
Currently there is a revival of interest in the research of recovery processes for polyphenols from olive oil waste but also from grape waste, tea leaves and all kinds of other plants [47–50]. Although polyphenols are a source of trouble in waste water



**Figure 1.8:** Some polyphenols present in olive oils. (A) tyrosol, (B) hydrotyrosol, (C) Oleuropein. Oleuropein are typical tyrosol esters with (cell-wall) carbohydrates. Hence, these compounds are not only present in the olive but also in the leaves. Caffeic acid and verbascoside are other polyphenols. In red wine other polyphenols are present but their structure is very similar

**Table 1.4:** Specific solvents for recovering “goodies”

Target	From	Solvent	Increase in yield (%)
Cartenoids	Palm, algae	Acetone, ethanol	Decolourisation deacidifying [36]
Polyphenols	Olive oil	Ethanol	Removal of oxidised polyphenols
Tocopherols	Palm oil	Conversion to methyl esters	10 times increase in yield [40]



**Figure 1.9:** Membrane unit (in installation) for pilot recovery of “goodies” from extractant solvent. The tank at the top is used for rinsing the membrane with permeate (courtesy of Solsep.com)

treatment, they are considered to have value for nutrition as well as for raw materials for organic synthesis. The first efforts to explore polyphenol waste sources were in the 1990s. A problem is that polyphenols tend to oxidize and polymerize in undefined circumstances. In that state they lose their extractability and their supposed beneficial properties. Polymerized phenols are especially difficult to handle and to break down in a wastewater system. Numerous trials have been and are devoted to extract active polyphenols like e.g., tyrosol (Mw ~138 Da), oleuropein (Mw ~540 Da) and many others. The challenge is to separate the interesting low molecular phenols from the worthless others. As such, large molecules and sediments are removed by physical techniques including centrifugation, sedimentation flocculation and/or micro- and ultrafiltration. The remaining solution is then fractionated by typical low-ultrafiltration and nanofiltration, which result in useful solutions of active components [51].

Nevertheless this is a rather complex way to acquire these components. Therefore other chemical and enzymatic treatments on typical olive oil residuals are being researched to release interesting polyphenols that are a little more defined. Subsequently the polyphenols can be extracted and recovered from the liquid.

## 1.4 Application scale and outlook

### 1.4.1 Application scale

As far as the application scale is concerned, a difference must be made between “membranes in biorefinery” and “membranes in vegetable oil and fat”. For the latter,