# Membranes in Biorefineries - GUIDELINE 2.0

Guideline for the integration of emerging membrane separation processes in biorefineries for research, industry and decision-makers

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[This guidance represents the current thinking on this topic, without any claim to completeness.]

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Project: IEA MD TCP Task 171

Programme:

klima+ energie fonds

Bundesministerium
Klimaschutz, Umwelt,
Energie, Mobilität,
Innovation und Technologie

iets
Industrial Energy-Related Technologies and Systems
An Implementing Agreement established under the auspices of the International Energy Agency

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## Preface

Within the transition from fossil-based industry to a renewable one, a huge focus is put on biorefining approaches. Within Europe and Austria several movements towards a biobased economy within the last years show the importance of this field. A key commitment of the European Green Deal is EU´s zero pollution ambition which includes a chemicals strategy for sustainability. The production and use of safe and sustainable chemicals shall include bio-based chemicals[1]. The European Green Deal strategy is aiming on a sustainable climate neutral and circular economy in Europe by 2050. The new circular economy action plan (CEAP) is setting several aims towards Europe's green transition. Also, at national level in Austria a bioeconomy strategy was taken up via an action plan giving an orientation of a sustainable economy concept until 2030, for fighting climate change, food- and water shortages as well as growing environmental impact[2].

*Figure 1: View of economic, social and ecological aspects of the Sustainable Development Goals (SDGs). (credit: Azote Images for Stockholm Resilience Centre)*

The objective of various initiates, concepts and strategies may be summarized in developing and applying new approaches towards replacing fossil fuels with renewable resources encompassing societal, industrial, scientific and economic sectors. Figure 1 shows a graphic of economic and societal aspects embedded in the biosphere connected to the UN Sustainable Development Goals.

National programmes as well as public policies on bioeconomy give an essential role on future sustainable development on biorefineries. Whereas among others one definition of a biorefinery can be: "a physical, chemical, or biological process which purifies, separates, refines, or transforms elements constituting biological assets from the kingdoms Monera, Protista, Plantae, Animalia, or Fungi, originating from the terrestrial or oceanic environment, in bioproducts for final use or that serve as raw material for other bioproducts" [3].

Along with the above stated movements and the expected growing role of biorefineries, the requirement for new process technologies and concepts becomes obvious. Membrane processes can play the role of key separation technologies within the bio-based industries. Potential, challenges and possible integration concept are discussed within this guideline.

# Content

List of Figures

List of Tables

# 1. Background

On the one hand, fossil carbon is the dominant energy and chemical source at present, however it is of limited availability. On the other hand, there is abundant renewable lignocellulosic biomass available for the utilization as a renewable resource in biorefineries.

The differences between fossil refineries and biorefineries can be summarized as follows. In fossil refineries, a fossil-based liquid feed is used, containing mainly carbon and hydrogen components and small amounts of nitrogen and sulphur. The fossil refinery uses as a first step a distillation, leading to the split into different streams such as light and heavy naphtha, jet fuel and diesel oil. Further processes such as cracking (for getting more “light” liquids), reforming (raising quality and volumes), treating (for separating unwanted molecules such as sulphur, nitrogen, heavy metals) and blending as the finishing process are applied in a sequence. In contrast to that, a biorefinery uses biomass feedstocks, which can be liquid or solid. An exemplary pathway leads from whole wood logs through chipping and further processing to intermediate platform chemicals (such as glucose, fructose, xylose, arabinose and further sugars). Through subsequent processing, building blocks, secondary chemicals, and intermediates are obtained, which are then converted to final products.

Crucial factors for the success of such biorefineries are energy and cost-efficient concentration and purification steps at industrial scale. Highly selective and energy efficient emerging membrane technologies have been identified as enabling technologies for future biorefineries. However, research and real-life applications, such as long-term experiences and integration guidelines for emerging membrane usage are needed. Lignocellulosic biomass (LCB) can be derived from waste residues of forestry, agriculture, industrial or municipal wastes. However, lignocellulosic biomass is composed of cellulose, hemicellulose and lignin in a very complex structure, which makes biorefining processes such as pre-treatment, hydrolysis and fermentation but also separation of products challenging. Numerous sectors such as the Food & Beverages, Biopharmaceutical, Fertilizer (based on manure, digestates, sludge), Pulp & Paper, Biotechnology and Bioplastics, Waste Water Treatment etc can act as a biorefinery, when more than just one resource/product is taken into account.

In pulp and paper biorefinery the main components cellulose, hemicellulose and lignin can be used for a variety of products. Cellulose can be used in nanocellulose (as reinforcing or control agent and viscosity modifier) specialty papers and packaging (as technical paper), graphic papers, casting and release papers (in form of textures for materials, functional films or automotive wraps), fibre composites (for automotive parts, furniture, audio speakers) or dissolving pulp (in applications of textiles, cellophane or pharmaceuticals).
Xylitol, furfural and substances synthesized from hemicellulose derived sugars can be applied in low-calorie sweeteners, toothpaste or recyclable plastics. Chemicals from lignin are used for binding or dispersion agents or emulsion stabilizers.

To name some more daily products of a wood biorefinery, additives for products or pre-processing steps can be found in ketchup, cucumbers pickles, cigarette filters, vanilla cookies or chewing gums.

# 2. Introduction

In biorefineries, not only the biomass conversion processes but also integration schemes for the separation and purification of biomass components and formed products streams are of utmost importance. Separation processes in biorefineries, compared to conventional chemical processes, may be severely hindered by factors such low feed concentration, product inhibition issues, and/or low product yield leading to very diluted streams. For this reason, separation and purification operations are factors influencing the overall cost effectiveness of biorefineries to a great extent, as they may account for 50–80% of the total production costs, which underlines the importance of implying appropriate technologies.

The main advantages of membrane separations are, among others, their high selectivity and low energy consumption. State-of-the-art membrane processes such as reverse osmosis (RO), microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) are well established in numerous industrial applications, for example in separation, concentration or purification steps. Due to the large variety of different components of biobased feedstocks, operation and integration must be adapted to the respective processes.

Membranes have already been used in biorefinery operations such as pre-treatment of waste, enzyme recovery, recycling and concentration of fermenting organisms, or removal of inhibitors, as well as in the form of membrane bioreactors where the biomass conversion and the separation take place at the same time. Traditional and emerging membrane processes together with the ongoing material research focused on functionalized membranes opens up new applications and possibilities to substitute the current state-of-the-art (SOTA) separation processes. However, the main challenge membrane operations are facing in biorefineries operations is fouling. In this regard, not only new materials or modification techniques for better anti-fouling properties of the membrane material are needed but also knowledge on impurities and foulants present since they determine the fouling behaviour. Such impurities may also require adaption and optimization of membrane processes such as adequate pre-treatment and cleaning strategies to allow long-term stable operation.

Within the international Task XVII potentials as well as challenges of the application of emerging and hybrid membranes processes are examined. Existing knowledge is put together, transferred and exchanged among the partners. Austria is part of the international consortium, leading the subtask on emerging membrane processes. IETS Task XVII - Membranes in Biorefineries is coordinated by Frank Lipnizky, University of Lund. The consortium includes partner from industry and academia from Austria, Denmark, Germany, Portugal, Sweden, Italy, the Netherlands and France.

This guideline was developed within the nationally funded IEA TCP Task 17 in 2021 and is herein extended. The objective of providing this guideline is to give an overview of emerging membrane technologies, map the actions done so far and foster know-how transfer within the international consortium, including integration concepts of membrane applications in biorefineries, such pre-treatment and cleaning approaches. The aim of this guideline is to support and enable the integration of potential membrane technologies in biorefining industry. This guidance shows possible integration concepts of membranes in biorefineries as well as recommendations for R&D, technology development, research, industry, and decision -maker.

# 3. Emerging membrane technologies

Conventional filtration is a mature, commercially available solid–liquid separation technology. It is widely used in biomass pre-treatment steps but also in the recuperation of crystals from precipitation/crystallization, the separation of pre-hydrolysate slurry and post-distillation slurry [4]. Membrane-based processes have the following additional advantages:

*1) They provide a large surface area (each of the pores) to bring the aqueous phase in contact with the extractant in a compact way;*
*2) The modularity of the membrane elements allows for a continuous operation while being easily scalable both in parallel or in series (if higher purity is needed);*
*3) The transfer rate, expressed in terms of a mass transport coefficient, can be optimized by adjusting the volume flow ratio.*

A drawback of membrane processes is the additional resistance of the membrane. Depending on the wetting properties of the membrane (hydrophilic/hydrophobic) either the feed solution or the extractant fills the pores of the membrane. However, the predictability and precise control of all hydrodynamic conditions is a significant advantage outweighing the loss in mass transport due to the membrane [5].
Membrane processes can be classified by their main driving forces in either pressure-, charge- or chemical potential driven. Examples of the application of pressure driven membranes in biorefineries based on pore size are for example separations of…

…activated carbon from sugar – conventional filtration
…biological cells from proteins – microfiltration (MF)
…proteins from salt – ultrafiltration (UF)
…sugar from salt – nanofiltration (NF)
…salt from water (desalination) – reverse osmosis (RO).
(whereas MF and UF are the most used processes.)

However, the use of alternative methods such as emerging membrane processes offers a solution to make the treatment of material streams more sustainable and efficient. These include, for example, forward osmosis (FO), membrane distillation (MD), liquid membrane permeation (LMP), pervaporation (PV) and membrane-assisted crystallization (MAC). In the biorefinery concept, the material use of the components is combined with energy efficiency measures through partly selective separation mechanisms. The essential point here is that processes bring additional benefits as well as an upgrade of existing production processes without generating a surplus in energy supply costs. In thermally driven membrane processes such as membrane distillation, the thermal energy requirement can be covered by waste heat utilization due to the low process temperatures. In industrial plants, such as paper mills, unused waste heat potentials can be ideally integrated. To meet the requirements of treating material flows with different demands, the possibility or necessity of combining emerging processes arises as a support to the state of the art of membrane processes in multi-stage separation concepts. Integration concepts for sustainable and efficient loop closure using membrane separation processes in biorefineries are needed. In the following a short description of the above-named emerging technologies is given:

## 3.1 Forward osmosis

Forward osmosis (FO) is an osmotic process that can be used as an alternative to pressure-controlled membrane processes. It is used to separate water and solutes such as molecules, ions or larger particles using a semipermeable membrane. The driving force in this process is the osmotic pressure difference, which is given by two differently concentrated process streams. Thereby, less $CO_2$ relevant energy is consumed compared to reversed osmosis (RO).

**Specific technology requirement:**

In FO, tailored membranes are required. However, most currently available membranes have been designed and optimized for pressure-controlled processes, which are often not suitable for FO due to concentration polarizations (=formation of a boundary layer at the membrane; this effect reduces the pressure difference across the membrane layer which limits the water flow).

**State-of-the-Art:**

Forward osmosis is a promising emerging solution for energy efficient water use. The low energy consumption, the achievement of higher concentrations and higher retentions, as well as the absence of solvents for the extraction are among the advantages of FO[6]. However, due to different operating conditions, experimental setups, and data interpretation, it is still difficult to evaluate the potential of FO applications to the industrial sector[7].

**Challenges:**

One of the main challenges in FO is the recycling of draw solution, to maintain the driving force and achieve the product. Various hybrid recovery approaches are described in literature. Furthermore, development of mainly TFC (thin film composite) membranes is sought to be able to provide higher stability and mechanical strength for different conditions, such as flow velocity and pressure[8]. The potential of fouling is high and once the membrane gets plugged the process stops and the cleaning steps are expensive[9]. Therefore, long-term fouling behavior and membrane cleaning methods must be investigated, and an energy and economic evaluation is required[7].

**Available membranes/modules:**

- Flat plate FO membrane: stacked plate and frame modules or wound spiral modules.
- Hollow fiber FO membrane: assembled hollow fiber modules
- Tubular membranes/ modules

## 3.2 Membrane distillation

Membrane distillation (MD) is an emerging thermal separation technology that allows evaporation of water through a porous hydrophobic membrane. Driven by the difference in vapour pressure the process allows evaporation to take place at ambient pressure and lower temperatures than conventional free surface evaporation approaches. As clear permeate evaporates through the membrane, non-volatile organic and inorganic compounds are left behind leading to a highly concentrated solution of significantly reduced total volume. Membrane distillation is widely used for seawater and brackish water desalination, wastewater treatment and concentration/crystallization applications of different industrial areas.

**Specific technology requirement:**

Membrane properties play an important role in the efficiency of the process. These include the physical properties, the interaction between vapor molecules and membrane surface, as well as the thermal properties and their effect on temperature polarization and mass transfer. Membranes made of polytetrafluoroethylene (PTFE) are particularly attractive because they have low surface energy, low conductivity and good thermal stability. However, other polymeric membranes made of polypropylene (PP) or of polyvinylidene fluoride (PVDF) are also widely used, as well as zeolite and ceramic membranes as recent studies show[10].

**State-of-the-Art:**

Interest in membrane distillation is increasing due to the low-grade heat used and minimal demands on the membrane applied. In addition to that, because of the low operating temperatures also renewable sources (e.g., solar energy) or waste heat can be used[11]. Currently, research is being conducted on novel materials for higher permeate flux, by means of constant heating or high temperature at the membrane surface, and mitigation of temperature polarization[12].

**Challenges:**

Apart from fouling, membrane pore wetting occurs from time to time due to losses of membrane hydrophobicity, which in turn leads to a degradation of the separation performance [10],[13]. Other factors to be improved are the relatively low permeate flux compared to pressure-controlled membrane processes and the still high cost of the modules. Temperature polarization is also a critical factor, since once it occurs, the temperature of the main liquid differs from the interface temperature of the membrane, which in turn has a negative effect on distillate flux and energy efficiency [12],[11] ,[10].

**Available membranes/modules:**

Polypropylene (PP)
Polytetrafluoroethylene (PTFE)
Polyvinylidene fluoride (PVDF)
PP/PTFE, zeolite and ceramic membranes.

The membranes can be flat (plate, spiral wound) or tubular (hollow fiber, capillary, pipe) in different module configurations.

## 3.3 Pervaporation

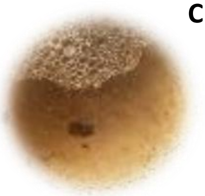
Pervaporation (PV) is used to purify components that are difficult to separate from a liquid mixture (primarily to separate water or methanol from a solvent mixture). The membrane separates the liquid phase (feed) and the gaseous phase (permeate). The driving force of this process is the difference in chemical potential, corresponding to the concentration gradient between the phases on the opposite sides of the membrane. Low energy consumption, no need of entrainer/chemicals, independent operation of vapor-liquid equilibrium such as simple and continuous mode are the characteristic features of a PV.

**Specific technology needs:**

Three types of membranes might be applied as follows: Membranes made of hydrophilic polymers are used for the separation of water from organic solutions and hydrophobic membranes are used for the purification of organic substances in aqueous solutions, especially for the recovery of ethanol, methanol, etc.. The extraction of organic compounds from aqueous solutions takes place via organophilic membranes (e.g. mixtures of amines, aldehydes and alcohol)[14]. Factors influencing the process include temperature, feed concentration and composition, and membrane thickness.

**State-of-the-Art:**

Membranes specifically optimized for the separation problem allow for selective separation of individual organic compounds from organic mixtures. Recent research is working on the for example, the removal of aromatic compounds from fuels, which is difficult due to the similar chemical composition[15].



**Challenges:**

In the future, research will be conducted in finding new membrane technologies, considering selectivity, stability and productivity. The goal is to develop high-performance PV membranes with long-term stability. The limitations of pervaporation systems at industrial level are so far low performance, short lifetime, high cost, as well as bio generation of base chemicals and still restricted scaling[14].

**Available membranes/modules:**

- Hydrophilic membranes: polyvinyl alcohol, cellulose acetate or polyimide.
- Hydrophobic membranes: polyoctylmethylsiloxane, polydimethylsiloxane, polyvinylidene fluoride (PVDF), polydimethylsiloxane (PDMS), polytrimethylsilyl-1-propyne (PTMSP), etc.
- Organophilic membranes

Plate & frame as well as tubular modules are commercially available.

## 3.4 Liquid Membrane Permeation

Liquid membrane permeation (LMP) is a kinetically controlled process in which extraction and re-extraction from a feed phase occurs in one step. Characteristic of this process is that the donor phase (feed phase), which contains the solute (=targeted compound), is separated from the receiving phase (=stripping phase) by a membrane holding the organic solvent phase (=liquid membrane). At the interface between the feed phase and the liquid membrane, the solute dissolves into the solvent phase. After passing through the liquid membrane, the re-extraction takes place at the interface between the liquid membrane and the stripping phase. The driving force for the transport of the solute is solution diffusion. This means that the solute dissolve in the liquid membrane and diffuse through the membrane due to a concentration gradient.

**Specific technology requirement:**

Solutes have different solubilities, as well as diffusion coefficients, making selective solubility an important consideration. Carriers can be added to the solvent phase to facilitate mass transfer and increase the efficiency by forming a reversible and selective bond with the solute. Classifications take place by module configuration, transport mechanisms, applications, carrier type, as well as by type of membrane support [16]. Knowledge of the relative diffusivities of the solutes can help in the selection of the membrane, as the membrane material must be able to withstand the process conditions.

**State-of-the-Art:**

Currently, the most important applications for LMP are the recovery of metals, the removal of organic pollutants, the enrichment of active pharmaceutical ingredients, and the separation of gaseous substances. Especially in analytical chemistry, it serves as a solute accumulation method because of the low amount of organic solvents, smaller sample volume and shorter analysis time compared to conventional accumulation methods [17]. In food industry, LMP is also used for recovery of flavors from fruits and concentration, as well as sterilization of liquid foods and beverages, without affecting the taste[17,18]. Supported membranes can also be applied in wastewater treatment and extraction of metal salts. The advantage is the low chemical consumption, as well as the high degree of separation, high selectivity and efficient use of energy and material.

**Challenges:**

Due to rising pressure differences, emulsion formation and blocking of the pores by solids, instability occurs in the liquid membranes. However, continuous impregnation, gelation or cross-linking of the liquid membrane etc., can increase the stability[17]. Also, the low permeate flux and high investment/operating costs have often prevented LMP from commercial use [16].

**Available membranes/modules:**

Polyethylene- composite membranes

## 3.5 Membrane-assisted crystallization

Membrane-assisted crystallization (MAC) is a technology based on macroporous hydrophobic membranes contacting the feed solution and pure water or vacuum on the opposite side. This technology differs from membrane filtration processes: under a partial pressure gradient established between the two membrane sides, the solvent (water) vaporizes at the feed/membrane interface, diffuses through the pores and condenses at the distillate side. Unique advantages of this method are[19]:

(i) accurate control of the trans-membrane flux of solvent that drives the solution through specific supersaturation pathways within the metastable zone (enhancing crystals formulation: particle shape/size distribution, polymorph/hydrated forms selection, impurity inclusion control);

(ii) chemical-physical properties of the membrane and topography as tools to modulate the free energy barrier to (heterogeneous) nucleation and, ultimately, to control the crystallization kinetics. Antisolvent configurations are also available [20].

**Specific technology requirement:**

Membrane properties play an important role in the efficiency of the process. These include the physical-chemical properties that modulate the interactions between target molecules to be crystalized and membrane surface, and the mass-transfer properties which affect the supersaturation rate. Membranes made of polypropylene (PP) are particularly attractive because they have good thermal stability and resistance to wetting. However, other polymeric membranes made of polyvinylidene fluoride (PVDF) or polytetrafluoroethylene (PTFE) can be used.

**State-of-the-Art:**

Interest in membrane-assisted crystallization is growing due to the possibility to recovery valuable materials from highly concentrated streams, that can be concentrated with MAC beyond the operating range of reverse osmosis, up to supersaturation. Furthermore, low grade heat or renewable sources (e.g. solar energy) can be used because of the low required operating temperatures, thus minimizing the energy demands of the process.

**Challenges:**

Apart from fouling that is intrinsically related to the liquid-solid phase transition, membrane wetting might occur when low-surface energy (hydrophobic) molecules are present in the feed, which in turn leads to a degradation of separation performance[21]. Opposite to MD, the relatively low permeate flux compared to pressure-controlled membrane processes are beneficial for the improved control of the supersaturation rate. While temperature polarization can affect the interface temperature of the membrane, which in turn has an influence on the local supersaturation values.

**Available membranes/modules:**

Polypropylene (PP)
Polyvinylidene fluoride (PVDF)
Polytetrafluoroethylene (PTFE)

The membranes can be flat (plate) or tubular (hollow fiber, capillary) in different module configurations.

## 3.5 Challenges of membrane applications in biorefineries

Compared to conventional chemical processes, the separation in biorefineries may be severely hindered by factors such as (in case of water-based biorefineries): low feed concentration, product inhibition issues, and/or low product yield leading to very diluted (aqueous) streams that resemble more wastewater streams than typical chemical reactor effluents [22]. This being the reason why many times separation and purification operations are the biggest factors influencing the overall cost effectiveness of biorefineries. As an example, in the bio-production of succinic acid the separation and purification procedures account for 50–80% of the total production costs [23].

Separations are based on physical and chemical differences between species as well as the nature of the mixture. Typical physical factors include size, shape, compressibility, density, and viscosity. Chemical factors include solubility, hydrophobicity/hydrophilicity, polarity, $pK_a$, boiling and freezing points and specific molecular interactions [24].

The separation processes can be classified into

a) Phase-change or equilibrium-based Separations
b) Affinity-Based Separations
c) Solid-Liquid Separations
d) Permeation methods where a medium is used (membranes)

Membrane operations are extremely relevant as advanced separation technologies. Due to versatility, separation efficiency, energy savings, and economic benefits of membrane operations, their use in biorefineries is becoming more and more relevant. Membranes have been already heavily used in biorefinery operations such as pre-treatment of waste, enzyme recovery, recycling and concentration of fermenting organisms, removal of inhibitors, etc... Also, in the form of membrane bioreactors where the biomass conversion and the separation take place at the same time. The multiple available traditional and emerging membrane processes together with the heavy material research focused in functionalized membranes opens up new applications and possibilities to substitute the current State-of-the-Art (SOTA) separation processes.

Membrane processes have a great potential in virtually all the separation operations found in biorefineries. However, one pressing challenge membrane operations are facing in biorefineries is fouling. In this regard, not only new materials or modification techniques for better anti-fouling properties are needed but also knowledge on impurities and foulants present in the streams is required, since they determine the fouling behaviour. Such impurities may also require adaption and optimization of membrane processes to allow long-term stable operation. Table 1 summarizes emerging membrane technologies such as membrane distillation, membrane-assisted crystallization and pervaporation with SOTA technologies such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). The key difference between the emerging and conventional membrane technologies is the driving force and the associated separation principle. The driving force in state-of-the-art membrane processes MF, UF, NF and RO is the pressure difference, with the applied pressures increasing from the single-digit to the triple-digit bar range (2-150 bar) in the order mentioned. The separation of pervaporation, membrane distillation and membrane-assisted crystallization, on the other hand, is based on different partial vapor pressure differences between the feed and permeate sides. Along with different degrees of separation or treatment, the technologies differ in membrane materials, structure, thickness as well as in porosity and pore size. The membranes can be flat (plate, spiral wound) or tubular (hollow fiber, capillary, pipe) in different module configurations. Applications range from classical seawater desalination to selective separation of valuable components in various industrial spades.

*Table 1: Overview of characteristics of currently used membrane separation processes in biorefineries*
*(adapted from He et al., 2011; Basile et al., 2015; Bokhary et al., 2017; Ohlrogge & Ebert, 2006; Chen et al., 2013; Staudt et al., 2010 & Van der Bruggen, 2013).*

| | **Membrane Distillation (MD)** | **Membrane-assisted Crystallization (MAC)** | **Pervaporation (PV)** | **Microfiltration (MF)** | **Ultrafiltration (UF)** | **Nanofiltration (NF)** | **Reverse Osmosis (RO)** |
|---|---|---|---|---|---|---|---|
| **Driving Force** | Vapor pressure difference 2) | Vapor pressure difference | Vapor pressure difference 4) | Pressure <2 bar 3) | Pressure 1-10 bar 3) | Pressure 5-35 bar 3) | Pressure 15-150 bar 3) |
| **Separation principle** | Vapor-liquid equilibrium 5) | Vapor-liquid equilibrium | Solution diffusion mechanism 2) | Sieve mechanism 1) | Sieve mechanism 1) | Solution diffusion mechanism 1) | Solution diffusion mechanism 3) |
| **Membrane structure** | Symmetric or asymmetric porous membrane 1) | Symmetric or asymmetric porous membrane | Homogeneous or composite membrane 1) | Symmetric or asymmetric porous membrane 1) | Asymmetric porous membrane 1) | Composite membrane 1) | Composite membrane 3) |
| **Membrane material** | Hydrophobic polymer 1) | Hydrophobic polymer | Polymer, ceramic, organic-inorganic 1) | Polymer, ceramic 1) | Polymer, ceramic 1) | Polymer 1) | Organic polymers (cellulose and polyamide derivatives ) 3) |
| **Membrane thickness (µm)** | 20–100 1) | 50–100 | ~0,1 or less (Top layer) 1) | ~10-150 1) | ~150 1) | Top layer: ~150 1)<br>Bottom layer: ~11) | 150 3) |
| **Pore size (nm)** | 10–5.000 2) | 50–5.000 | Non-porous (dense) 1) | ~50–10.000 1) | ~1–100 1) | <2 1) | 0,1-1 3) |
| **Module configuration** | Plate module, tube module, Capillary module 1) | Plate module, tube module, Capillary module | Plate module, tube module, hollow fibre module 1) | Plate module, tube module, hollow fibre module 1) | Plate module, tube module, hollow fibre module, spiral wound-, capillary-module 1) | Plate module, tube module, Spiral wound module 1) | Plate module, tube module, hollow fibre module, spiral wound-module 3) |
| **Application examples** | Recovery of valuable components from wastewater 7); Production of distilled water 7); … | Recovery of valuable components as solids from waste streams and brines; Production of distilled water; | Process water treatment 6), Dewatering of organ. Solvents 6)… | Clarification & Concentration in the Beverage Industry 6); Recovery of Lignin, Hemicellulose and Enzymes 1); ... | Separation of Oil/Water Emulsions 6); Recovery of Lignin, Hemicellulose and Enzymes 1); ... | Filtration of acids and alkalis 6); recovery of lignin, hemicellulose and removal of fermentation inhibitors 1); ... | Seawater and brackish water desalination 6); recovery of lignin, hemicellulose and removal of fermentation inhibitors 3)... |
| | *1) He et al.[25];, 2011; *2) Basile et al., 2015[26];; *3) Bokhary et al.[27];, 2017; *4) Ohlrogge & Ebert[28], 2006; *5) Chen et al.[29], 2013; *6) Staudt et al.[30], 2010 *7) Van der Bruggen[31], 2013 | | | | | | |

Due to their very special characteristics, the above-shown technologies have individual criteria for their applications.

# 4. Integration Example for Membranes in Biorefineries

Biorefinery approaches are most important closing the loop strategies of the circular economy. However, one of the main challenges in biorefineries, besides the effective conversion of biomass, are the separation and purification of the products, which have the largest effect on the overall economics of biorefineries. For this reason, separation technologies are becoming increasingly important in a future circular economy scenario and are examined herein.

At the beginning of the present work, the state of the art regarding membrane approaches in biorefineries was screened. Biomass conversion, separation and purification can be summarized as the units where the greatest need for action exists in terms of ecological and economical solutions. In these process steps, current solutions were compared with novel options and their potential was outlined. In addition, specific potential process or wastewater streams were identified for further value-added use. For this purpose, qualitative and quantitative parameters were considered. In exchange with the national and international consortium, in dialogue with industrial partners and with the help of literature, integration points for the application of the emerging membrane processes were identified.

The state of the art of separation technologies which are currently most commonly used in the biorefinery sector is reaching from distillation, affinity-based separation processes, solid-liquid methods such as precipitation, crystallization to membrane filtration processes. These membrane technologies are of great importance as advanced separation technologies, due to their versatility, separation performance, energy savings, and economic advantages. Already widely used in biorefineries, membranes are used for the

- Pre-treatment of waste
- Enzyme recovery
- Recycling and concentration of fermentation organisms
- Removal of inhibitors, etc.
- In the form of membrane bioreactors, where biomass conversion and separation occur simultaneously.

The variety of available traditional and emerging membrane processes, as well as the intensive materials research in the field of functionalized membranes, open new applications and opportunities to replace the current SOTA separation processes. Several factors affect the suitability of membrane processes, including feed material properties, membrane properties, operating conditions, and type of pre-treatment. However, a major challenge for membrane processes in biorefineries is fouling. In this context, not only new materials or modification techniques for better anti-fouling properties are needed, but also knowledge about the impurities and foulants present in the streams. Such foulants may also require adjustment and optimization of membrane processes to allow long-term stable operation. Specific streams from the paper industry were taken and the components of importance to the application of emergent membrane processes were highlighted to evaluate the potential of their use. Regarding feed (process or wastewater stream) properties, the presence of compounds such as extracellular polymeric substances (EPS), soluble microbial products (SMP), and dissolved inorganics can cause membrane fouling and/or wetting. In most membrane processes, the solids content is not as crucial as the interaction of the solids with each other and with the membrane. For example, some solids may form a porous fouling layer (i.e., a cake layer) that has minimal TMP accumulation during the filtration cycle and is ideal for direct filtration regardless of total suspended solids (TSS) or turbidity. Other solids, on the other hand, even with low turbidity or TSS, can form a dense fouling layer that offers significant resistance to flow.

In direct filtration of wastewater in the pulp and paper industry, organic and inorganic fouling of the membrane are the predominant mechanisms, as wood hydrolysate contains various substances, including carbohydrates, extracts, and lignin [32]. As another example, during the recovery, fractionation, and purification of lignin and hemicelluloses from wood hydrolysates using UF, wood hydrolysates have a high tendency to foul, as these streams contain hemicelluloses, lignin, and wood extracts, such as fatty and resin acids [33]. Among them, lignin is the most crucial contaminant, so most pre-treatment strategies focus on lignin removal.

One of the goals of this work was to highlight integration examples of membrane technologies as part of biorefineries. One example specific to the pulp and paper industry is presented in more detail, along with other interesting applications found in the literature and summarized in Table 2. It includes the quantities generated and the composition as a basis for the integration of membrane processes in, for example, the streams black liquor from the Kraft process, sulfite liquor, sludges, and bleaching (waste) waters. The composition does not include the complete breakdown, but only the compounds in the respective medium that are considered crucial for the use of membrane processes regarding treatment objectives, fouling, purification and pre-treatment.

*Table 2: Overview of process and wastewater streams as potential integration points for emerging membrane processes in biorefineries, including food and pulp and paper industry. The table does not show the total composition but only certain components of interest for respective applications.*

| Application | Raw material | Quantity produced | Composition | Source |
|---|---|---|---|---|
| **Rice production** | Rice husks | 120 Mt per year worldwide | 31 wt% cellulose, 22.5 wt% hemicellulose, 22.3 wt% lignin, 13.8 wt% ash, 2.3 wt% extractives (on a dry basis) | 34 |
| **Silage** | Grass silage | 4.7 t per year in Austria | 5-25 g/kg glucose, 5-61 g/kg fructose, 85-177 g/kg lactate, 3-30 g/kg acetate, 0.8-5.7 g/kg propionate | 35, 36 |
| | Corn silage | 9,2 million tons per year worldwide | 32,5 wt% dry matter.<br>20 wt% starch, 24 wt% cellulose, 25 wt% hemicellulose, 5,4 wt% lignin and 7,6 wt% proteins (on a dry basis). | 37, 38 |
| **Sugar production** | Sugar cane Bagasse | 220 Mt per year worldwide | Sugar content 81.3 g/l, of which 68.6 g/l xylose, 11.5 g/l glucose and 1.2 g/l arabinose. | 39, 40 |
| | Sugar cane Bagasse | 490 million tons per year worldwide | 45-50% water, 40-45% fibre, 2-5% dissolved sugars<br>Fibers: 40-50% cellulose, 25-35% hemicellulose, 20-30% lignin. | 41 |
| | Press sludge | 55 million tons per year worldwide | 50-65% water, 15-30% fibre, 5-14% waxes, 5-15% sugar, 5-15% proteins. | 41 |
| **Pulp and Paper** | Kraft black liquor | 13 billion tons per year worldwide | 31 wt% lignin, 29 wt% organic acids, 7 wt% other organic compounds, 33 wt% inorganic components (based on dry basis). | 42, 43 |
| | | | 127-210 g/l, dry solids, 40-71 g/l lignin, 20-43 g/l organic acids | 43,44 |

| | | | | |
|---|---|---|---|---|
| | Spent sulfites liquor | 90 billion tons per year worldwide | 137 g/l Lignosulfonates | [45,46] |
| | Paper sludge | 99 million tons of paper in Europe. 11 million tons of Waste generated | 30.6% cellulose, 8% lignin, 12.1% sugars, 41.6% inorganic materials (Al, Si, Ca, Cu, Fe, or Mg) | [47,48] |
| | Kraft pulping effluent | 80% of all pulping | 43.9 wt% glucan, 9.4 wt% xylan, 22.5 wt% protein, 6.4 wt% ash (P, Fe, K, Mg, Mn) (% dry matter) | [49] |
| | Bleaching effluent | 50 kg/t lutro at CS | 0.66 – 1% TS, 6000 mg/L COD, Cl 40 mg/l, 100-400 mg/l fibre | Case Study AEE INTEC |
| **Food industry** | Wastewater from the food industry (potato, corn, wheat, pineapple) | | 18-31 g/l starch, 0.8-26 g/l, 360-920 mg/l Kjeldahl-nitrogen, 75-108 mg/l phosphate, 40-88 mg/l sulfate. | [50,51] |
| | Municipal food waste | 1.3 billion tons per year worldwide | 52.3% Carbohydrates, 12.8% proteins, 25.8% fats, 2.3% ash (mass based) | [52,53] |
| | Baking waste (bread) | | 83.6 g/L glucose, 9.5 g/L fructose 619 mg/L FAN | [54] |
| | Fruit peels (potato, mango, orange) | | High carbohydrate content (30% of the fruit is waste) | [55] |
| | Coffee pulp | | Coffee Pulp (w/w): proteins (9-11%), lipids (2-17%), cellulose (13-27%), tannins (4.5%), pectins (6.5%), reducing sugars (12.4%) and non-nitrogen extracts (57-63%).<br>Coffee pulp hydrolysate (g/L): glucose (20-30), xylose (15-25), saccharose (5-11) and arabinose (0.7-10) | [56] |

As this is a non-extensive list, only a few integration examples are given in detail, further examples such as the in situ carboxylic acid extraction from fermentation broth [57] and the application in of Hydrothermal Carbonisation in combination with membrane distillation are subject to current research questions.

The following chapter shows a collection of more detailed integration examples of different hybrid membrane technologies in biorefinery applications.

*Table 3: Overview of integration examples.*

| **Source/ Feedstock** | **Technology** | **Product** |
|---|---|---|
| Biocatalytic reactor for the production of L-malic acid | Enzymatic Membrane Reactor (EMR); membrane-assisted crystallization (MAC) | Fumaric acid |
| Organosolv stream (Fabiola TM) | Nanofiltration and pervaporation/vapor permeation | Lignin and monomeric sugars |
| Olive oil washing wastewater (OOWW) | Ultrafiltration, Nanofiltration, Forward Osmosis | antioxidant phenolic compounds (PhC), water |
| Seaweed hydrolysate feed | Ultrafiltration and Nanofiltration | Monomeric sugars |
| Digestate sludge from wastewater treatment | Membrane Distillation | Ammoniumsulfate and water |
| Sweet sorghum silage press juice | Reactive extraction | Lactic acid |

## 4.1 Recovery of fumaric acid from a biocatalytic reactor for the production of L-malic acid by membrane-assisted crystallization (MAC)

The application of membrane-assisted crystallization is being investigated at the Consiglio Nazionale delle Ricerche – Istituto per la Tecnologia delle Membrane (CNR -ITM). The feed stream used is fumaric acid, which is a by-product of the production of phthalic anhydride by oxidation of o-xylene. The industrial use of fumaric acid, is severely limited by its low solubility. Its enzymatic conversion to L-malic acid by fumarase immobilized in an enzymatic membrane bioreactor (EMR) in asymmetric capillary membranes attained the maximum steady-state conversion efficiency of 80%. L-malic acid is used as an acidifying agent in foods [58]. Fumaric acid, which was not converted in the membrane bioreactor, was successfully crystallized [59]. The membranes were cleaned by extensive washing with distilled water (temperature 30-35 °C), before and after treatment with NaOH (0.5-1.0 wt%) and citric acid solutions (pH 3-4) to restore the original performance of the membranes. Regarding further application potentials of the technology, it is expected to be compatible with streams from other agro-industrial processes, such as lignocellulosic biomass and derivatives, in which biomolecules are also present.

## 4.2 Nanofiltration (NF) and Pervaporation/Vapor permeation (PV/VP) for lignocellulose fractionation

TNO, the Netherlands Organisation for applied scientific research, shared the integration example of nanofiltration and pervaporation membrane application for improving the fractionation of lignocellulosic biomass. Their patented process deals with the separation of lignin and monomeric sugars from a liquid stream from for instance the organosolv process, consisting of water and an organic solvent. The advantage of this process in respect to conventionally used (precipitation and centrifugation/decantation/filtration in small scale) distillation at large scale is the reduced energy demand and thus a cost reduction. Furthermore, both fractions, lignin and monomeric sugars such as the organosolv liquor can be further used. The nanofiltration membrane might be comprised of a ceramic carrier and a polymeric top layer consisting of sulfonated polyether ether ketone. For the pervaporation step any water selective membrane such as polyvinyl alcohol-based polymeric membranes, polyimide-based membrane, zeolite membrane, silica membranes or organic-inorganic hybrid silica membranes can be used[1] .

## 4.3 Treatment of olive mill wastewater with Ultrafiltration (UF), Nanofiltration (NF), Forward Osmosis (FO)

At the Universitat Politècnica de València, a hybrid membrane process of forward osmosis, ultrafiltration and nanofiltration is used to recover phenolic components and water. As part of a circular economy concept for olive mill wastewater, the recovery of antioxidant phenolic compounds (PhC) and the reclamation of wastewater for future reuse are presented. The hybrid process includes membrane processes, adsorption/desorption, and biological treatment. The process provides for pre-treatment followed by the membrane process stage. The first option provides for ultrafiltration followed by nanofiltration, while the second provides for direct osmosis only. In both cases, the adsorption and desorption stage follows, which includes an evaporator to recover part of the ethanol used to extract the phenolic compounds. Finally, the residual streams are treated by biological treatment with SBR.

As can be seen in Figure 2, both processes contemplate a pre-treatment, followed by the membrane process stage. The first option contemplates an ultrafiltration followed by a nanofiltration, while the second only contemplates direct osmosis. In both cases, the adsorption and desorption stage follow, which includes an evaporator to recover part of the ethanol used to extract the phenolic compounds. Finally, the residual streams are treated by biological treatment with SBR.
The two-phase continuous centrifugation process is the most widely used in Spain for olive oil production. The wastewater generated, called olive oil washing wastewater (OOWW), was the object of this study. First, a pre-treatment (flotation, sedimentation and filtration (60 µm)) was considered, to then proceed with ultrafiltration (UF)[60],[61]. Forward osmosis (FO) using (HFFO.6 and FTSH2O) was also tested for this purpose with fermentation brines from table olive production as draw solutions. In this case de hollow fiber membrane HFFO.6 was selected. Then, PhC from FO and NF concentrates

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[1] https://patents.google.com/patent/WO2016131828A1/en

were recovered with 40 g/L of the MN200 adsorption resin (Purolite) and a 50% ethanol/water solution as eluent[4].

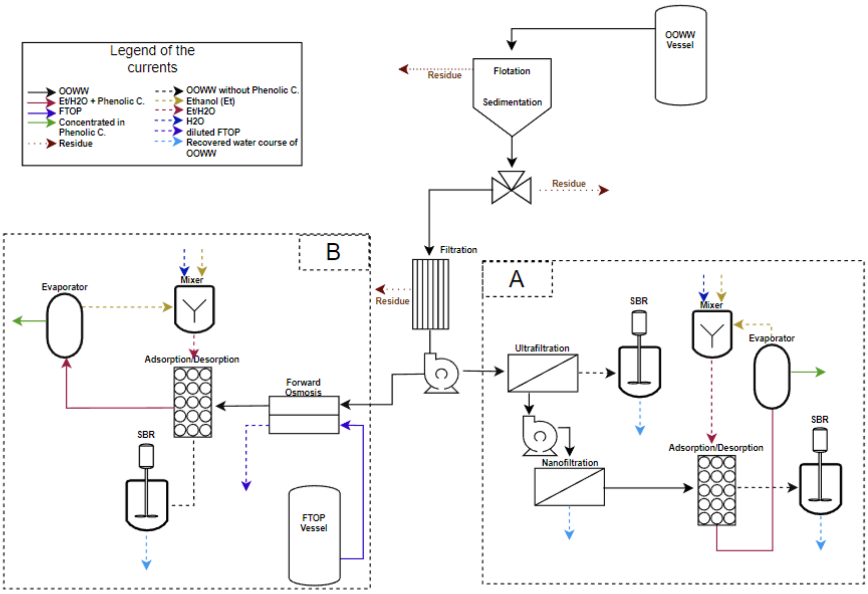

*Figure 2:Proposed processes for the recovery of phenolic compounds and treatment of olive oil washing wastewater (OOWW)*

The streams without PhC, together with the UF retentate, were submitted to a biological treatment[5] where the feasibility of a sequencing batch reactor to reduce the organic load was analyzed. By means of both proposed processes, it was possible to obtain a concentrate rich in phenolic compounds such as the recovery of water courses for its reincorporation in the process as machinery washing water.

For each kilogram of olives processed through a two-phase centrifugation process, 0.5 liters of OOWW are generated. The final flow to be treated was 54.75 $m^3$/day, which is rounded to 55 $m^3$/day. However, residual water is only generated during the harvest season and the olive oil process, during the months of October to January/February. Finally, the cost for process A including UF and NF membrane processes is 7.24 euros/$m^3$ OOWW treated[2], while for process B considering only the FO membrane process it is 6.86 euros/$m^3$ OOWW treated[2]. It is important to point out that the costs are competitive with those currently existing for wastewater treatment from agro-industries. On the other hand, a concentrate rich in phenolic compounds is obtained, which has a high commercial value (reference value from Sigma Aldrich: tyrosol: 14.5 euros/g; hydroxytyrosol: 13.48 euros/g).

## 4.4 Digestate sludge treatment from wastewater by membrane distillation (MD)

The example below shows how membrane distillation can be integrated into a wastewater treatment plant. Following the anaerobic stage in the digestion tower and after sludge dewatering or drying, the liquid stream ("centrate water") is fed into the MD. The goal of this approach is to recover ammonium in the form of ammonium sulfate, which can be used as fertilizer. The integration example of

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[2] For energy consumption it was considered: Power of 17.5 and 22 kW, for option A and B respectively; working day of 8 h/day; Light price of €0.20/kWh (Cost €35.69/day); days Operation 120 days/year. With SBR operating 24 hours. Useful membranes life 5 years.

membrane distillation for the selective recovery of ammonia is discussed in detail with long-term tests and fouling mitigation in chapter 5.

## 4.5 Sweet sorghum silage press juice for isolation of lactic acid

Experiments on the isolation of lactic acid were carried out by means of reactive extraction from sugar millet silage pressed juice. Pressed juice concentrate with a solids content of 40 wt% served as the starting material for the extraction experiments. After pre-treatment by centrifugation, dilution with water and filtration, the feed stream had a solids content of 13 wt%, a lactic acid concentration of 0.43 mol/L and a pH of 4.00. Two-phase extraction experiments were carried out with this feed stream. Different extractants, solubilizers and diluents were tested.

Carbohydrate-containing process streams offer the advantage that various end products can be produced by fermentation, such as carboxylic acids [62]. Reactive extraction of carboxylic acids is a well-established process and provides the basis for membrane extraction [63]. Since silage is already subjected to natural fermentation and therefore contains lactic acid, silage was selected as a representative process stream.

In the first step, the pressed juice concentrate was prepared. Different extractants, solubilizers and diluents were then tested in the two-phase extraction experiments. The extraction trials were evaluated for extraction efficiency and emulsion formation. From the extraction experiments, four solvent phases with high efficiency and low emulsion formation were selected for re-extraction experiments. The results were published in "Reactive extraction of lactic acid from sweet sorghum silage press juice" in Separation and Purification Technology 282 (2022) 120090 (DOI: 10.1016/j.seppur.2021.120090).

The results show that the composition of the solvent phase plays a key role in the extraction process, affecting both emulsion formation and extraction efficiency. Depending on the solvent phase, the volume fraction of emulsion varied from 2.6 to 42.3 vol%. The following four solvent phases with high extraction efficiency and low emulsion formation were selected for back extraction experiments:

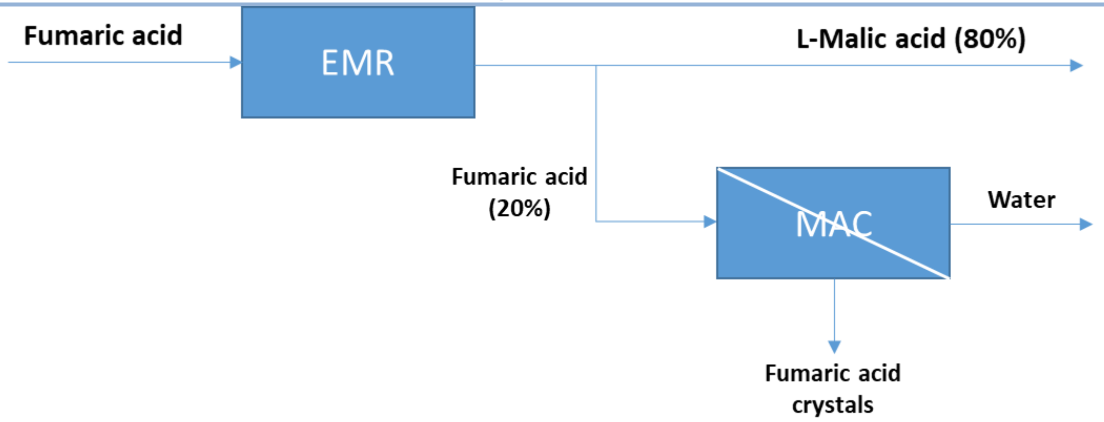
- Dioctylamine/aliquat336:1 octanol:n nonane (15:15:35:35 wt%) at 25 °C.

- Trioctylamine/aliquat336:1 octanol:n undecane (15:15:35:35 wt%) at 25 °C

- Dioctylamine:1 octanol:n nonane (30:35:35 wt%) at 50 °C

- Trioctylamine:1 octanol:n nonane (30:35:35 wt%) at 50 °C.

The back-extraction experiments showed that effective back-extraction of lactic acid from the loaded solvent phase was possible using 0.3 M NaOH and 0.3 M $NaHCO_3$. In another step, the isolation of lactic acid from pre-treated sugar millet silage pressed juice concentrate was investigated using continuous membrane extraction. Continuous operation was not possible here because deposits occurred on the membrane surface. To reduce deposits and enable continuous operation, the pre-treatment of the silage must be investigated and optimized, for example by means of a multi-stage membrane process [64].

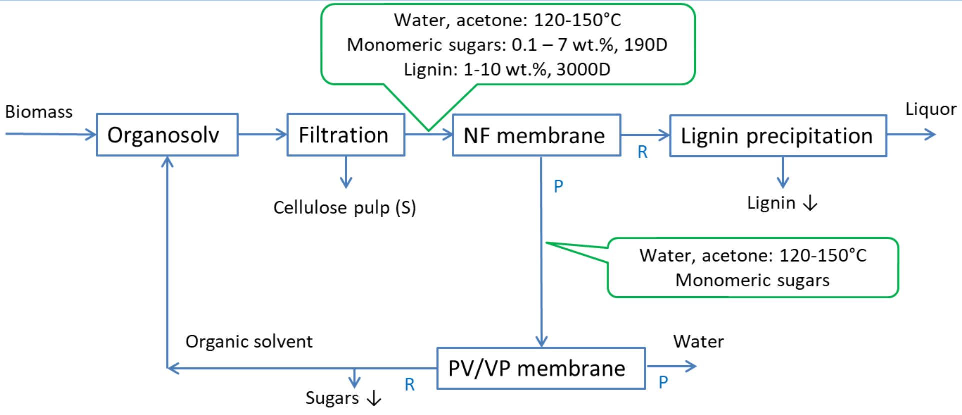
| Institution/contact | Integration scheme |
|---|---|
| Consiglio Nazionale delle Ricerche – Istituto per la Tecnologia delle Membrane (CNR-ITM)<br>Gianluca Di Profio<br>g.diprofio@itm.cnr.it |  |
| **Feedstock stream** | |
| Fumaric acid obtained as by-products from production of phthalic anhydride by oxidation of o-xylene | |
| **Pre-treatment** | |
| Pre-treatment can be necessary to enrich the phase downstream to the production of phthalic anhydride in fumaric acid | |

| Membrane process | Module & Membrane | Treatment capacity | | Production capacity |
|---|---|---|---|---|
| | | Per hour | Per membrane area | |
| Enzymatic membrane bioreactor (EMR)<br>Membrane-assisted crystallization (MAC) | MD020CP-2N modules (Microdyn) each containing 40 hollow fibers made in polypropylene (PP) | 0.60 - 0.65 kg/h | ~15 kg/m$^2$ | 2 L of solution (3.9x10$^{-2}$ M of fumaric acid and 1.6x10$^{-1}$ M of L-malic acid) recirculating through the membrane per each batch. Amount produced of fumaric acid: 0.50 g/L per batch |

| Membrane area deployed | Process inputs | | Highlights | Challenges and development goals |
|---|---|---|---|---|
| 0.1 m$^2$ of total membrane area per module | Chemicals | ☐Yes<br>☐No | The industrial application of fumaric acid, obtained as by-products from production of phtalic anhydride, is greatly limited by its low solubility. Its enzymatic conversion to L-malic acid by fumarase immobilized in asymmetric capillary membranes, more soluble and used as acidulant in foods, has been analysed[65], with maximum steady-state conversion degree of 80% . The possibility to recover the unreacted fumaric acid present in the outlet stream coming from a membrane bioreactor for the synthesis of L-malic acid, was demonstrated[66]. | Membrane cleaning is necessary, based on abundant washing with distilled water (temperature of 30-35 °C) before and after treatment with NaOH (0.5-1.0% w/w) and citric acid (pH 3-4) solutions, provided to restore the initial membrane performance. |
| | Thermal energy | ☒Yes<br>☐No | | |
| | Electrical energy | ☒Yes<br>☐No | | |

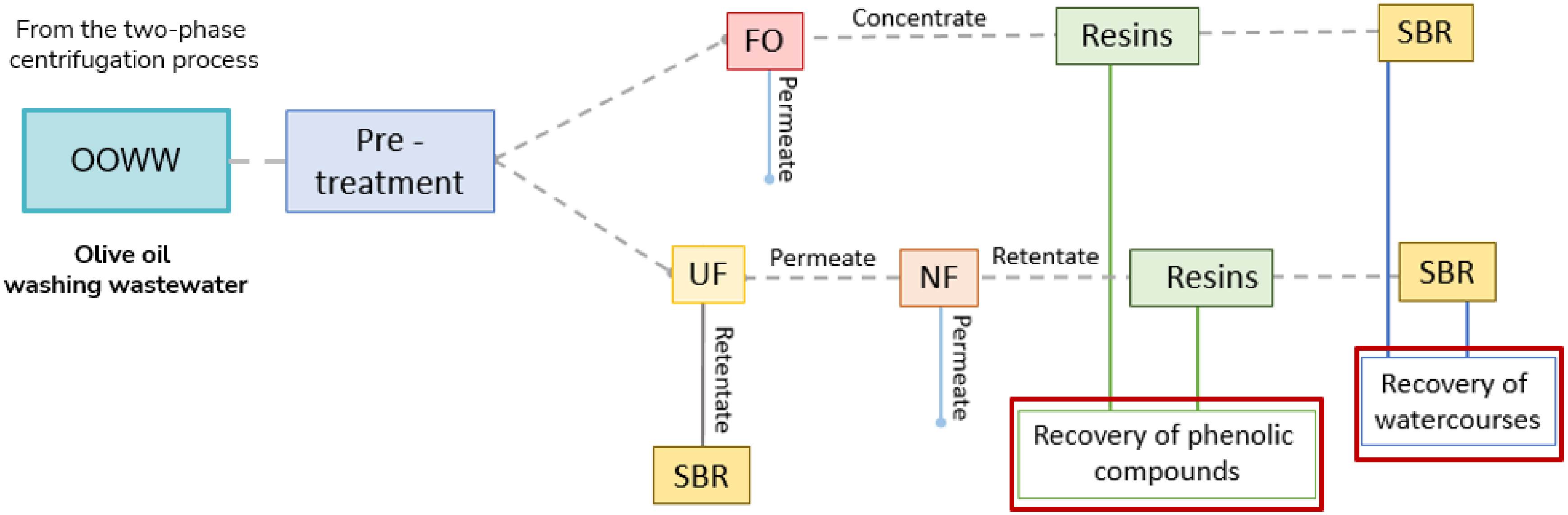
| TRL | | Further potential applications | Sources: |
|---|---|---|---|
| Application | Membrane operation | This technology is expected to be compatible with streams from other agro-industrial processes, such as lignocellulosic biomass and derivate, where biomolecules are also present. | 65, 66 |
| 3/4 | 3/4 | | |

## Lignocellulosic biomass fractionation (organosolv)

| Institution/contact | Objective | Feedstock stream | Integration point |
|---|---|---|---|
| TNO<br>Soraya.sluijter@tno.nl<br>Yvonne.vanDelft@tno.nl | Separate monomeric sugars from lignin and water/organic solvent mixture. | Organosolv stream (Fabiola ™) |  |
| **Pre-treatment** | **Membrane process** | **Module type** | |
| **Filtration** | Nanofiltration; pervaporation | Polymer on ceramic tubular support | |

| Challenges and development goals | | | Highlights | Further potential applications |
|---|---|---|---|---|
| Full process demonstration with real process mixtures | TRL | 4-5 | Two membrane processes (nanofiltration and pervaporation) to improve lignocellulosic biomass fractionation | Other monomeric sugar or water/organic solvent mixtures |
| | **Thermal energy** | Patent: WO2016131828A1 | | |

| Valorization of olive oil washing wastewater by means of a hybrid system: Membrane processes, Adsorption/Desorption and Biological Treatment. | |
|---|---|
| **Objective** | Recovery of phenolic compounds and recovery of watercourses. |
| **Contact** | Research Institute for Industrial, Radiophysical and Environmental Safety (ISIRYM),<br>Universitat Politècnica de València, C/Camino de Vera s/n, 46022, Valencia, Spain<br>Magdalena Cifuentes-Cabezas (magcica@upv.es), María Cinta Vincent-Vela, José Antonio Mendoza-Roca, Silvia Álvarez-Blanco |
| **Feedstock stream** | Olive Oil Washing Wastewater;<br>Wastewater obtained at the outlet of the vertical centrifugation (olive oil washing) obtained from the olive oil production process by centrifugation in two phases.<br>This olive oil production process is currently used in Spain. It uses less water than triphasic centrifugation (more widely used in other Mediterranean countries), so it is expected that more countries will opt for this more environmentally friendly option in the future. |
| **Capacity** | 55 m3/day only from October to January/February (olive oil production) |
| **Pre-treatment** | A three-stage pre-treatment was planned. The first stage consisted of natural flotation, sedimentation, and cartridge filtration (60 µm)[67]. |
| **Membrane process** | Ultrafiltration[67], [68], Nanofiltration[69], Forward osmosis |



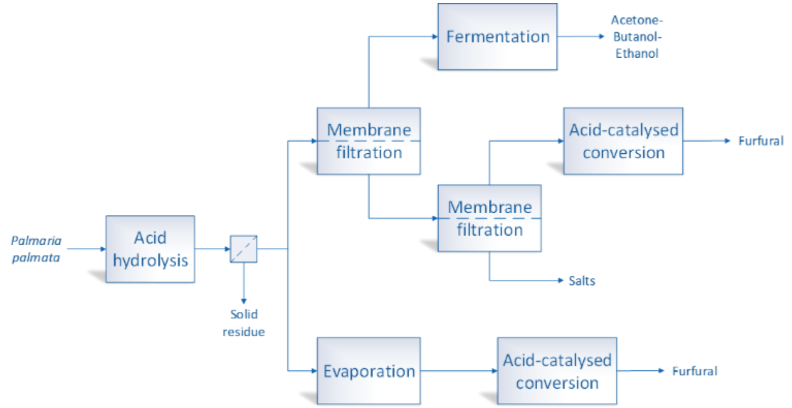
| **Module type/ Membrane material** | **Challenges and development goals** |
|---|---|
| FO: FTSH2O flat sheet membrane (Fluid Technology Solutions, USA) made from cellulose triacetate (CTA). The other membrane tested corresponded to the hollow fiber membrane HFFO.6 (Aquaporin Inside, Denmark), with an active layer of polyamide thin film composite (TFC) with integrated aquaporin proteins. | The main disadvantage comes when it comes to the different characteristics of the olive oil washing residual water. Since this depends on the characteristics of the olive and everything that affects it. Therefore, it is a wastewater with fluctuating characteristics, for this reason the process must be suitable to treat the water regardless of its variation, be it organic matter or phenolic compounds. Regarding membrane processes, the main disadvantage comes with the forward osmosis process. Unlike ultrafiltration and nanofiltration membranes, FO is a process little or not studied with OOWW. On the other hand, there are currently few FO membranes on the market. This limits finding a suitable membrane. |

| **Highlights** | **Further potential applications** |
|---|---|
| Compared to other processes proposed both to recover phenolic compounds from mill wastewater and to treat them, the proposed process does not consider chemicals. It is a process based on physical separation, which makes it friendly to the environment. | This practice is expected to be compatible with wastewater from other agro-industrial processes, such as wastewater from berry and wine production. Where compounds with high antioxidant characteristics (phenolic compounds) are also present. It is important to point out that this process would be a basis to begin studies, since the characteristics of each wastewater will govern the treatment process. |

**Literature:** [67,68, 69, 70, 71]

Acknowledgment: Spanish Ministry of Economy, Industry and Competitiveness through the project CTM2017-88645-R. The European Union through the Operational Program of the Social Fund (FSE) through ACIF-2018 and BEFPI-2021 grand. Universidade Nova de Lisboa - Associate Laboratory for Green Chemistry-LAQV which is financed by national funds from FCT/MCTES (UIDB/50006/2020 and UIDP/ 50006/2020).

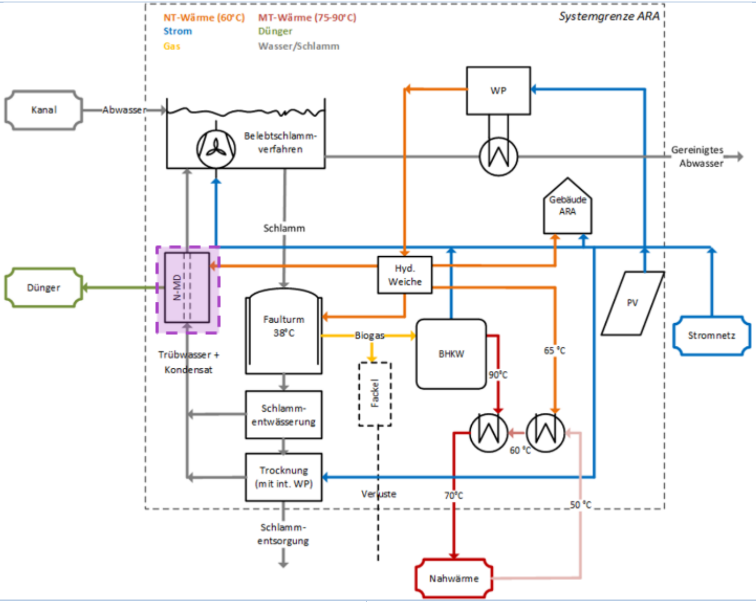
## (Seaweed) hydrolysate, separation of sugars and salts.

| **Institution/contact** | **Objective** | **Feedstock stream** | **Integration scheme** |
|---|---|---|---|
| TNO<br>Soraya.sluijter@tno.nl<br>Yvonne.vanDelft@tno.nl | Separate (monomeric) sugars from salt water stream. Remove salts to enable/improve fermentation. Separate different sizes of sugars. | Seaweed hydrolysate feed |  |

| **Pre-treatment** | **Membrane process** | **Membrane material** |
|---|---|---|
| Filtration, potentially RO | Nanofiltration | Polymeric membrane |

| **Process inputs** | | | **Highlights** | **Challenges and development goals** |
|---|---|---|---|---|
| Fermentable sugars (glucose + mannitol) 15 g/L; salts ($Na^+$, $K^+$): 13.6 g/L | Chemicals | ☐Yes<br>☒No | Sugar loss < 3%, reaching the defined syrup quality with respect to sugar (92% retention) and salt concentration for fermentation | Investigations on pH level and membrane surface area (modelling), optimization related to economics |
| | Thermal energy | ☒Yes<br>☐No | | |
| | Electrical energy | ☒Yes<br>☐No | | |

| **TRL** | | **Further potential applications** |
|---|---|---|
| **Application** | **Membrane operation** | Other salt sugar separations |
| 4 | 5 | |

| **Selective recovery of ammonia/ water purification** | | | | |
|---|---|---|---|---|
| **Objective** | **Feedstock stream** | **Highlights** | | **Integration point** |
| Remove/recover ammonia from WWTP effluent and produce a fertilizer in the form of an Ammonium Sulphate (AS) solution. | Digestate sludge supernatant (after dewatering of sludge) | Ammonia recovery up to 99%;<br>Effluent <10 mg TAN/l;<br>CF of N-NH4 concentration from feed to permeate up to 5; High purity of the product | |  |
| **Production capacity** | **Challenges and development goals** | **TRL Application** | **TRL Membrane operation** | |
| ~ 100 l ammonium sulfate at 6.4 g NH4 l$^{-1}$ | Towards higher product (AS) concentration in the permeate and solid product. | 4-5 | 4-5 | |

| **Pre-treatment** | **Membrane process** | **Module / Membrane** | **Treatment capacity** | | **Membrane area deployed** |
|---|---|---|---|---|---|
| | | | Per day | Per membrane area | |
| Filtration of TS and particles/cartridge filter (200 µm) | MD | Plate and frame / PP | ~ 1 m$^3$/day | 0,07 m$^3$/m$^2$ membrane | Up to 14 m$^2$ |

| **Membrane process inputs** | | | | | |
|---|---|---|---|---|---|
| **Chemicals** | ☒Yes<br>NaOH<br>$H_2SO_4$ | **Thermal energy** | ☒Yes<br>13,6 kWh$_{th}$ pro kg NH3 | **Electrical energy** | ☒Yes<br>Only for recirculation pumps |

| **Further potential applications** | **Further info sources** |
|---|---|
| Biogas plants, slaughterhouses, any ammonia-rich stream. | ThermaFlex project: https://thermaflex.greenenergylab.at/thermaflex/?lang=en<br>Guillen et al, 2023 [72]<br>Contact: b.muster@aee.at |

# 5. Long-term studies

There is little literature available on long-term studies and experiences with emerging membrane technologies operating with real process fluids. One study that could be carried out within the period of IEA IETS Task 17 2018-2022 was a long-term evaluation of membrane distillation for ammonia recovery. Operational details have been published in ([73]), while membrane analysis and cleaning results have recently extended the work.
It is the aim of IEA IETS Task 17 to further collect such long-term studies in order to enhance trustability in emerging membrane operation and enable industrial deployment of the technologies.

## 5.1 Long- term study Membrane Distillation (MD)

In the long-term tests on ammonium removal by means of membrane distillation in the wastewater treatment plant (WWTP), operation was guaranteed over a period of 3 months and about 700 hours, without any major maintenance effort.

Wastewater treatment plants have great potential to act as hubs of energy and resource supply in the future. While currently wastewater treatment plants often consume energy, new intelligent concepts make it possible to transform the plants into energy suppliers.

One of the most energy-intensive processes in wastewater treatment plants is nitrogen removal in the nitrification/denitrification (N/DN) process, with specific electrical energy demand values ranging from 5 to 15 kWh/kg TN [74]. A look at global data shows the world's inefficient use of ammonia - only 16 percent of the nitrogen fertilizer produced annually is used, with the rest lost to water and the atmosphere, with nitrogen synthesis via the Haber-Bosch process requiring 1-2 percent of annual global energy consumption [75]. To improve energy and resource efficiency in wastewater treatment plants, a study on selective ammonium removal from wastewater treatment plants using membrane distillation was carried out as part of the "Thermaflex" and "IEA IETS Task 17" projects. The aim is to reduce the nitrogen load in wastewater treatment plants (main clarifier, digestion tower) and to produce ammonium sulfate for regional fertilizer applications as a by-product. By increasing the pH, the ammonium bound in the water is converted into the form of free ammonia, which diffuses across the membrane. On the permeate side, the ammonia is bound as ammonium sulfate. While traditional nitrogen removal in the wastewater treatment plant requires electricity and releases the nitrogen into the atmosphere as $N_2$, membrane distillation can be operated at very low temperatures of 30 to 40 °C and allows the nitrogen cycle to be closed.

In December 2020, a pilot plant was installed at the Gleisdorf wastewater treatment plant as a container plant to treat the centrate water by membrane distillation after separation of the sewage sludge. In order to determine optimal operating conditions, the operating parameters were evaluated in laboratory tests and implemented in the pilot plant. In the first pilot phase, 100 liters of centrate water were treated in batch operation at a time; later, the plant was further automated to allow 24-hour operation and thus to be able to gather long-term experience.

*Figure 3: A membrane distillation unit installed in a container was installed for a two-month real operation at the wastewater treatment plant Gleisdorf (from right to left : container unit from outside, container from inside, membrane distillation module), (Source: AEE INTEC).*

In the first operation phase the target of high ammonium recovery could be demonstrated with 96% ammonium removal in 100l feed after 2 operation time. The ammonium concentration of the treated centrate water was below 10 mg/l ammonium nitrogen. Compared to standard conditions, the water vapor passage through the membrane accompanying ammonia diffusion was reduced by 94 percent, demonstrating far more selective removal of ammonium than previously possible [76].

In the second pilot phase, optimization was carried out regarding a lower requirement for caustic soda and long-term operation was demonstrated at a reduced pH value of the feed of pH 8.7. In this phase, the pilot plant was modified, equipped with further automated control, and could be operated continuously 24 hours a day, treating about 1 $m^3$ of feed water per day. The feed water was passed through the membrane distillation (14 $m^2$ membrane area) in 100 liter batches at a time until almost complete ammonium removal. The permeate was not exchanged and thus the concentration was continuously increased. The results show that the plant was able to achieve ammonium removal of over 90 percent over several weeks at pH 8.7, and the ammonium concentration was reduced to less than 20 mg/L. The permeate reached an ammonium sulfate concentration of about 23 g/l (corresponding to a nitrogen concentration $N\text{-}NH_4$ of 5g/l ) during this pilot phase. This concentration settled as a stable product concentration. Measures to increase this even further have since been implemented in laboratory tests. The energy requirement in the second pilot phase was 16 $kWh_{th}$/kg NH4, although in this operation only the feed side has to be heated to 38 °C, or in an integrated operation the heat of the centrate water can be partly used directly after sludge removal by a centrifuge [77] .

A crucial point of the evaluation was the stability of the process and the necessary cleaning. The plant proved to be very robust and operating problems arose during the pilot phase only with regard to the pre-cleaning system, which is currently very simple and whose filters had to be replaced again and again. The membrane distillation continued to run constantly even after intermediate shutdowns. In several operating campaigns, no drop in treatment efficiency was observed for weeks, with the plant being flushed with citric acid on the feed side for 2 hours after each campaign (approx. 5-15 days). For example, ammonium removal was > 99 percent in two comparable treatment cycles before and after acid flushing.

### 5.2 Fouling and Cleaning

During the ongoing long-term operation with the pilot plant, it was not possible to optimize the cleaning. Therefore, the module was subsequently opened and the membranes were exposed to various cleaning tests. Differences in cleaning efficiency due to different cleaning methods could not be detected in the subsequent ammonium tests.

Figure 4 shows an example of the achieved N-$NH_4$ membrane flux for some cleaning procedures. A similar flux could be achieved before and after cleaning. Thus, with an error of +/- 3%, which must be expected in the experiments, no significant difference can be detected. It is interesting to note that there is a tendency for a slight decrease in N-$NH_4$ flux after the cleaning procedures.

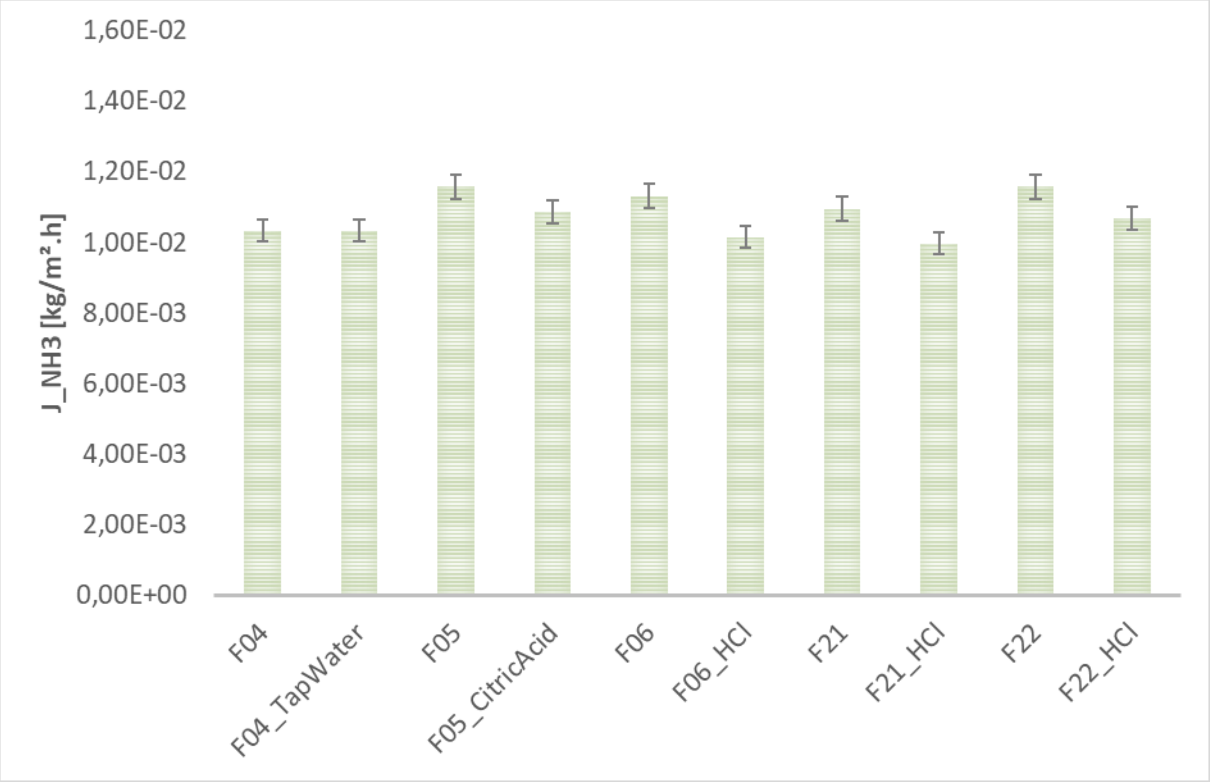


*Figure 4: Ammonia flux in the reference tests of different membrane pieces before (F04, F05, F06, F21, F22) and after (F04_TapWater, F05_CitricAcid, F06/F21/F22_HCl) different cleaning procedures.*

A new (virgin), an unpurified (fouled), and a purified (fouled&cleaned; 0.05 M HCl, 40 min) membrane were selected for SEM/EDX analysis.

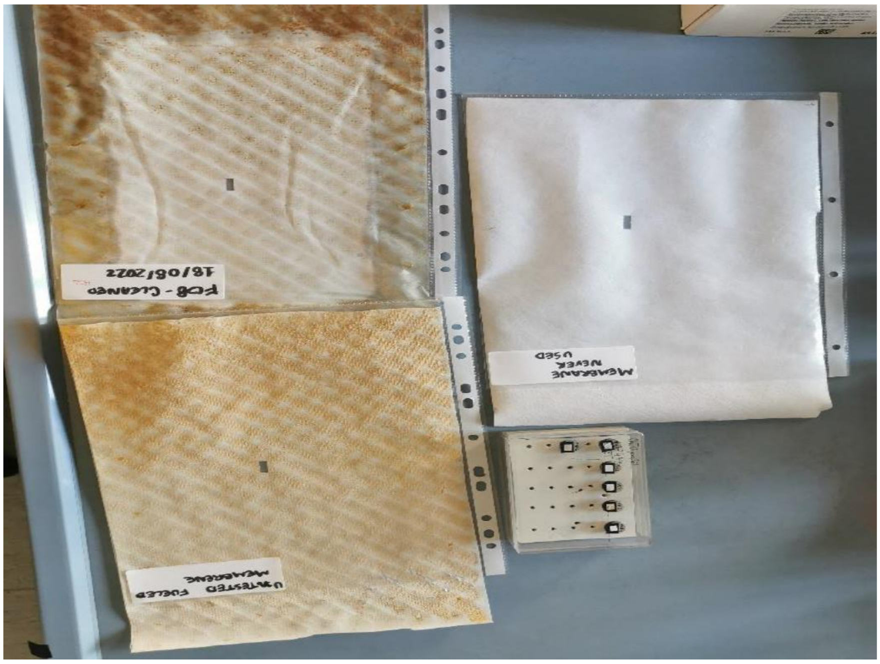


*Figure 5: Photo of the selected membranes for SEM/EDX analysis*

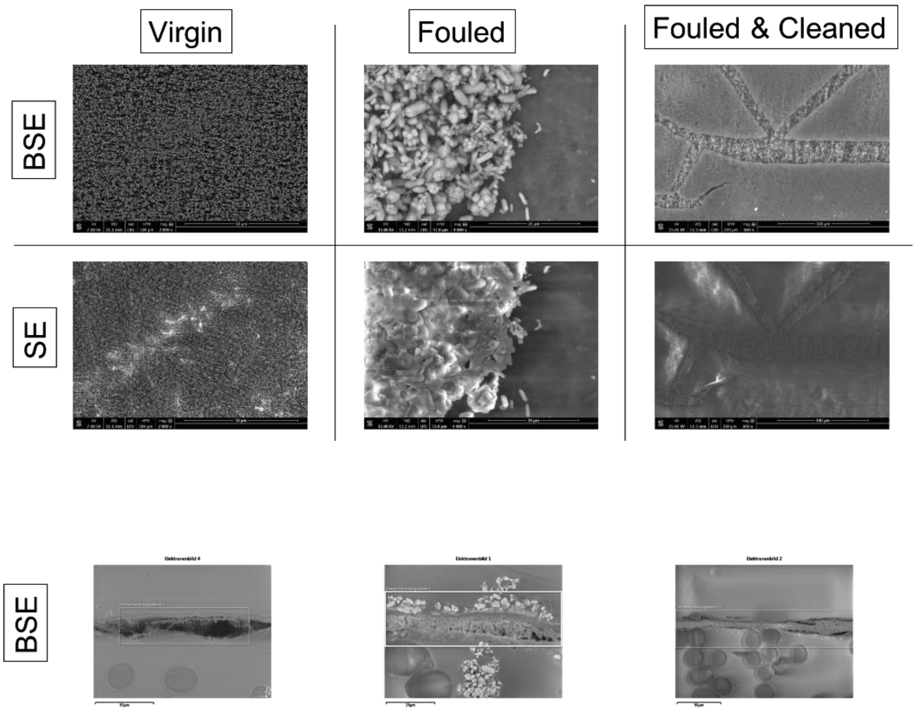


*Figure 6: SEM Images of the membrane at the surface (top) and in cross-section (bottom), FELMI-ZFE.*

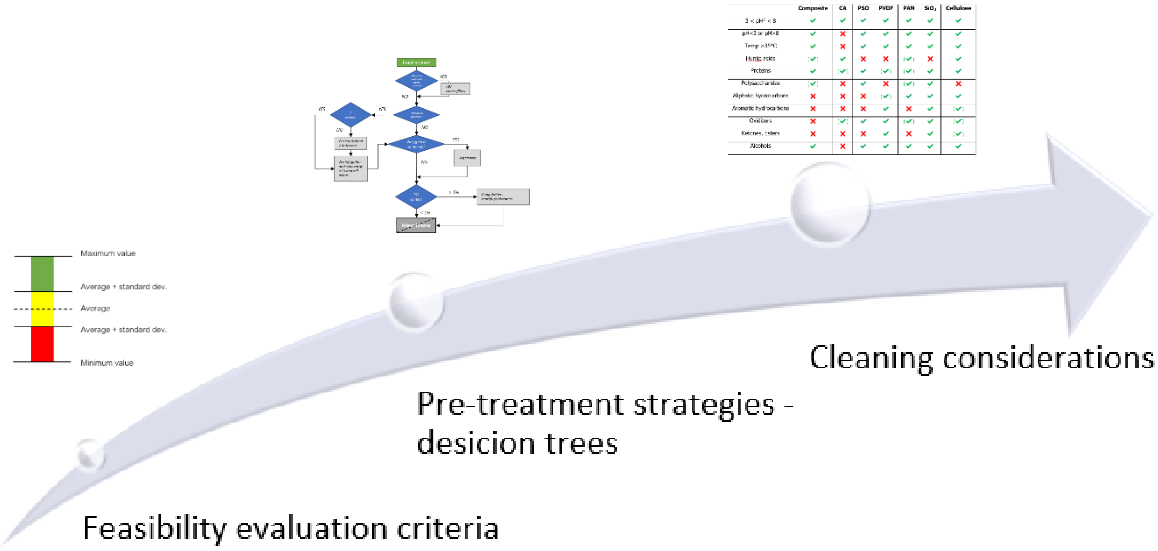
The pictures show clear crystal deposits on the uncleaned membrane, which are significantly reduced after cleaning. However, a thin layer remains under the crystal deposits on the membrane, which is not removed after cleaning, but only gets cracks.

The further EDX results show that the crystal deposits are mainly inorganic scaling (probably $CaCO_3$), which can be well cleaned from the membrane by acid cleaning. Interestingly, the thin top layer - which cannot be cleaned by the selected cleaning methods - is rich in N as well as Si and P, according to the analyses. This could therefore be a layer of protein fragments that had either still been in the centrate water or had re-agglomerated from protein degradation products over the operating time. The fact that protein layers are difficult to clean has already been shown in other work [78]. It is also hypothesized that this layer accumulates on the membrane over the operating time but does not have a negative effect on the $N\text{-}NH_4$ flux.

# 6. Possibilities of how to evaluate integration of feasibility of membrane usage

Within this guideline a possible way of dealing with a separation question in a biorefining approach shall be addressed. In this chapter the reader will be led through general feasibility criteria depending on both membranes and feed media, and decision making on pre-treatment methods and cleaning strategies.

The identification of optimal process conditions is a challenging task due to the complexity of the fouling phenomenon and all the factors that play a role in it. In literature most of the studies have been exploring the effect of temperature, pressure, velocity and volume reduction factor/recovery factor.



|  | Composite | CA | PSO | PVDF | PAN | $SiO_2$ | Cellulose |
|---|---|---|---|---|---|---|---|
| $3 < pH^2 < 8$ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| pH<3 or pH>8 | ✓ | ✗ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Temp >35°C | ✓ | ✗ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Humic acids | (✓) | ✓ | ✗ | ✗ | (✓) | ✗ | ✓ |
| Proteins | ✓ | (✓) | ✓ | (✓) | (✓) | ✓ | ✓ |
| Polysaccharides | (✓) | ✗ | ✓ | ✗ | (✓) | ✓ | ✗ |
| Aliphatic hydrocarbons | ✗ | ✗ | ✗ | (✓) | ✓ | ✓ | ✓ |
| Aromatic hydrocarbons | ✗ | ✗ | ✗ | ✓ | ✗ | ✓ | (✓) |
| Oxidizers | ✗ | (✓) | ✓ | ✓ | (✓) | ✓ | (✓) |
| Ketones, Esters | ✗ | ✗ | ✗ | ✓ | ✗ | ✓ | (✓) |
| Alcohols | ✓ | ✗ | ✓ | ✓ | ✓ | ✓ | ✓ |

*Figure 7: Evaluation method for emerging membrane applications in biorefineries concerning feasibility, pre-treatment and cleaning consideration.*

In general, improving hydrodynamic conditions via higher velocities contributes to reduce the polarization effects and the fouling while increasing the volume reduction factor can be detrimental to fouling. Temperature has shown opposite effects as it can, on the one hand, increase permeate flux but on the other, it can reduce for example the floc size and as a consequence increase the filtration resistance and the fouling.

The different available membranes have additional limiting conditions in their operation. These operational limits are related to the membrane material and will have an effect on their lifetime and might limit the pre-treatment choice.

For example, cellulose acetate (CA) used for RO, NF and UF applications has limitations with respect to pH and temperature. It also has low resistance to biofouling since it can be used by the microorganisms as a substrate. Polysulfone (PSO) also used in UF and MF applications has exceptional temperature and pH resistance. This is why PSO is mostly used in food and dairy applications. However, they don’t tolerate oil, grease, fat and polar solvents. Polyvinylidenedifluoride (PVDF) main advantage is its high resistance to hydrocarbons and oxidizing environments. New composite (TFC) or thin-film membranes (TFM) have good temperature and pH resistance, but do not tolerate oxidizing environments. Although their specific composition is proprietary, generally speaking, a thin-film composite membrane consists of a PSO membrane as support for the very thin skin layer which is polymerized in situ on the PSO UF membrane. Other materials such as polyacrylonitrile (PAN), ceramic materials ($SiO_2$) and cellulose (hydrolyzed cellulose acetate) are also used to fabricate membranes.

The following table shows the chemical resistance of some of these membrane materials, it has been modified from the Membrane Filtration Handbook Practical Tips and Hints published by Osmonics in 2001[79].

*Table 4: Chemical resistance of some of these membrane materials. Modified (Wagner, 2001).*

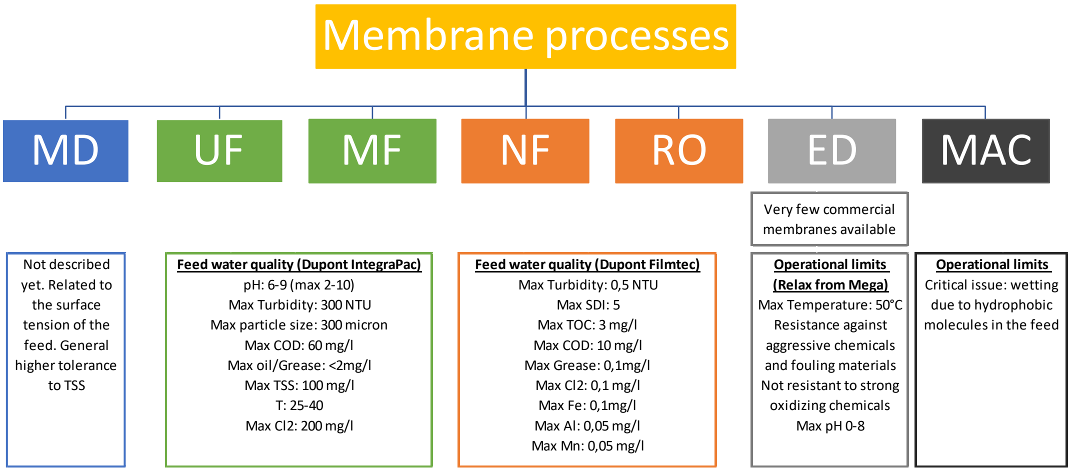
| | **Composite** | **CA** | **PSO** | **PVDF** | **PAN** | **$SiO_2$** | **Cellulose** |
|---|---|---|---|---|---|---|---|
| 3 < pH[3] < 8 | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| pH<3 or pH>8 | ✓ | ✗ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Temp >35°C | ✓ | ✗ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Humic acids | (✓) | ✓ | ✗ | ✗ | (✓) | ✗ | ✓ |
| Proteins | ✓ | (✓) | ✓ | (✓) | (✓) | ✓ | ✓ |
| Polysaccharides | (✓) | ✗ | ✓ | ✗ | (✓) | ✓ | ✗ |
| Aliphatic hydrocarbons | ✗ | ✗ | ✗ | (✓) | ✓ | ✓ | ✓ |
| Aromatic hydrocarbons | ✗ | ✗ | ✗ | ✓ | ✗ | ✓ | (✓) |
| Oxidizers | ✗ | (✓) | ✓ | ✓ | (✓) | ✓ | (✓) |
| Ketones, Esters | ✗ | ✗ | ✗ | ✓ | ✗ | ✓ | (✓) |
| Alcohols | ✓ | ✗ | ✓ | ✓ | ✓ | ✓ | ✓ |

✓ high resistance

(✓) either that the information is based on theory or that practical results have proved to be dubious

✗ low resistance

Figure 8 summarizes some of the water quality requirements specific for different membrane processes. These requirements are dictated by the manufacturers and as we have seen, depend on many membrane characteristics. The graph contains examples of commercial product of Dupont (US) and Mega (CK).



Very few commercial membranes available

Not described yet. Related to the surface tension of the feed. General higher tolerance to TSS

**Feed water quality (Dupont IntegraPac)**
pH: 6-9 (max 2-10)
Max Turbidity: 300 NTU
Max particle size: 300 micron
Max COD: 60 mg/l
Max oil/Grease: <2mg/l
Max TSS: 100 mg/l
T: 25-40
Max Cl2: 200 mg/l

**Feed water quality (Dupont Filmtec)**
Max Turbidity: 0,5 NTU
Max SDI: 5
Max TOC: 3 mg/l
Max COD: 10 mg/l
Max Grease: 0,1mg/l
Max Cl2: 0,1 mg/l
Max Fe: 0,1mg/l
Max Al: 0,05 mg/l
Max Mn: 0,05 mg/l

**Operational limits (Relax from Mega)**
Max Temperature: 50°C
Resistance against aggressive chemicals and fouling materials
Not resistant to strong oxidizing chemicals
Max pH 0-8

**Operational limits**
Critical issue: wetting due to hydrophobic molecules in the feed

*Figure 8: Typical feed water quality and/or operational limits for different membrane processes.*

---

[3] The pH limitations stated by most membrane manufacturers are in reality the limitations presented by the overall membrane configuration or membrane system rather than by the membrane material itself, the weakest material in the whole system determines the limitation. For example, PE backer materials have limited resistance to high pH.

In addition to the described general aspects of membrane processes, in the following chapter a methodological approach on an evaluation pathway is given:

## a. Feasibility decision criteria

For the evaluation of the potential of implementing a membrane separation process, such as membrane distillation (MD), liquid membrane permeation (LMP), pervaporation (PV), and forward osmosis (FO), primarily theoretical and technological bases of each membrane separation process can be used. In the work by J. Ressler, an evaluation method was developed, to select membrane processes in the pulp and paper industry, which is summarized below.

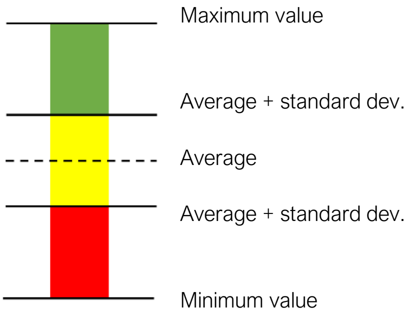


*Figure 9: Schematic classification of an evaluation criterion according to the traffic light system with included standard deviation.*

The evaluation method itself is performed using a traffic light system (green, yellow or red see Figure 9). Evaluation criteria consisting of quantitative and qualitative points were established for each of the membrane separation processes considered. For quantitative evaluation criteria (for example, transmembrane flux [$Lm^2/h$]), the resulting color was defined by numerical values (for example, by the color red for low transmembrane flux). The range (= highest and lowest numerical value) and subdivision (= the limit up to which a traffic light color is valid) for the classification according to the traffic light system were made specifically according to the criterion of evaluation for the respective membrane separation process. A qualitative evaluation criterion is, for example, the existence of results of scientific experiments. The classification was based on the definition of the evaluation criterion.

In order to prevent a "sharp delimitation" of fixed color values, a variable color value was implemented by linear interpolation.

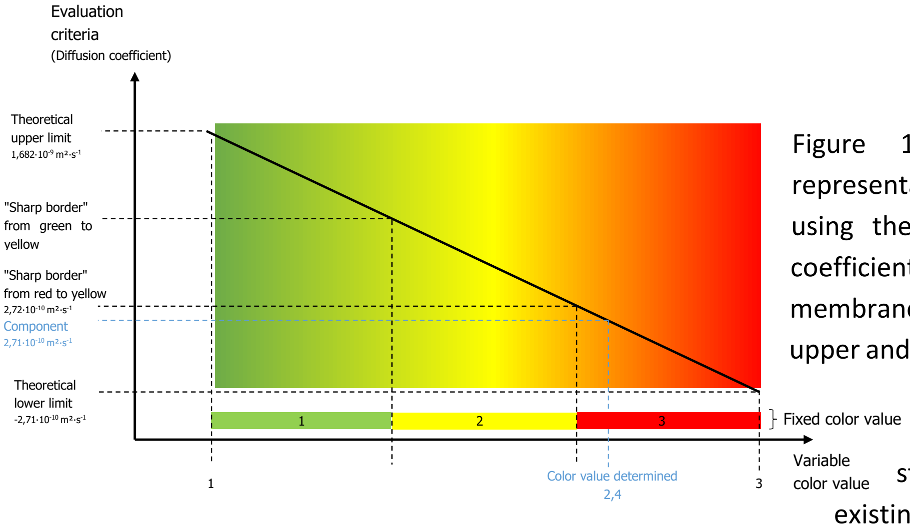


*Figure 10: Schematic representation of linear interpolation using the example of the "diffusion coefficient" evaluation criterion in liquid membrane permeation.*

Figure 10 shows the schematic representation of linear interpolation using the example of the "diffusion coefficient" evaluation criterion in liquid membrane permeation. The theoretical upper and lower limits, in the case of the diffusion coefficient, were defined by taking the standard deviation of all existing diffusion coefficients.

The arithmetic mean of all color values within a technology can then be summed up and used for evaluation. Table 5 show the following evaluation criteria for the process of membrane distillation MD: partial vapor pressure difference, transmembrane flux and feed temperature with the respective classification in the color code.

*Table 5: Presentation of the evaluation criterion for membrane distillation including classification with color code.*

<table>
<tr><td colspan="3"><i>Evaluation criterion:</i> Partial vapor pressure difference<br>The partial vapor pressure difference [mbar] represents the driving force of the MD. When the partial vapor pressure of a component is higher than that of water (pi> pW) it permeates through the membrane, otherwise it is concentrated in the feed stream (pi<pW). The lower the partial vapor pressure difference (Δp=|pw-pi|), the lower the probability of selective separation or concentration of the component. The classification and the bandwidth of the color range are determined according to the median of all partial vapor pressure differences of the components to be evaluated with respect to water (bandwidth of a color range = zero to median). (pW = partial vapor pressure of water; pi = partial vapor pressure of the component).</td></tr>
<tr><td rowspan="3"><i>Classification</i></td><td>🟩</td><td>The partial vapor pressure difference (Δp) is >58 mbar.</td></tr>
<tr><td>🟨</td><td>The partial vapor pressure difference (Δp) is in the range of 29-58 mbar or could not be determined.</td></tr>
<tr><td>🟥</td><td>The partial vapor pressure difference (Δp) is <29 mbar. The partial vapor pressure of the component approaches that of water and it becomes increasingly difficult to selectively separate or concentrate the component.</td></tr>
<tr><td colspan="3"><i>Evaluation criterion: Transmembrane flux</i><br>The performance of a membrane in MD is indicated, among other things, by the transmembrane flux [L·m$^2$/h.]. The values collected are from empirical studies. The classification is determined according to the mean value of the transmembrane fluxes of the components to be evaluated of all membrane separation processes, as surveyed in the conducted literature research. Within the classification, a finer evaluation is performed by linear interpolation.</td></tr>
<tr><td rowspan="3"><i>Classification</i></td><td>🟩</td><td>Transmembrane flux ≥5 L·m$^2$/h.</td></tr>
<tr><td>🟨</td><td>No/missing data or empirical studies are available.</td></tr>
<tr><td>🟥</td><td>Transmembrane flux <5 L·m$^2$/h.</td></tr>
<tr><td colspan="3"><i>Evaluation criterion: Feed temperature</i><br>The technologically optimum working range of the MD is at operating temperatures in a range of 30 95 °C, not taking into account the waste heat potential. Therefore, it is recommended that the feed stream (and therefore the waste liquor and condensate stream) be within this temperature range so that additional energy input is not required.</td></tr>
<tr><td rowspan="3"><i>Classification</i></td><td>🟩</td><td>A sufficient temperature of the feed stream (≥30 °C) is given to operate the MD without additional energy supply.</td></tr>
<tr><td>🟨</td><td>Temperature of the feed stream is unknown.</td></tr>
<tr><td>🟥</td><td>Sufficient temperature of the feed stream (<30 °C) is not given and additional energy supply is required to operate the MD optimally.</td></tr>
</table>

## b. Pre-treatment strategies

Especially in the pulp and paper industry, a high fouling tendency due to wood hydrolysates can be expected as a challenging factor for a wide application of membrane processes. Due to the complexity of the components and the lack of studies on membrane fouling, there is a lack of detailed information on the properties and type of particles that can cause fouling. However, it can be determined whether the particles cause deposition of material on the membrane surface, for example, by their size or by their organic or inorganic composition, which are critical factors in the fouling process [80].

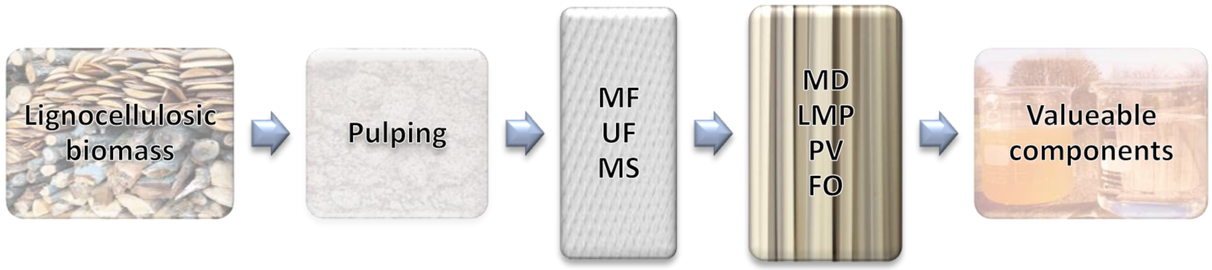


*Figure 11: Possible process for pre-treatment of waste liquor from pulp production. MF...microfiltration, UF...ultrafiltration, MS... mechanical skimming, MD... membrane distillation, LMP...liquid membrane permeation, PV...pervaporation, FO...forward osmosis (adapted from Bokhary et al, 2016).*

Pre-treatment strategies may be of different kind. Figure 11 gives an overview of how different membrane operations can be combined in hybrid processes. The objective can lay in diminishing fouling, as well as increasing the permeates quality. How effective a pre-treatment method works, depends on the type (agent), amount (dosage), temperature, feed and membrane characteristics. Foulants might be degraded, inactivated or removed. In pulp and paper mills effluents strategies such as coagulation, activated carbon adsorption, laccase addition, pH adjustment or ozone oxidation are applied [81]. For example, pre-treatment of waste liquor with microfiltration or ultrafiltration prior to the use of emerging membrane separation technologies not only helps to reduce fouling, but also facilitates subsequent membrane cleaning. Using the recovery of tall oil soap in the course of ultrafiltration as an example, it is shown that concentration of this can be accomplished by upstream mechanical skimming[82]. This procedure could also be applied to newer technologies of membrane separation processes. The following figure shows a possible sequence for pre-treatment of waste liquor from pulp production.

The management of membrane fouling through the incorporation of pre-treatment methods has gained increasing popularity in membrane technologies, since they not only prevent or delay fouling but also potentially increase permeate output and quality.

Most of the examples of proposed pre-treatment strategies to reduce membrane fouling that can be found in literature are related to pressure driven membrane operations (mainly UF) and the pulp and paper industry[81]. Very few examples can be found for other membrane separation technologies like FO [83] or other bio sectors like algae cultivation/harvesting [84] or biogas digestates [85], [79].

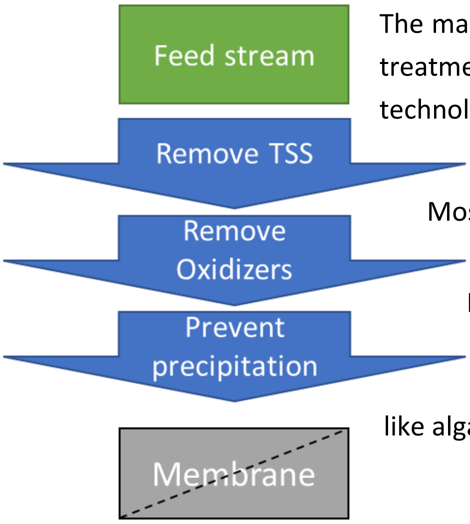


*Figure 12: General pre-treatment strategy prior to membrane operations.*

Pre-treatment prior to membrane filtration is extremely important and the nature and thoroughness of the pre-treatment is, in many cases, determining the overall plant performance. A good pre-treatment strategy can be summarised in these 3 rules. Additionally, rule number 3 applies to the operation of the plant too:

- Remove harmful suspended solids
- Remove oxidizers
- Prevent precipitation in the plant

One single recipe for a pre-treatment strategy cannot be given for all the variety of different bio streams. However, within this work the authors tried to set up a decision tree for the two categories (general waste (see Figure 13) and pulp and paper streams (see Figure 14)) in order to help the user to follow a method for the integration of a membrane technology. Special cases have to individually be adapted.

As an example, in order to perform membrane-assisted crystallization in biorefinery applications, transfer of the target material to be purified into a buffer compatible with the crystallization protocol and adjustment of the concentration of the molecule to concentrations optimal for crystallization (pre-treatment step) can be necessary. Defining a pre-treatment procedure for the solution, based on simple filtration operations in order to remove eventual molecules present in the clarified fermentation broths and which can be at the origin of the membrane fouling/wetting is therefore requested.

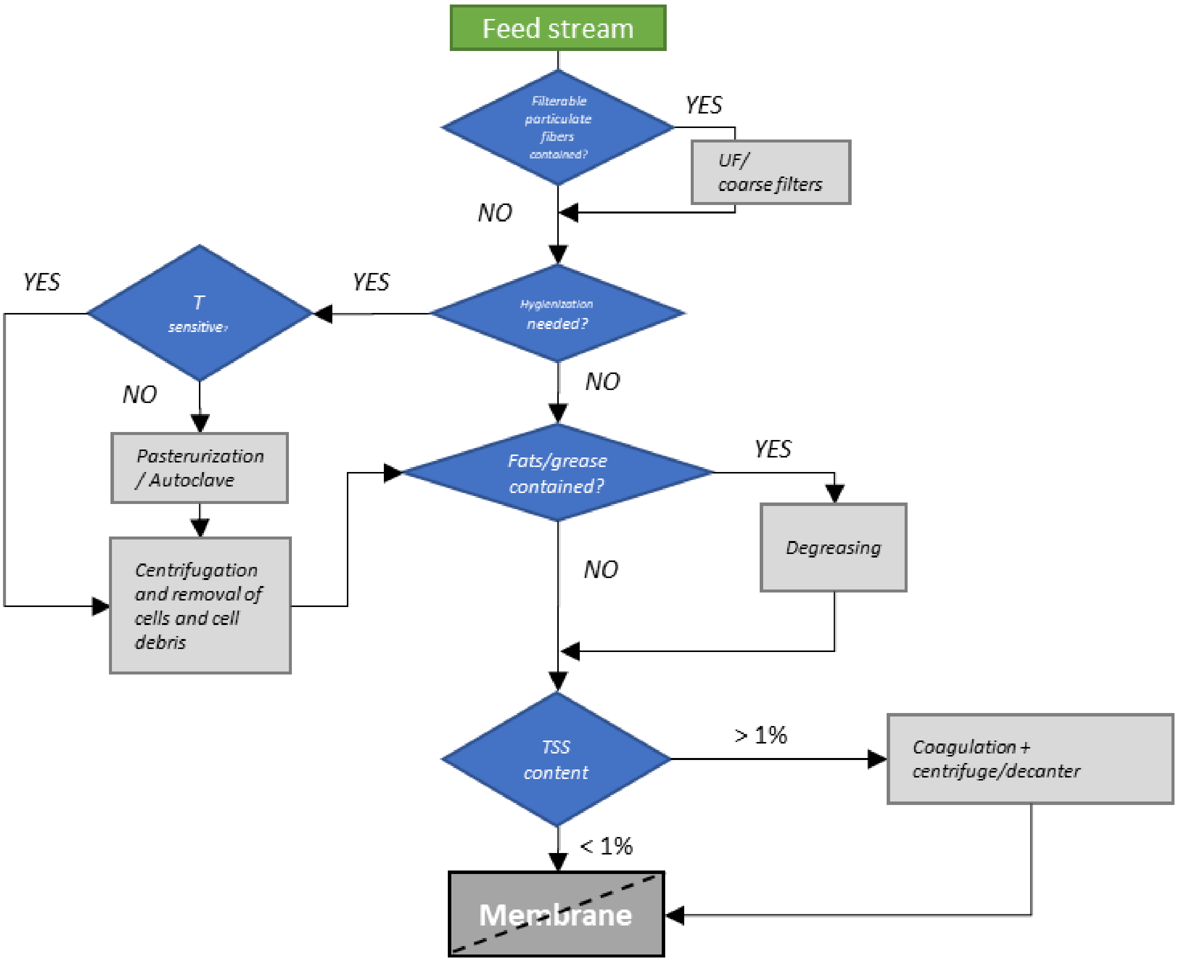


*Figure 13: Method for approaching a pre-treatment application of a general bio waste stream (Questions to be raised in rhombus, to be answered with yes or no, leading to a possible treatment step (rectangular boxes).*

Following the methodological approach of Figure 13, the bio stream of interest needs to be evaluated towards the following points. If there is filterable particulate matter such as fibres in the liquid stream, as a first step a coarse filter or UF can be applied. Else the question whether disinfection is needed should be addressed (i.e. in communal waste water). If there are any concerns on hygiene, while having a temperature sensitive media the pathways towards centrifugation and cell / cell debris removal might be approached. Having a non-sensitive media an additional previous step in form of pasteurization or autoclavation can be done. Does the substrate additionally include fats or greases, a degreasing step might be appropriate. Having a final look at the TSS content, at higher than 1% TSS a coagulation and centrifugation/decanting step could be applied before starting the membrane operation.

A little more specific and stepwise approach is shown with Figure 14. Here, a pulp and paper stream is given. After deciding on the membrane process to be applied as a first step the feed stream needs to be characterized towards its main foulants. This can either directly lead to the design of the pre-treatment or lead through the membrane selection (in terms of material, module and so forth) and the identification of operation limits of process and membrane (in terms of pH, T, TSS etc.). Three specific removal steps are given in the rhombus boxes suggesting TSS removal with MF, coagulation or polymeric ads., phenol removal through activated carbon or laccase addition and lignin degradation with AOPs before application of the chosen membrane process.

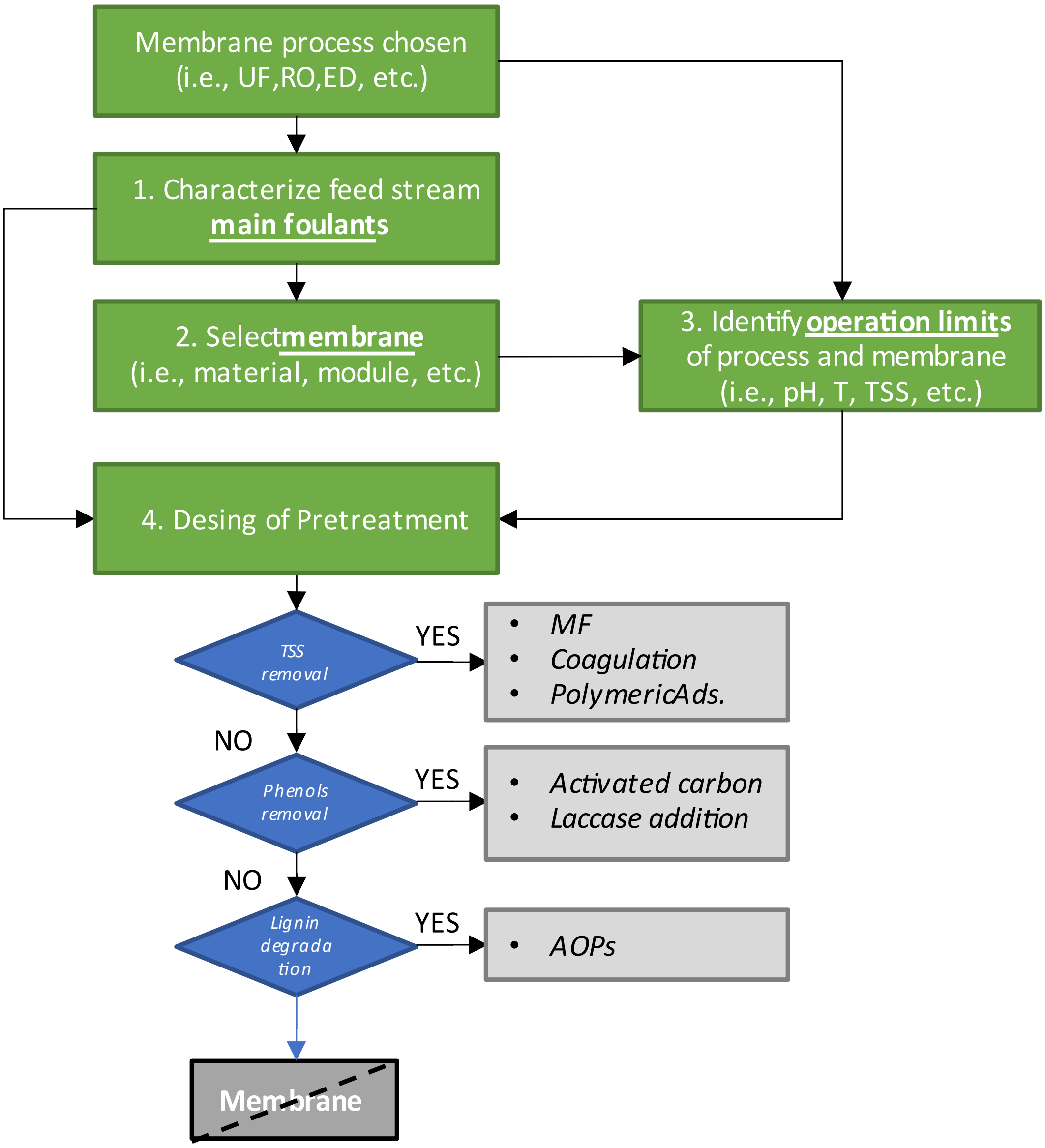


*Figure 14: Stepwise approach towards membrane integration with pulp and paper streams*

Additionally, to the stepwise approaches given by the decision tress above, more details on pre-treatment steps as found in literature, including pH adjustment, pre-filtration, coagulation. Polymeric adsorbents activated carbon adsorption, laccase addition and oxidation, are mentioned as follows:

### pH Adjustment

The pH adjustment is in general the first step in pre-treatment. The pH defines the polarity of the foulant particles and the membrane surface. In general, the negative polarity of the particles increases with more basic pH values. Pulp and paper mill effluents can be both extremely alkaline or acidic; therefore, a pH change can modify the membrane foulant interactions greatly and potentially diminish the membrane fouling. In general, it has been observed that alkaline conditions reduce membrane fouling.

Koivula et al. used alkaline pH (NaOH) for the pre-treatment of hydrolysates from birch and spruce as a preliminary step to destabilize the lignin network. High pH transformed some of the carboxylic acids into salts reducing their ability to stabilize the lignin network. However, at neutral pH carboxylic acid groups are repelled by the negatively charged membrane, which might reduce fouling. However, the authors noticed no significant influence of the pH adjustment in the filtration capacity. One important drawback of this method is that large volumes of pulp and paper wastewaters need large quantities of chemicals which renders this method as economically inefficient [86].

It is good to remind here that pH is a limiting operational factor for some membranes, this has to be taken into account when using this pre-treatment method. A specified pH-limitation may be flexible to some degree and can be exceeded for short periods and under the right conditions without detrimental effects. Low pH is usually not as problematic as high pH. Exceeding pH limitations with elevated temperatures is almost guaranteed to cause problems [79].

Pre-filtration

MF is very much applied prior UF and NF for the reduction of membrane fouling in the forest industry, for example during the separation of hemicelluloses extracted from wheat bran or in the treatment of wastewater from mechanical pulping mills or Kraft black liquor, showing good results in maintaining the filtration capacity of the UF system. However, important hemicellulose losses have been reported.

Coagulation

Coagulation is a common method used in wastewater treatment. It is a simple, economic method that facilitates the aggregation of the suspended/unstable particles prior sedimentation/filtration and it is very efficient in the removal of colour and chemical oxygen demand (COD). However, limited research on its use in the reduction of membrane fouling and enhancement of the permeability of pulp and paper process water is available[87] . The coagulation process is very dependent on the pH value and pulp and paper effluents might be very alkaline or acidic, therefore adjusting the pH for the coagulation process can be economically not feasible.

Polymeric adsorbents

Polymeric adsorbents can be also used to reduced fouling prior membrane filtration operations to reduce colloidal suspended matter. But also, to remove lignin and lignans by addition of an uncharged polyacrylate adsorbent. In general, hydrophobic and uncharged hydrophobic adsorbents are used to remove hydrophobic molecules and non-polar compounds. Again, this method can be very efficient for fouling prevention of UF membranes but it is also associated with major hemicellulose losses. Development of specific selective polymeric adsorbents to decrease hemicellulose losses due to adsorption is needed.

Activated carbon (AC) adsorption

Pre-treatment by AC adsorption prior to membrane filtration has also been employed to prevent membrane fouling. The capacity of AC is dependent on different factors such as its pore size, carboxylic portion, and surface area. A major problem with AC in larger-scale and industrial applications is that a great amount of solid waste is generated [32]. Adjusting the pH of pulp and paper wastewater to decrease membrane fouling can be less expensive in comparison with AC; however, this depends on the buffer capacity of the wastewater [81]. Alternatively, charcoal adsorption has also been proposed for the removal of phenolic compounds from wood hydrolysate [88].

Addition of activated and inactivated laccase

Laccase is a copper-containing oxidase that utilizes $O_2$ as oxidant and also oxidizes phenolic rings to phenoxy radicals and has been used as pretreatment to minimize fouling. It is considered eco-friendly because it requires $O_2$ as co-substrate for the catalysis and it yields water as the sole by-product. In literature some examples of utilization of laccase for removal of phenolics via precipitation in the pulp and paper industry can be found. It has been reported that the initial effect of the addition of laccase is to reduce the permeability of the filtration membrane, because of the formation of a gel layer, but after that no further flux decay occurs. Laccase has been also used in combination with adsorption onto bentonite to treat lignin and hemicelluloses [89].

Oxidation

Advanced oxidation processes (AOPs) can be very useful in the reduction of membrane fouling. AOPs can partially degrade high molar mass lignin compounds and this can improve filtration capacity by reducing the feed viscosity and minimizing the gel layer formation. Methods such as pulsed corona discharge (PCD) or ozonation have been studied and their application before membrane filtration proved to diminish membrane fouling. Regarding the PCD, the process decreased the average molar weight of hemicelluloses to some extent which may lead to hemicellulose losses [81].

## c. Cleaning Strategies

Cleaning operations are unavoidable in membrane operations. The planning and designing of proper cleaning processes is of outmost importance. The cleaning objective is to restore the system’s flux capacity and remove any fouling/scaling or biofouling agents without damaging the membrane or other heat and chemical-sensitive parts (i.e., gaskets).

Parameters that enhance the cleaning efficiency (assuming no damage to the membrane and system) are: temperature, pressure and flow rate, concentration of the cleaning agents and residence time.

Temperature decreases the viscosity of the cleaning solution and increases its turbulence hence increasing the reaction rate of the cleaning agents (i.e., protein hydrolysis). However, depending on the fouling agents an increase of temperature while cleaning can be detrimental, for example carbonates precipitate at higher temperatures and some proteins can be denaturalized and worsen the fouling problem. In any case, for complex foulant agents’ mixtures it is recommended to use formulated cleaning agents and combine acid and alkaline solutions to avoid mineral precipitation (acid solutions) and promote protein solubilization (alkali solutions).

Not only the type of cleaning agent is important during cleaning operations, their concentration and the order of application will also determine the quality of the cleaning treatment. As an example, cleaning with acid after an alkaline wash is a common dairy industry practice, as the reverse sequence would lead to protein aggregation when casein is present.

Regarding pressure and flow velocity the cleaning operations membranes should operate under low transmembrane pressures and as high cross-flow velocity as the system allows in order to limit additional cake layer formation during the cleaning process [79].

# 7. Recommendations for future applications, research questions.

Due to the complexity and inhomogeneity of process- and wastewaters in the pulp and paper sector, research challenges remain for future membrane applications to allow their final demonstration in industrial environment. Topics such as the selectivity of a recovery step, the purification of the desired product, the process stability and flexibility are of great importance. Further, reliable process data are required for an implementation into the pulp and paper industry, and more successful pilot operations to show robust and reliable operations in real environments as best practice examples to deploy the technologies on larger scale are needed.

Process streams form the pulp and paper industry contain a lot of interesting compounds like lignin, hemicellulose, tall oil, furfural, or carboxylic acids. Depending on which of the compounds shall be isolated, different questions need to be addressed. However, to summarize the most important once, the following recommendations are given:

- Studies on tailored and cost-effective protocols for respective selection of pre-treatment agents preferably of high performance, low cost and reduced hemicellulose degradation[81].
- New membrane developments (configuration and fabrication). Advanced membranes – e-beam irradiation; 3D printing of membranes, membranes without halogenated elements (PP instead of PTFE)

  Sustainable materials are the backbone of green production – to enable truly environmental-friendly production techniques, the materials applied must be sustainably produced, endure a long-life time and show good recyclability or potential for after-life products. Membrane operations are already state of the art technologies in many industrial sectors, including gas separation, wastewater treatment, food processing, etc. and the interest towards the application of membrane operations to other industrial processes is increasing. In general, they enable a more sustainable and circular production (i.e.: better energy and resource efficiency) and higher quality and safer products. Additionally, membrane operations achieve concrete benefits for manufacturing and processing, in fact, they are precise and flexible processing techniques, able to maximize phase contact, integrate conversion and separation processes with improved efficiency and significantly lower energy requirements compared to conventional ones. However, in the majority of cases the origin, production footprint and after-life use of membrane materials is not questioned, yet. In order to reach these goals, membranes with enhanced mechanical and thermal properties are required, tailor-made to specific challenges in order to reach high performance in a long-life time. Impactful material/fabrication/modification innovation, with proven excellent performance and flexibility must be translatable into a technically feasible and scalable membrane fabrication process.

Current research themes to address these issues are:

i. Membrane surface engineering, e.g., membrane modification via E-beam or cold plasma modification to tailor the polymeric structure (crosslinking, pore size) and to functionalize surfaces.

ii. Development of more sustainable materials (non-halogenated polymers, such as PP or PE instead of PTFE/PVDF or biopolymers) with suitable thermal and mechanical properties

iii. Development of novel membrane structures via 3D printing

iv. Model-based membrane design based on transport and fouling models to overcome existing bottlenecks:

   In case of membrane surface engineering, for example, the ability to control and obtain a desired performance through a modified membrane material via E-beam/Cold Plasma is non-trivial and there is a research gap on how these adjustable membrane properties will affect the membrane performance especially for new applications. If effectively correlations between membranes structure, thermo-mechanical properties and performance could be established, this approach could be applied to any polymeric membrane and/or material and any application.

- Mechanisms to enhance selectivity via decoupling valuable transport driving force from others.
- Integrated membrane process designs, that allow coupling of various membrane processes.

  When components should be selectively separated, often several membrane processes must be integrated. Here, it is often not trivial how to integrate and select a final configuration, specifically when several valuable components should be separated. Here, clear guidelines and strategies could be beneficial in future, ideally based on integrated modelling tools to model the interaction of various membrane separation processes and the respective process efficiency, energy demand and component purity.

- More elaborated effective combined physical and chemical membrane cleaning protocols, where the costs of the required chemicals don´t affect the economic feasibility of the overall membrane technologies that much and where environmental issues are also regarded [81].

- Further data is required on the identification of major foulants by advanced membrane autopsy and characterisation techniques, for addressing the complexity and the high fouling propensity of P&P effluents [81].

- Identification of optimal operating conditions, in terms of hydrodynamics, feed and membrane characteristics [81].

- Long-term pilot studies in 24h operation to evaluate stable operating scenarios and determine maintenance requirements.

- Establishment of research on membrane reactors, for in-situ removal of valuable substances from reaction processes in biorefineries.
- Modifying the membrane surface by functionalization in order to achieve the compatibility with the final clarified solution to avoid fouling/wetting in membrane-assisted crystallization.

# 8. Discussion

Biorefineries without any doubts have a huge potential in future industry. Benefits of lignocellulosic biorefineries are of course the production of valuables and biofuels or energy but also include economic development in rural areas, the sustainable waste management and the general benefits on climate change, such as greenhouse gas emissions reduction. However, irregular biomass supply chains, market uncertainties, and scale-up challenges still harm the complete break-through.

The awareness of the benefits for all participants of industrial symbiosis must be risen. Industrial symbiosis of biobased materials can bring players together such as feedstock utiliser, energy producer, energy consumer, waste utilizer, fertilizer producer, fertilizer consumer etc… and thereby foster closing loops and creating circular economy, whereas the re-use of agro- process- and post-consumer residues results in cost-competitiveness and environmental benefits.

Decision Support Tools for in general bioeconomy approaches could help in future for evaluating the impact of economic, environmental, technical, social, policy or legal and supply chain aspects of different scenarios. In Task 11 the I-BIOREF Decision Support Tool is being developed at the moment, which aims to provide with this software platform a multidisciplinary approach for support in identification and mitigation of bioeconomy projects.
A detailed integration of membrane units to the technical part of such decision support tool could strengthen the application of membranes in biorefineries.

Within the IEA TCP Task 17 project and the development of this guideline the potential of emerging membrane processes in biorefining approaches could be clearly seen. However, there are, just as mentioned in the chapter above still several challenges and research questions to be answered. The objective of providing this guideline is to give an overview of the emerging membrane technologies, map the actions done so far and strengthen know-how transfer within the international consortium, including integration concepts of membrane applications in biorefineries, such pre-treatment and cleaning approaches. The aim of this guideline is to support and enable the integration of potential membrane technologies in biorefining industry. This guidance shall give possible integration concepts of membranes in biorefineries as well as recommendations for R&D, technology development, research, industry and decision -maker. This guideline will be extended to further biorefining applications.

# 9. Recent Publications and Contacts of Task 17

Article

2023

Elena Guillen-Burrieza et al., ‘Recovery of Ammonia from Centrate Water in Urban Waste Water Treatment Plants via Direct Contact Membrane Distillation: Process Performance in Long-Term Pilot-Scale Operation’, Journal of Membrane Science 667 (February 2023): 121161, https://doi.org/10.1016/j.memsci.2022.121161.

2022

Paul Demmelmayer, Marlene Kienberger, Reactive extraction of lactic acid from sweet sorghum silage press juice, Separation and Purification Technology 282 (2022) 120090, 2022, Englisch, 8, https://www.sciencedirect.com/science/article/pii/S1383586621017950 zu finden.

M. Battestini Vives, J. Thuvander, A. Arkell and F. Lipnizki: Low-molecular-weight lignin recovery with nanofiltration in the kraft pulping process. Membranes, 2022, 12, 310. https://doi.org/10.3390/membranes12030310. (Subtask B)

M. Sjölin, M. Sayed, J. Thuvander, F. Lipnizki, R. Hatti-Kaul, O. Wallberg: Effect of membrane purification and concentration of sucrose in sugar beet molasses for the production of 5-Hydroxymethylfurfural, Chemical Engineering Research and Design, https://doi.org/10.1016/j.cherd.2022.01.007. (Subtask A)

2021

K.S. Burts, T.V. Plisko, M. Sjölin, G. Rodrigues, A.V. Bildyukevich, F. Lipnizki and M. Ulbricht. Development of antifouling polysulfone membranes by synergistic modification with two different additives in casting solution and coagulation bath: Synperonic F108 and polyacrylic acid, Materials 2022, 15(1), 359; https://doi.org/10.3390/ma15010359. (Subtask C)

K.S. Burts, T.V. Plisko, A.V. Bildyukevich, G. Rodrigues, M. Sjölin, F. Lipnizki and M. Ulbricht: Development of polysulfone ultrafiltration membranes with enhanced antifouling performance for the valorisation of side streams in the pulp and paper industry. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 632 (2022), 127742. (Subtask C)

F. Lipnizki, G. Rudolph, J. Thuvander, B. Al-Rudainy and M. Battestini Vives: Anwendungspoten-tial von Membranprozessen im Konzept der Lignocellulose-Bioraffinerien (Application potential of membrane processes in the concept of lignocellulose biorefineries). Chemie Ingenieur Technik, 93 (2021), http://doi.org/10.1002/cite.202100018. (Subtask B)

2020

K. Knozowska, A. Kujawska, G. Li, J. Kujawa, M. Bryjak, W. Kujawski, F. Lipnizki, L. Ahrné, J.K. Kujawski: Membrane assisted processing of acetone, butanol, and ethanol (ABE) aqueous streams. Chemical Engineering and Processing - Process Intensification, 166 (2021) http://doi.org/10.1016/j.cep.2021.108462. (Subtask E)

T. Hliavitskaya, T. Plisko, S. Pratsenko, A. Bildyukevich, F. Lipnizki, G. Rodrigues, M. Sjölin: Development of antifouling ultrafiltration PES membrane for concentration of hemicellulose. Journal of Applied Polymer Science. https://doi.org/10.1002/app.50316. (Subtask C)

T. Hliavitskaya, T. Plisko, A. Bildyukevich, F. Lipnizki, G. Rodrigues, M. Sjölin: New PES-PRAESTOL 859 UF membranes for hemicellulose purification. Chemical Engineering Research and Design, 162 (2020), 187–199. (Subtask C)

G. Rudolph, A. Hermansson, A.-S. Jönsson and F. Lipnizki: Investigating adsorptive membrane fouling of thermomechanical pulping process water with QCM-D. Separation and Purification Technology, (2020), https://doi.org/10.1016/j.seppur.2020.117578. (Subtask C)

A.V. Bildyukevich, T.V. Plisko, F. Lipnizki, S.A. Pratsenko: Correlation between membrane surface properties, polymer nature and fouling in skim milk ultrafiltration. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 605 (2020), 125387. (Subtask C)

T. Virtanen, A. Lopatina, B. Al-Rudainy, G. Rudolph, H. Schagerlöf, L. Puro, M. Kallioinen and F. Lipnizki: Analysis of ultrafiltration membrane fouling by Brunauer-Emmet-Teller nitrogen adsorption/desorption technique, Scientific Reports 10, 2020, 3427, doi.org/10.1038/s41598-020-59994-1. (Subtask C)

M. Sjölin, J. Thuvander, O. Wallberg and F. Lipnizki: Purification of sucrose in sugar beet molasses by utilizing ceramic nanofiltration and ultrafiltration membranes. Membranes, 2020, 10, 5. doi.org/10.3390/membranes10010005. (Subtask A)

**2019**

B. Al-Rudainy, M. Galbe, F. Lipnizki and O. Wallberg. Galactoglucomannan recovery with hydrophilic and hydrophobic membranes: Process performance and cost estimations. Membranes, 2019, 10:9(8):99. doi.org/10.3390/membranes9080099. (Subtask B)

G. Rudolph, T. Virtanen, M. Ferrando, C. Güell, F. Lipnizki and M. Kallioinen: A review of in situ real-time monitoring techniques for membrane fouling in the biotechnology, biorefinery and food sectors, Journal of Membrane Science, 588, 2019, doi.org/10.1016/j.memsci.2019.117221. (Subtask C)

J. Thuvander, F. Lipnizki and A.-S. Jönsson: On-site recovery of hemicelluloses from thermomechanical pulp mill process water by microfiltration and ultrafiltration. Journal of Wood Chemistry and Technology, 39, 2019, doi: 10.1080/02773813.2019.1565865. (Subtask B)

M. Zhou, H. Sandström, M. Belioka, T. Pettersson and T. Mattsson: Investigation of the cohesive strength of membrane fouling layers formed during cross-flow microfiltration: The effects of pH adjustment on the properties and fouling characteristics of microcrystalline cellulose. Chemical Engineering Research and Design, 149, 2019, 52-64. (Subtask C)

D. Humpert, M. Ebrahimi, A. Stroh and P. Czermak Recovery of lignosulfonates from spent sulfite liquor using ceramic hollow-fiber membranes. Membranes, 2019, 9, 45; doi:10.3390/membranes9040045. (Subtask B)

M. Zhou and T. Mattsson: Effect of crossflow regime on the deposit and cohesive strength of membrane surface fouling layers. Food and Bioproducts Processing, 115, 2019, 185-193. (Subtask B)

N.T. Faria, S. Marques, F. C. Ferreira and C. Fonseca, Production of xylanolytic enzymes by Moesziomyces spp. using xylose, xylan and brewery's spent grain as substrates, New Biotechnology, 49, 2019, 137-143, ISSN 1871-6784, doi: 10.1016/j.nbt.2018.11.001. (Subtask B)

M.V Santos., N.T. Faria, C. Fonseca, F.C. Ferreira, Production of mannosylerythritol lipids from lignocellulose hydrolysates: tolerance thresholds of Moesziomyces antarcticus to inhibitors. 94 (4), 2019, 1064-1072, J. Chem. Technol. Biotechnol. ISSN: 1097-4660, ISSN 0268-2575. doi:10.1002/jctb.5853. (Subtask B)

**Conferences**

**2022**

M. Sjölin, M. Sayed, J. Thuvander, R. Hatti-Kaul, O. Wallberg, Frank Lipnizki: Impact of sugar beer molasses purification by ultra-and nanofiltration on the 5-Hydroxymethylfurfural production, Filtech 2022, 2022, Cologne, Germany. (Subtask A)

**2021**

K.S. Burts, T.V. Plisko, A.V. Bildyukevich, G. Rodrigues, M. Sjölin, F. Lipnizki and M. Ulbricht: Development of polysulfone ultrafiltration membranes with enhanced antifouling performance for the valorisation of side streams in the pulp and paper industry, Euromembrane 2021, Copenhagen, Denmark. (Subtask C)

M. Battestini Vives, J. Thuvander, A. Arkell and F. Lipnizki: From lab to pilot scale: Lignin recovery with nanofiltration in the kraft pulping process, Euromembrane 2021, Copenhagen, Denmark. (Subtask B)

G. Rudolph, A.-S. Jönsson and F. Lipnizki: Ultrafiltration of process streams from lignocellulosic biorefineries: Insights on membrane fouling and cleaning, Euromembrane 2021, Copenhagen, Denmark. (Subtask C)

M. Sjölin, S. Herrlin, O. Wallberg, J. Thuvander and F. Lipnizki: Purification of galactoglucoman-nan in the liquid fraction from steam pretreatment of soft wood using ultrafiltration membranes, Euromembrane 2021, Copenhagen, Denmark. (Subtask A)

M. Battestini Vives, J. Thuvander, A. Arkell and F. Lipnizki, Scaling up nanofiltration of kraft black liquor for lignin recovery, 18th Network Young Membrains Meeting, 2021, Lund, Sweden. (Subtask B)

M. Battestini Vives, J. Thuvander, A. Arkell and F. Lipnizki: Producing biofuel from lignin: How close are we? PhD Conference on Sustainable Development, 2021, Lund, Sweden. (Subtask B)

F. Lipnizki, J. Thuvander, G. Rudolph and M. Battestini Vives: Anwendungspotential von Membranprozessen im Konzept Lignocelluloser-Bioraffinerien, DGMT Jahrestagung 2021, "Membranen zum Schutz von Klima und Ressourcen", Germany. (Subtask B)

**2020**

F. Lipnizki, J. Thuvander, B. Al-Rudainy, A. Arkell, O. Wallberg and A.-S. Jönsson: New membrane-based concepts for ligno-cellulosic biorefineries: Status and challenges, ICOM 2020, 2020, London, UK. (Subtask B)

T.V. Plisko, K.S. Burts, M. Sjölin, G. Rodrigues, M. Mateus, A.V. Bildyukevich, M. Ulbricht and F. Lipnizki: Development of pH-sensitive membranes with enhanced antifouling performance for the valorisation of side streams in the pulp industry, ICOM 2020, 2020, London, UK (Keynote). (Subtask C)

M. Battestini Vives, K. Li, J. Thuvander, C. Hulteberg, A. Arkell and F. Lipnizki: Performance of nanofiltration membranes for the recovery of lignin from kraft black liquor in the production of renewable fuels, ICOM 2020, 2020, London, UK. (Subtask B)

M. Sjölin, J. Thuvander, F. Lipnizki and O. Wallberg: The effect of ultrafiltration and nanofiltration membranes upstream a 5-Hydroxymethylfurfural production process from sugar beet molasses, ICOM 2020, 2020, London, UK. (Subtask A)

G. Rudolph, A.-S. Jönsson and F. Lipnizki: Studying membrane fouling in lignocellulosic biorefiner-ies with QCM-D, ICOM 2020, 2020, London, UK. (Subtask C)

G. Rudolph, T. Virtanen, H. Schagerlöf, L. Puro, M. Kallioinen and F. Lipnizki: Brunauer-Emmett-Teller analysis – a suitable method for membrane fouling in lignocellulosic biorefineries? ICOM 2020, 2020, London, UK. (Subtask C)

F. Lipnizki, J. Thuvander, B. Al-Rudainy, A. Arkell, O. Wallberg and A.-S. Jönsson: New membrane-based concepts for ligno-cellulosic biorefineries: Status and challenges, ICOM 2020, 2020, London, UK. (Subtask B)

**2019**

F. Lipnizki, G. Rudolph and J. Thuvander: Membrane processes in ligncellulosic biorefineries: Status, potential and challenges. PERMEA 2019, 2019, Budapest, Hungary. (Subtask B)

F. Lipnizki, J. Thuvander and G. Rudolph: Membrane opportunities in lignocellulosic biorefineries, Engineering with Membranes, 2019, Båstad, Sweden. (Subtasks B and C)

G. Rudolph and F. Lipnizki: New developments in fouling and cleaning of membrane processes in lignocellulosic biorefineries. Treesearch Progress Conference, 2019, Norrköping, Sweden. (Subtask C)

M. Sjölin, J. Thuvander, O. Wallberg and F. Lipnizki: Purification and retention of sucrose in sugar beet molasses by utilizing ceramic nanofiltration membranes, Engineering with Membranes, 2019, Båstad, Sweden. (Subtask A)

G. Rudolph, T. Virtanen, F. Lipnizki and M. Kallioinen: In situ real-time monitoring techniques for membrane fouling in food, biorefinery and biotechnology industries, Engineering with Membranes, 2019, Båstad, Sweden. (Subtask C)

**Editions**

F. Lipnizki and S. Luque: Engineering with Membranes – Membranes for a sustainable future, Conference proceedings, Båstad, Sweden, 2019. (Subtasks A to F)

**Books**

F. Lipnizki, J. Thuvander and G. Rudolph: Membrane processes and applications for biorefineries. In: Membranes in Environmental Applications by A. Basile, A. Figoli and Y. Li, Elsevier B.V., Amsterdam, 2019. (Subtasks A – F)

**Reports**

J. Buchmaier, B. Muster, E. Guillen, S. Meitz, Membranes in Biorefineries - Guideline for the integration of emerging membrane separation processes in biorefineries for research, industry and decision-makers, AEE, Austria. (Subtask E)

List of Contacts on Membrane Technologies:

| Company | Contact Person | Topics |
|---|---|---|
| AEE INTEC | Judith Buchmaier<br>j.buchmaier@aee.at<br>Bettina Muster<br>b.muster@aee.at | Membrane Distillation (MD), Closing the Loop |
| Aquaporin A/S | Jörg Vogel<br>jvo@aquaporin.com | Forward Osmosis FO, Closing the Loop, Reduction in water consumption<br>RO with biomimetic membranes (e.g. Low Energy BWRO) |
| Pentair X-Flow | Ania Pacak<br>ania.pacak@pentair.com | Microfiltration, Ulfrafiltration, Nanofiltration |
| Pentair X-Flow | Erik Vriezekolk<br>erik.vriezekolk@pentair.com | Microfiltration, Ulfrafiltration, Nanofiltration |
| Nova University of Lisbon | Joao Crespo<br>jgc@fct.unl.pt | Membrane Filtration, Ultrafiltration, Reverse Osmosis |
| Consiglio Nazionale delle Ricerche – Istituto per la Tecnologia delle Membrane (CNR-ITM) | Gianluca Di Profio | Membrane Distillation (MD), Membrane-assisted Crystallization (MAC) |
| Aalborg University | Morten Christensen<br><mlc@bio.aau.dk>; | Membrane Distillation (MD) Forward Osmosis (FO) |
| LiqTech International A/S | Victor Candelario<br>vcl@liqtech.com | Liquid Membrane Permeation (LMP), Membrane fabrication |

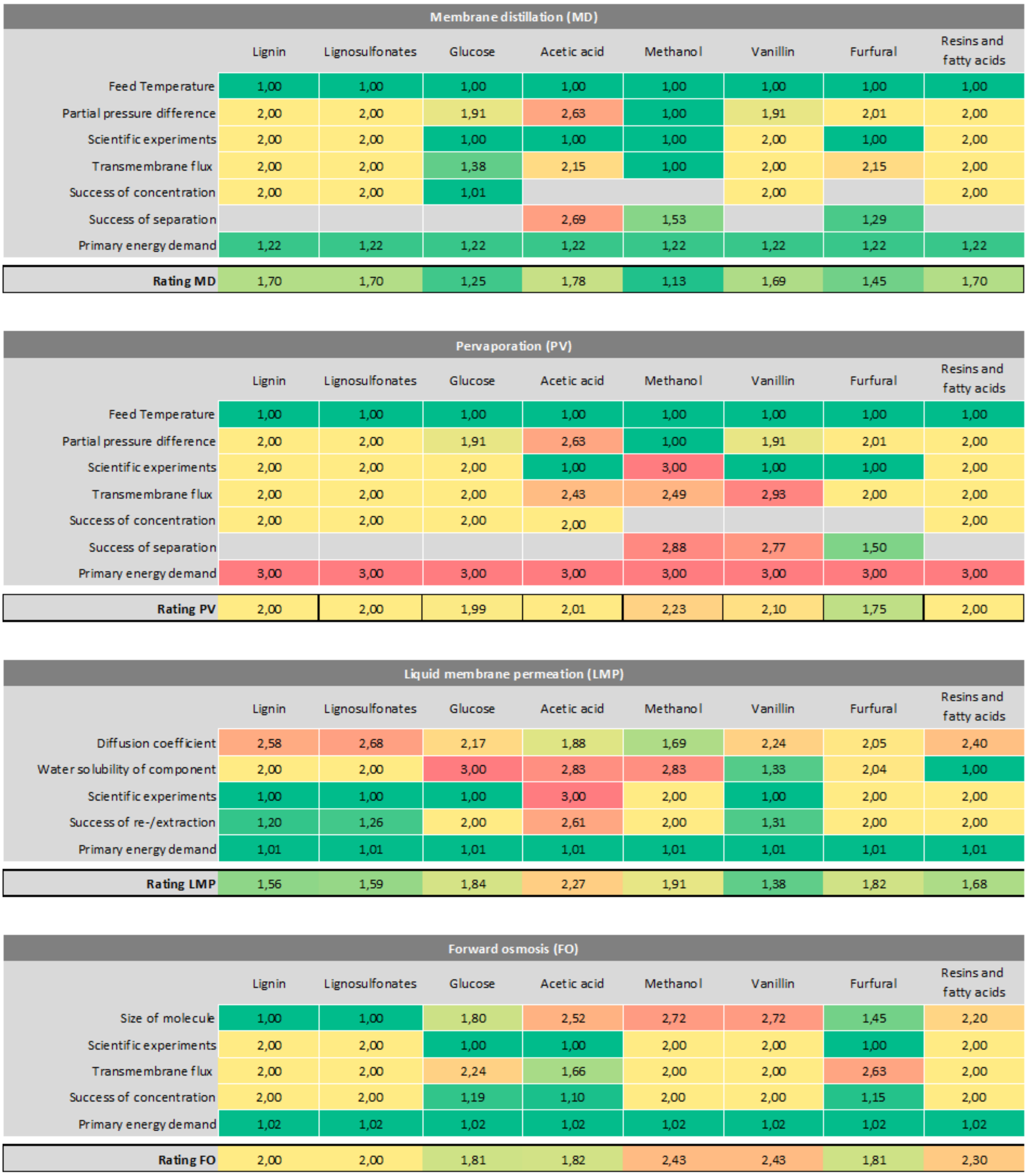
| | | |
|---|---|---|
| Ecohelix AB | Petri Oinonen<br>petri@ecohelix.se | Forward Osmosis (FO), Closing the Loop |
| Ecohelix AB | Oskar Schmidt<br>oskar@ecohelix.se | Sustainable materials |
| AlfaLaval | Aurélie Dupuy<br>aurelie.dupuy@alfalaval.com | Forward Osmosis (FO), Closing the Loop; Reduction in Water Consumption, polymeric membrane manufacturing |
| University of Southern Denmark | Knud Villy Christensen<br>kvc@kbm.sdu.dk | Membrane Distillation (MD), Forward Osmosis (FO), Reduction in Water Consumption |
| TNO- Netherlands Organisation for Applied Scientific Research | Soraya Sluijter<br>soraya.sluijter@tno.nl | Microfiltration, Ulfrafiltration, Nanofiltration, Forward Osmosis |

# 10. Annex

In J. Reßlers work the developed methodology described in Chapter 5 -Possibilities of how to evaluate integration of feasibility of membrane usage has been applied to the pulp and paper industry for the separation of the following components:

- Lignin
- Lignosulfonates
- Glucose
- Acetic acid
- Methanol
- Vanillin
- Furfural
- Resins
- Fatty acids

Based on the technology-related data and the defined evaluation criteria with the classification by means of color codes, a matrix with evaluation of the potential for separation of the components was be prepared for each process.



**Membrane distillation (MD)**

| | Lignin | Lignosulfonates | Glucose | Acetic acid | Methanol | Vanillin | Furfural | Resins and fatty acids |
|---|---|---|---|---|---|---|---|---|
| Feed Temperature | 1,00 | 1,00 | 1,00 | 1,00 | 1,00 | 1,00 | 1,00 | 1,00 |
| Partial pressure difference | 2,00 | 2,00 | 1,91 | 2,63 | 1,00 | 1,91 | 2,01 | 2,00 |
| Scientific experiments | 2,00 | 2,00 | 1,00 | 1,00 | 1,00 | 2,00 | 1,00 | 2,00 |
| Transmembrane flux | 2,00 | 2,00 | 1,38 | 2,15 | 1,00 | 2,00 | 2,15 | 2,00 |
| Success of concentration | 2,00 | 2,00 | 1,01 | | | 2,00 | | 2,00 |
| Success of separation | | | | 2,69 | 1,53 | | 1,29 | |
| Primary energy demand | 1,22 | 1,22 | 1,22 | 1,22 | 1,22 | 1,22 | 1,22 | 1,22 |
| **Rating MD** | 1,70 | 1,70 | 1,25 | 1,78 | 1,13 | 1,69 | 1,45 | 1,70 |

**Pervaporation (PV)**

| | Lignin | Lignosulfonates | Glucose | Acetic acid | Methanol | Vanillin | Furfural | Resins and fatty acids |
|---|---|---|---|---|---|---|---|---|
| Feed Temperature | 1,00 | 1,00 | 1,00 | 1,00 | 1,00 | 1,00 | 1,00 | 1,00 |
| Partial pressure difference | 2,00 | 2,00 | 1,91 | 2,63 | 1,00 | 1,91 | 2,01 | 2,00 |
| Scientific experiments | 2,00 | 2,00 | 2,00 | 1,00 | 3,00 | 1,00 | 1,00 | 2,00 |
| Transmembrane flux | 2,00 | 2,00 | 2,00 | 2,43 | 2,49 | 2,93 | 2,00 | 2,00 |
| Success of concentration | 2,00 | 2,00 | 2,00 | 2,00 | | | | 2,00 |
| Success of separation | | | | | 2,88 | 2,77 | 1,50 | |
| Primary energy demand | 3,00 | 3,00 | 3,00 | 3,00 | 3,00 | 3,00 | 3,00 | 3,00 |
| **Rating PV** | 2,00 | 2,00 | 1,99 | 2,01 | 2,23 | 2,10 | 1,75 | 2,00 |

**Liquid membrane permeation (LMP)**

| | Lignin | Lignosulfonates | Glucose | Acetic acid | Methanol | Vanillin | Furfural | Resins and fatty acids |
|---|---|---|---|---|---|---|---|---|
| Diffusion coefficient | 2,58 | 2,68 | 2,17 | 1,88 | 1,69 | 2,24 | 2,05 | 2,40 |
| Water solubility of component | 2,00 | 2,00 | 3,00 | 2,83 | 2,83 | 1,33 | 2,04 | 1,00 |
| Scientific experiments | 1,00 | 1,00 | 1,00 | 3,00 | 2,00 | 1,00 | 2,00 | 2,00 |
| Success of re-/extraction | 1,20 | 1,26 | 2,00 | 2,61 | 2,00 | 1,31 | 2,00 | 2,00 |
| Primary energy demand | 1,01 | 1,01 | 1,01 | 1,01 | 1,01 | 1,01 | 1,01 | 1,01 |
| **Rating LMP** | 1,56 | 1,59 | 1,84 | 2,27 | 1,91 | 1,38 | 1,82 | 1,68 |

**Forward osmosis (FO)**

| | Lignin | Lignosulfonates | Glucose | Acetic acid | Methanol | Vanillin | Furfural | Resins and fatty acids |
|---|---|---|---|---|---|---|---|---|
| Size of molecule | 1,00 | 1,00 | 1,80 | 2,52 | 2,72 | 2,72 | 1,45 | 2,20 |
| Scientific experiments | 2,00 | 2,00 | 1,00 | 1,00 | 2,00 | 2,00 | 1,00 | 2,00 |
| Transmembrane flux | 2,00 | 2,00 | 2,24 | 1,66 | 2,00 | 2,00 | 2,63 | 2,00 |
| Success of concentration | 2,00 | 2,00 | 1,19 | 1,10 | 2,00 | 2,00 | 1,15 | 2,00 |
| Primary energy demand | 1,02 | 1,02 | 1,02 | 1,02 | 1,02 | 1,02 | 1,02 | 1,02 |
| **Rating FO** | 2,00 | 2,00 | 1,81 | 1,82 | 2,43 | 2,43 | 1,81 | 2,30 |

Figure 1a: Representation of the evaluation matrix of the technologies membrane distillation, pervaporation, liquid membrane permeation and forward osmosis.

Table 1a shows the summary evaluation matrix of all previously analyzed membrane technologies with respect to the identified valuable substances. The color range (color value) is from green (1) as a very suitable membrane separation process to the color range (color value) red (3) as a less suitable membrane separation process for the recovery of a component. In order to ensure a comparable evaluation of all membrane separation processes, the primary energy requirement, the scientific experiments carried out and the yields of the component under consideration were used as evaluation criteria. These represent those criteria that allow a uniform evaluation to be made across all membrane separation technologies. The potential of concentration or separation of the given components with one of the considered emerging membrane processes is summarized in Table 1a.

Table 1a: Evaluation matrix of all membrane separation processes with respect to the potential for separation (yellow values)/concentration (blue values) of lignin, lignosulfonate, glucose, acetic acid, methanol, vanillin, furfural, resins and fatty acids.

| **Concentration/ Separation** | | | | |
|---|---|---|---|---|
| **Separation Technology / Components** | **Membrane distillation (MD)** | **Liquid membrane permeation (LMP)** | **Pervaporation (PV)** | **Forward osmosis (FO)** |
| **Lignin** | 1,74 | 1,08 | 2,33 | 1,67 |
| **Lignosulfonates** | 1,74 | 1,10 | 2,33 | 1,67 |
| **Glucose** | 1,08 | 1,34 | 2,33 | 1,07 |
| **Acetic acid** | 1,64 | 2,22 | 2,00 | 1,04 |
| **Methanol** | 1,26 | 1,67 | 2,96 | 1,67 |
| **Vanillin** | 1,74 | 1,12 | 2,26 | 1,67 |
| **Furfural** | 1,18 | 1,67 | 1,81 | 1,06 |
| **Resins and fatty acids** | 1,74 | 1,67 | 2,33 | 1,67 |

Looking at the columns assigned to the technologies in Table 1a, the green color is predominant for MD, LMP and FO, while for PV the orange range is predominant. It should be noted that the lower rating of PV compared to the other membrane separation technologies is related to the higher primary energy demand. However, compensation can be achieved since the process is able to separate low concentrations of components due to the high selectivity of the membranes.

When looking at the components line by line, the best recovery for lignin and its derivative lignosulfonate is achieved by the LMP. Here, a very good (re-)extraction success can be achieved by the emulsion-supported liquid membrane configuration. However, it should be mentioned that larger molecules, such as lignin, require higher amounts of carrier for the extraction process which is coupled to a negative impact on the economics.

Concentration of glucose could be best evaluated using MD and FO technologies. However, membrane fouling with increasing test duration has been observed in scientific experiments. Also, by combining FO with nanofiltration (NF-FO hybrid process), good concentration yields of glucose can be achieved. Acetic acid and furfural also yield good results of concentration in FO applications. When acetic acid is concentrated by FO, significant concentration polarization at the membrane has occured, which reduces water flux. Vacuum MD may be a promising method for complete removal of furfural as it provides good separation success. Similarly, the recovery of methanol is best done by separation with MD, as good transmembrane flux and separation success can be achieved. LMP can be identified as a suitable membrane separation process to recover vanillin from aqueous solution by separation into the permeate. The selection of impregnated solvent in the microporous solid support (support body) plays an important role. For resins and fatty acids, both separation by LMP and concentration by MD and FO can be considered, since these components have a complex molecular structure and their vapor pressure is lower than that of water.

The assessment of the suitability of the individual technologies for the chosen components is obviously dependent to a certain extent on the current state of research, especially with regard to new membrane developments with special selectivity. However, for future assessments and also transfer to other industrial sectors and valuable materials, the developed technical assessment criteria form an important basis for evaluation, since the criteria based on the process principles, remain valid.

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