Membranes in Biorefineries - GUIDELINE

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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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 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.

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1. Background

On the one hand, fossil carbon is the dominant energy and chemical source at present, however they are 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 of fossil refineries and biorefineries are various. In fossil refineries a liquid feed, with mainly carbon and hydrogen components, and small amounts of nitrogen and sulphur, is used. The petrol 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, such as solid feeds. A rough pathway leads from whole wood logs through chipping, intermediate platforms (such as glucose, fructose, xylose, arabinose and further sugars) going through building blocks to secondary chemicals, intermediates and then to products and their usage.

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 be run as a biorefinery, when taking advantage of more than just one resource/product.

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 chemicals from sugars achieved from hemicellulose 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 or vanilla cookies or chewing gums.

2. Introduction

In the multitude of biorefinery applications, not only the biomass conversion process but also separation and purification of the biomass components and the products streams such as full integration schemes are of utmost importance. The separation 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 [4]. For this reason, often separation and purification operations are the factor influencing the overall cost effectiveness of biorefineries most. Separation and purification procedures in bio-production may account for 50–80% of the total production costs [5], 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, in example in separation, concentration or purification steps. Due to the large variety of different components of lignocellulosic feedstocks and its complexity design, operation and integration must be adapted to the respective processes.

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. as well as 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.

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 in the streams is required 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 Annex 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 industrial and academic partners. Austria is part of the international consortium, leading the subtask on emerging membrane processes. IETS Annex XVII - Membranes in Biorefineries is coordinated by Frank Lipnizky from the University of Lund. A previous Annex was running from 2013 to 2017, the continuation started in 2018 with a defined work programme until spring 2022 which shall be now extended for a following period. The established Annex is set up by a network of experts in the field of energy efficient separation methods including membranes. 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 Annex 17 project. The objective of providing this guideline is to give an overview of the emerging membrane technologies, map the actions done so far and include 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.

3. Emerging membrane technologies

Conventional filtration is a mature, commercially available solid–liquid separation technology. Widely used in the biomass pre-treatment steps but also in the recuperation of crystals from precipitation/crystallization, the separation of pre-hydrolyzate slurry and post-distillation slurry [6]. 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 the membrane extraction process 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 [7].
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) and pervaporation (PV). 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 upgrading of existing production processes and do not generate 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, often unused waste heat potentials can be ideally integrated. In order 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, much less CO_2 relevant energy is consumed compared to reversed osmosis (RO).

Specific technology requirement:

For FO, one needs membranes tailored to the process. 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 non-requirement of solvents for the extraction are among the advantages of FO[8]. However, due to different operating conditions, experimental setups, and data interpretation, it is still difficult to evaluate the potential of applying FO to the industrial sector[9].

Challenges:

One of the main challenges in FO is the recycling of draw solution, in order to maintain the driving force and achieve the product. Various hybrid recovery approaches are described in literature. Further 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[10]. The potential of fouling is high and once the membrane gets plugged and the process stops, the cleaning steps becomes expensive[11]. Therefore, long-term fouling behavior and membrane cleaning methods must be investigated, and an energy and economic evaluation have to be made[9].

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[12].

State-of-the-Art:

Interest in membrane distillation is increasing due to the low grade heat used and minimal demands on the membrane used. In addition to that, because of the low operating temperatures also renewable sources (e.g. solar energy) or waste heat can be used[13]. 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[14].

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 separation performance [12,15]. 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 [14,13,12].

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 in 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: Hydrophilic polymers are used for the separation of water from organic solutions and hydrophobic membrane tools 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)[16]. 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 processing of acidic solvents, for example, the removal of aromatic compounds from fuels, which is due to the similar chemical composition often difficult[17].

Challenges:

In the future, research will be conducted on other membrane technologies, taking into account selectivity, stability and productivity. The goal is to develop high-performance PV membranes with long-term stability. The limitations so far of pervaporation systems at industrial level are low performance, short lifetime, high cost, as well as bio generation of base chemicals and still restricted scaling[16].

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 material occurs in one step. Characteristic of this process is that the outer donor phase, which contains the material (=feed phase), is separated by means of a liquid membrane material from the inner receptor phase, which receives the material (=stripping phase). In the stripping phase, the re-extraction takes place. The driving force for the transport of the dissolved substance is solution diffusion. This means that the solutes 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. Carries can be used to increase this, as they facilitate mass transfer and increase efficiency by forming a reversible and selective bond with the material to increase its solubility. Classifications take place by module configuration, transport mechanisms, applications, carrier type, as well as by type of membrane support[18]. Knowledge of the relative diffusivities of the solutes can help in the selection of the particular membrane, as the membrane material must be able to withstand conditions completely and over the long term.

State-of-the-Art:

Currently, the most important applications for liquid membranes 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 due to the need for fewer organic solvents, smaller sample volume and shorter analysis time compared to conventional accumulation methods [19]. 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 [18,20]. 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 arising pressure differences, emulsion formation and blocking of the pores by the failure of solids, instability occurs in the liquid membranes. Continuous impregnation, gelation or cross-linking of the liquid membrane etc., can increase the stability [19]. Also, the low permeate flux and high investment/operating costs have often prevented LMP from commercial use [18].

Available membranes/modules:

Polyethylene- composite membranes

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 waste water streams than typical chemical reactor effluents [21]. 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 [22].

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 [23].

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 filtration 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 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 and membrane distillation, 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).

Technology	**Membrane Distillation (MD)**	**Pervaporation (PV)**	**Microfiltration (MF)**	**Ultrafiltration (UF)**	**Nanofiltration (NF)**	**Reverse Osmosis (RO)**
Driving Force	Vapor pressure difference	Vapor pressure difference	Pressure <2 bar	Pressure 1-10 bar	Pressure 5-35 bar	Pressure 15-150 bar
Separation principle	*Vapor-liquid equilibrium*	*Solution diffusion mechanism24*[Fehler! Textmarke nicht definiert.]	*Sieve mechanism* [1)]	*Sieve mechanism* [1)]	*Solution diffusion mechanism* [1)]	*Solution diffusion mechanism*
Membrane structure	*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*
Membrane material	*Hydrophobic polymer* [1)]	*Polymer, ceramic, organic-inorganic* [1)]	*Polymer, ceramic* [1)]	*Polymer, ceramic* [1)]	Polymer [1)]	*Organic polymers (cellulose and polyamide derivatives)*
Membrane thickness (µm)	20–100 [1)]	~0,1 or less (*Top layer*) [1)]	~10-150 [1)]	~150 [1)]	*Top layer:* ~150 *Bottom layer::* ~1 [1)]	150
Pore size (nm)	10–5.000 [Fehler! Textmarke nicht definiert.]	Non-porous (dense) [1)]	~50–10.000 [1)]	~1–100 [1)]	<2 [1)]	0,1-1
Module configuration	Plate module, tube module, Capillary module [1)]	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
Application examples	Recovery of valuable components from wastewater; Production of distilled water; …	Process water treatment, Dewatering of organ. Solvents…	Clarification & Concentration in the Beverage Industry; Recovery of Lignin, Hemicellulose and Enzymes 1); ...	Separation of Oil/Water Emulsions; Recovery of Lignin, Hemicellulose and Enzymes 1); ...	Filtration of acids and alkalis; recovery of lignin, hemicellulose and removal of fermentation inhibitors 1); ...	Seawater and brackish water desalination; recovery of lignin, hemicellulose and removal of fermentation inhibitors...

*1) He et al., 2011; *2) Basile et al., 2015; *3) Bokhary et al., 2017; *4) Ohlrogge & Ebert, 2006; *5) Chen et al., 2013; *6) Staudt et al., 2010 *7) Van der Bruggen, 2013

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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. 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 [24] . As another example, during the recovery, fractionation, and purification of lignin and hemicelluloses from wood hydrolysates using UF, wood hydrolysates in particular have a high tendency to foul, as these streams contain hemicelluloses, lignin, and wood extracts, such as fatty and resin acids [25]. 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 with regard to treatment objectives, fouling, purification and pre-treatment.

Table 2: Overview of process and wastewater streams as potential integration points for emerging membrane processes. The table does not show the total composition but only certain components of interest for respective applications.

Raw material	Quantity produced	Composition	Source
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).	[26,27]
		127-210 g/l, dry solids, 40-71 g/l lignin, 20-43 g/l organic acids	[27,28]
Spent sulfites liquor	90 billion tons per year worldwide	137 g/l Lignosulfonates	[29,30]
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)	[31,32]
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)	[33]
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	Industry Case Study AEE INTEC, (aiming: TS concentration; COD reduction wastewater)

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].

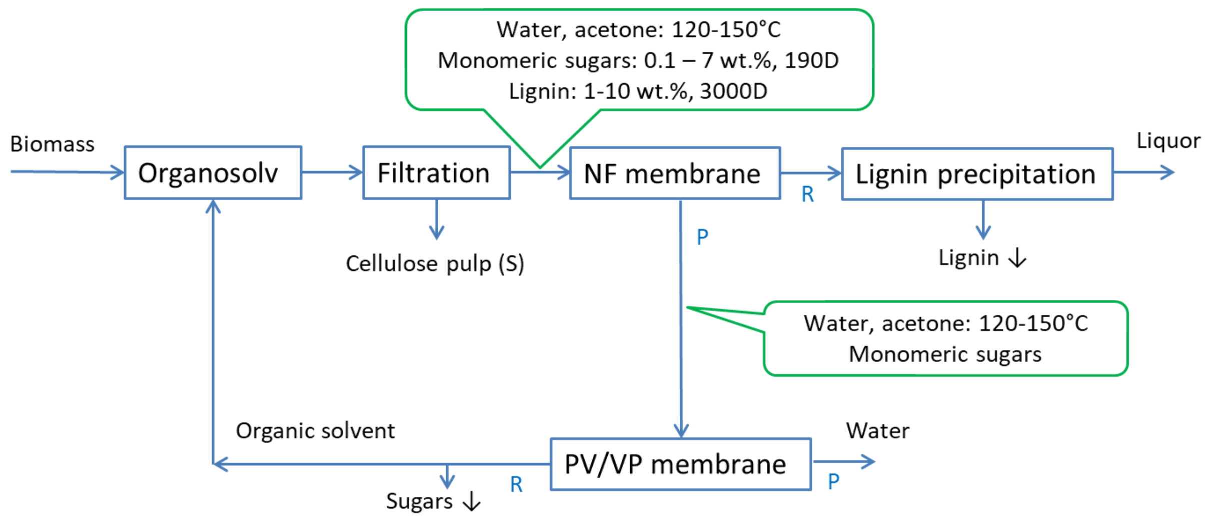

Figure 2: Scheme of TNOs 2-steps process (nanofiltration + pervaporation/vapor permeation) for lignocellulose fractionation

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

5. 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.

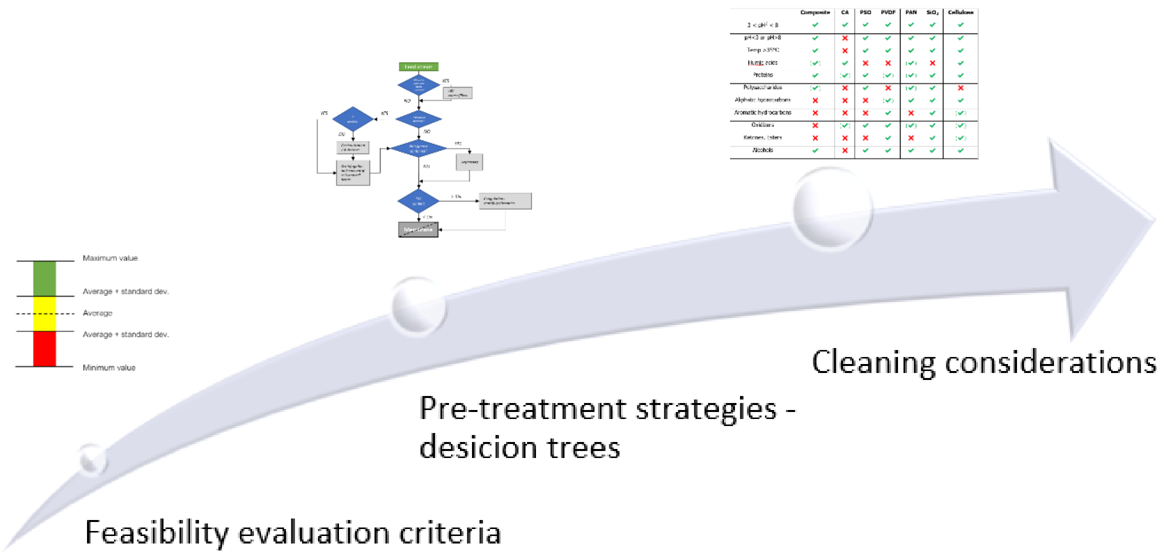

Figure 3: Evaluation method for emerging membrane applications in biorefineries concerning feasibility, pre-treatment and cleaning consideration.

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. 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[34].

Table 3: Chemical resistance of some of these membrane materials. Modified (Wagner, 2001).

	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	✔	✘	✔	✔	✔	✔	✔

✔ high resistance

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

✘ low resistance

Regarding the specific membrane processes (i.e., UF, RO, etc.) Figure 4 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).

[2] 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.

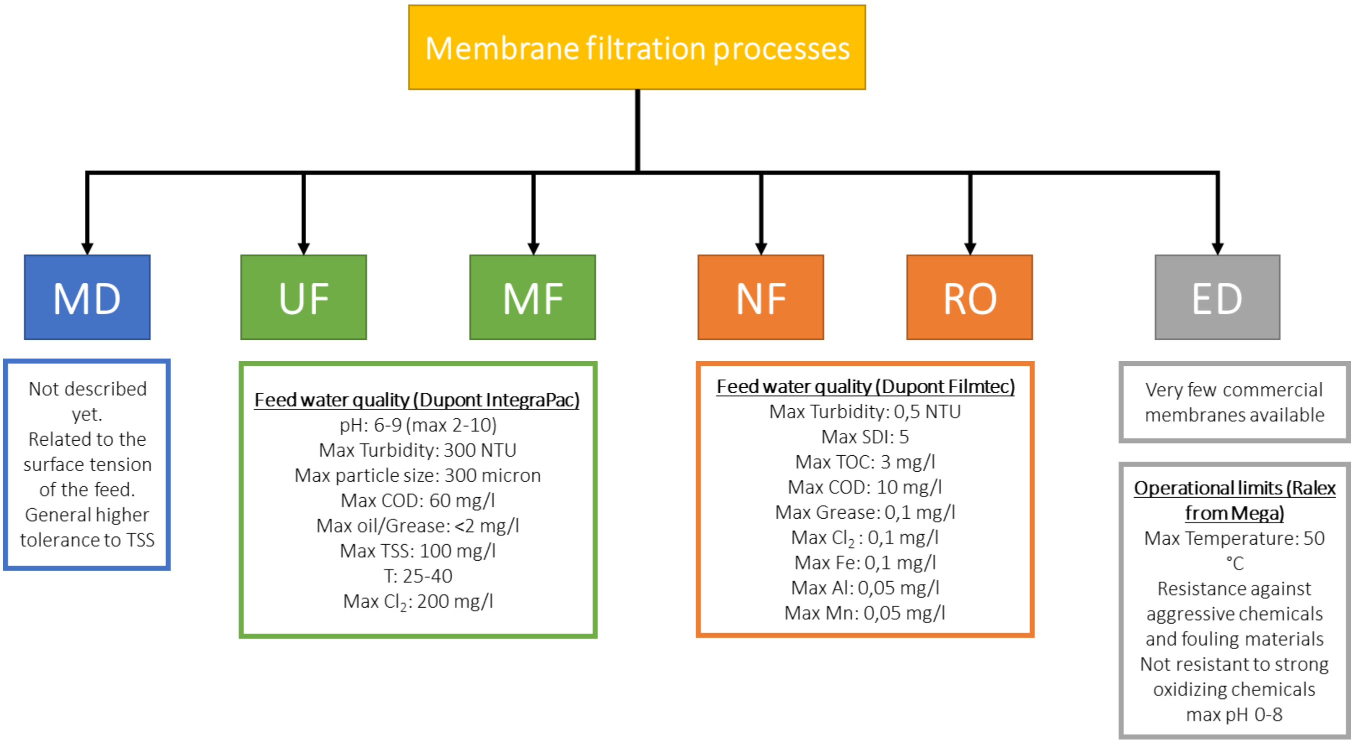

Figure 4: Typical feed water quality and/or operational limits for different membrane processes.

In addition to the described general aspects of membrane filtration 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.

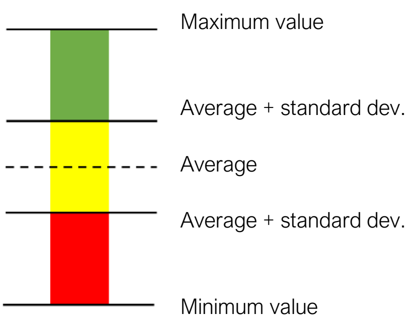

Figure 5: Schematic classification of an evaluation criterion according to the traffic light system with included standard deviation.

The evaluation method itself is performed using a traffic light system (green, yellow or red see Figure 5). 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.

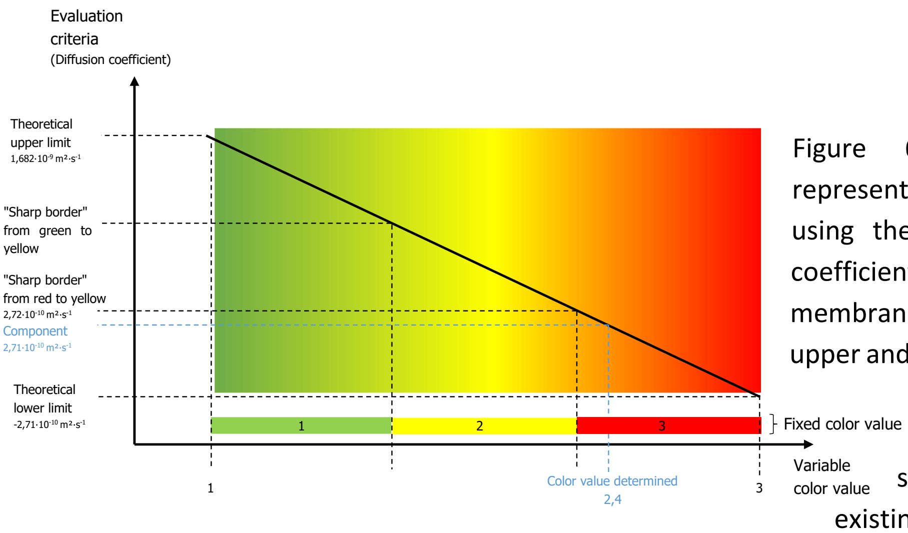

Figure 6: Schematic representation of linear interpolation using the example of the "diffusion coefficient" evaluation criterion in liquid membrane permeation.

Figure 6 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 4 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 4: Presentation of the evaluation criterion for membrane distillation including classification with color code.

Evaluation criterion: Partial vapor pressure difference The partial vapor pressure difference [mbar] represents the driving force of the MD. That component whose partial vapor pressure is higher than that of water (pi> pW) permeates through the membrane, otherwise the component 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).		
Classification		The partial vapor pressure difference (Δp) is >58 mbar.
		The partial vapor pressure difference (Δp) is in the range of 29-58 mbar or could not be determined.
		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.
Evaluation criterion: Transmembrane flux The performance of a membrane in MD is indicated, among other things, by the transmembrane flux [L·m²/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.		
Classificat ion		Transmembrane flux ≥5 L·m²/h.
		No/missing data or empirical studies are available.
		Transmembrane flux <5 L·m²/h.

Evaluation criterion: *Feed temperature*		
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.		
Classification		A sufficient temperature of the feed stream (≥30 °C) is given to operate the MD without additional energy supply.
		Temperature of the feed stream is unknown.
		Sufficient temperature of the feed stream (<30 °C) is not given and additional energy supply is required to operate the MD optimally.

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 [35].

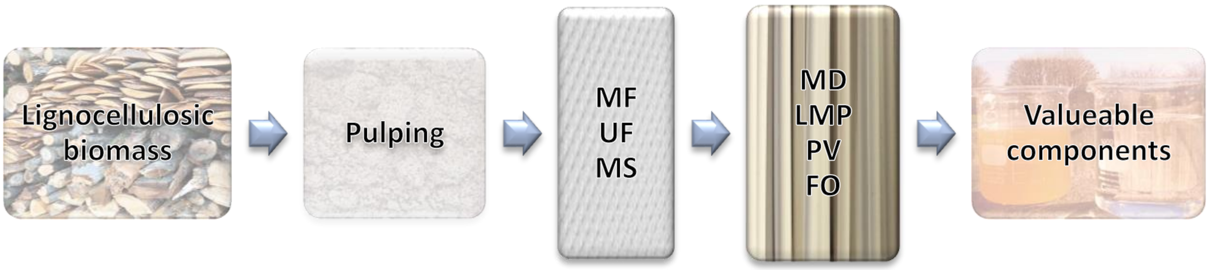

Figure 7: Possible process for pre-treatment of waste liquor from pulp production. MF...microfiltration, UF...ultrafiltration, MS... mechanical skimming, MD... membrane distillation, LMP...liquid membrane permeation, PV...pervaporation, FO...forward osmosis (adapted from Bokhary et al, 2016).

Pre-treatment strategies may be of different kind. Figure 7 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 [36]. 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[37]. 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.

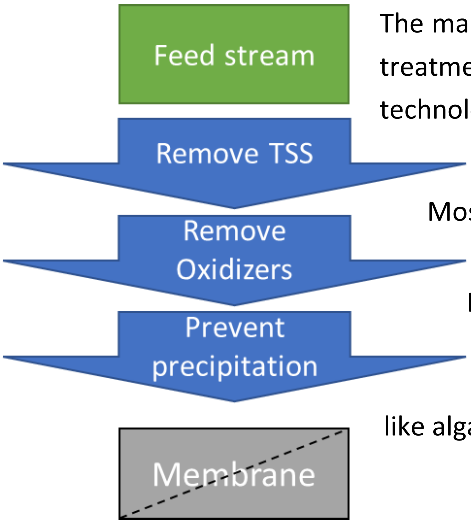

Figure 8: General pre-treatment strategy prior to membrane operations.

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[36]. Very few examples can be found for other membrane separation technologies like FO [38] or other bio sectors like algae cultivation/harvesting [39] or biogas digestates [40], [34].

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 9) and pulp and paper streams (see Figure 10)) in order to help the user to follow a method for the integration of a membrane technology. Special cases have to individually be adapted.

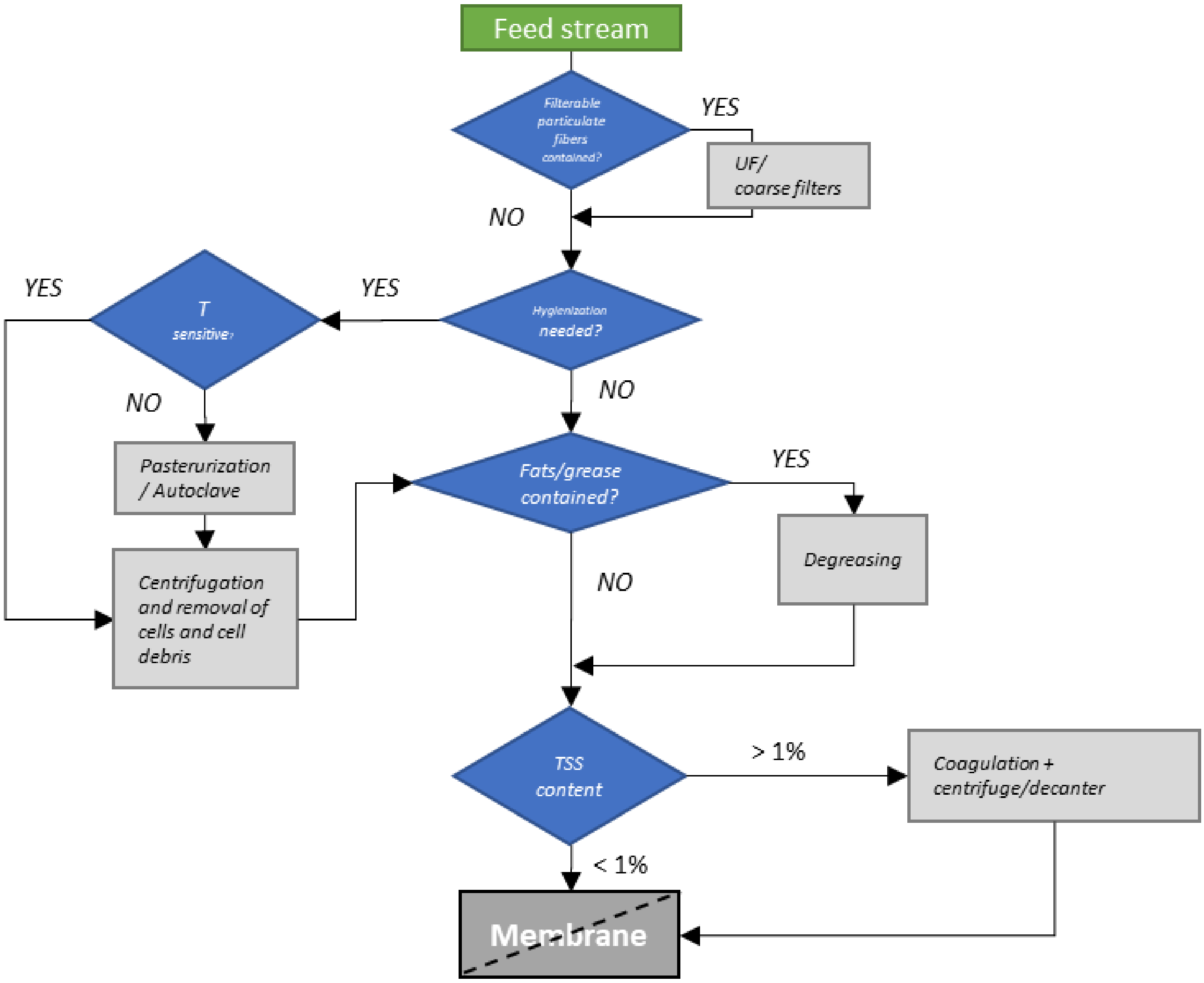

Figure 9: Method for approaching a pre-treatment application of a general bio waste stream (Questions to be raised in rhombus, to be answered with yes or no, leading to a possible treatment step (rectangular boxes).

Following the methodological approach of Figure 9, 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 10. 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.

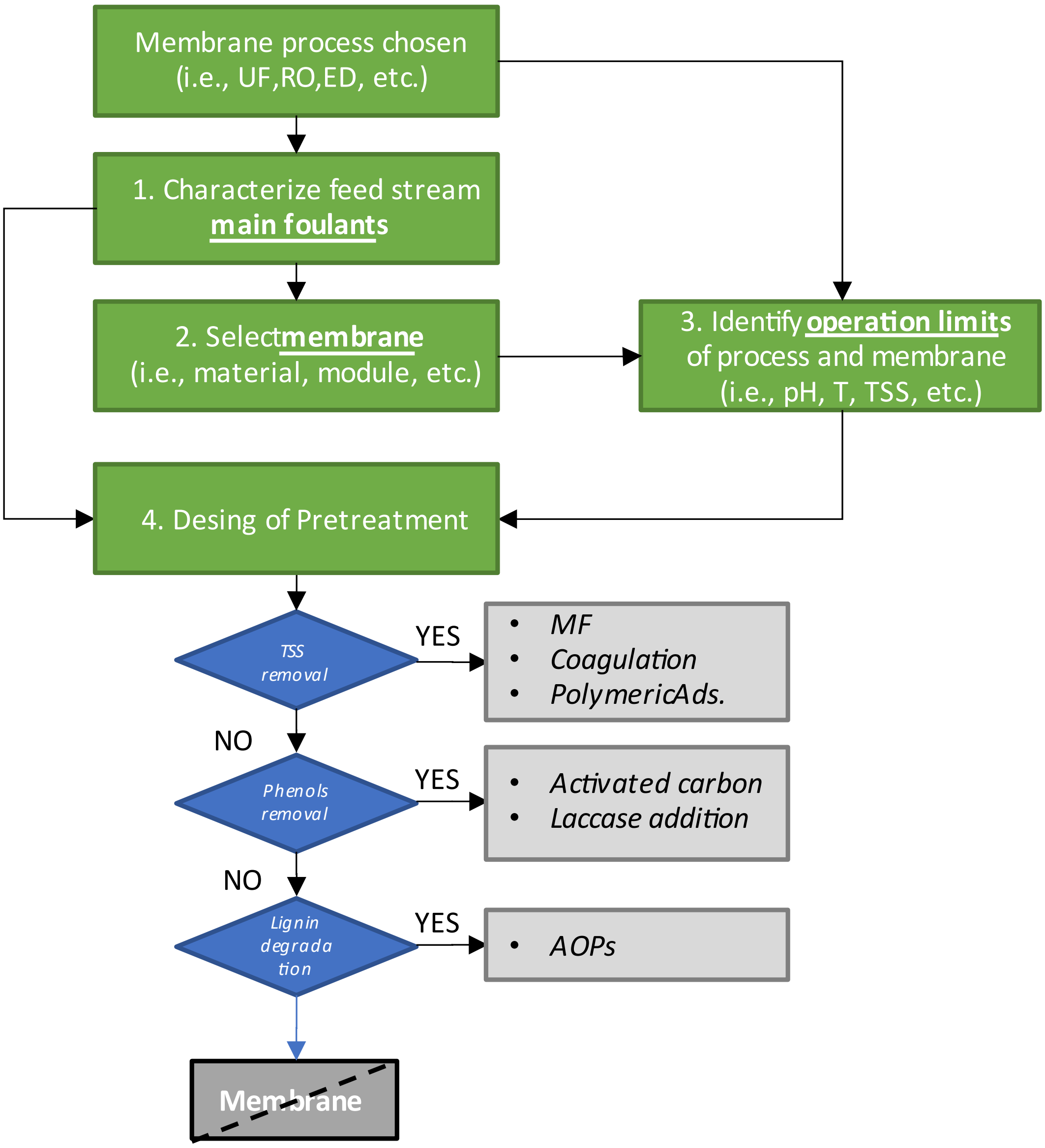

Figure 10: Stepwise approach towards membrane integration with pulp and paper streams

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:

<u>pH Adjustment</u>

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 [41].

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 [34].

<u>Pre-filtration</u>

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.

<u>Coagulation</u>

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[42] . 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.

<u>Polymeric adsorbents</u>

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.

<u>Activated carbon (AC) adsorption</u>

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 [24]. 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 [36]. Alternatively, charcoal adsorption has also been proposed for the removal of phenolic compounds from wood hydrolysate [43].

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 [44].

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 [36].

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 [Fehler! Textmarke nicht definiert.].

6. 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 in order 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[36].

- 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 particular 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 have to 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 [36].

- 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 [36].

- Identification of optimal operating conditions, in terms of hydrodynamics, feed and membrane characteristics [36].

- 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

7. 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 Annex 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.

8. Recent Publications and Contacts of Annex 17

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List of Contacts on Membrane Technologies:

Company	Contact Person	Topics
Aquaporin A/S	Jörg Vogel jvo@aquaporin.com	Forward Osmosis FO, closing the loop, Reduction in water consumption RO with biomimetic membranes (e.g. Low Energy BWRO)
Pentair X-Flow	Ania Pacak ania.pacak@pentair.com	Microfiltration, Ulfrafiltration, Nanofiltration
Pentair X-Flow	Erik Vriezekolk erik.vriezekolk@pentair.com	Microfiltration, Ulfrafiltration, Nanofiltration
Nova University of Lisbon	Joao Crespo jgc@fct.unl.pt	Membrane Filtration, Ultrafiltration, Reverse Osmosis
Aalborg University	Morten Christensen <mlc@bio.aau.dk>;	Membrane Distillation (MD) Forward Osmosis (FO)
LiqTech International A/S	Victor Candelario vcl@liqtech.com	Liquid Membrane Permeation (LMP), Membrane fabrication
Ecohelix AB	Petri Oinonen petri@ecohelix.se	Forward Osmosis (FO), Closing the Loop
Ecohelix AB	Oskar Schmidt oskar@ecohelix.se	Sustainable materials
AlfaLaval	Aurélie Dupuy aurelie.dupuy@alfalaval.com	Forward Osmosis (FO), Closing the Loop; Reduction in Water Consumption, polymeric membrane manufacturing
University of Southern Denmark	Knud Villy Christensen kvc@kbm.sdu.dk	Membrane Distillation (MD), Forward Osmosis (FO), Reduction in Water Consumption

9. 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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