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Membrane Operations in the Pulp and Paper Industry for the Recovery of Constituents: A State of the Art Review

Daniela Silva Benavidez, Paul Demmelmayer and Marlene Kienberger *

Institute of Chemical Engineering and Environmental Technology, Graz University of Technology, Inffeldgass 25c, 8010 Graz, Austria

* Correspondence: marlene.kienberger@tugraz.at

Abstract: The pulp and paper industry is one of the biggest industry sectors worldwide, whose market growth is expected to reach 370.12 billion USD by 2028. However, as a water-intensive process, the pulp and paper production generate huge volumes of contaminated effluents, some of which contain dissolved high-value chemical compounds, such as lignin, hemicellulose, or carboxylic acids. These compounds can be recovered using membrane operations. Thus, membrane operations represent a method to valorize effluents and byproducts from this industry sector and narrow the gap between biorefinery models and the pulp and paper production as an integrated biorefinery. The present review reviews the state-of-the-art-research and the state-of-the-art applications of membrane operations in the pulp and paper industry.

Keywords: membrane operations; pulp and paper industry; lignin; hemicelluloses; wood extractives; carboxylic acids; biorefinery; integrated biorefinery

1. Introduction

The advantages of membrane operations (MO), like low energy demand and their selectivity, are well described in the literature [1–5]. The application of MO in the pulp and paper industry (PPI) dates back to the 1970s [4,6,7]. However, just few applications have been studied (Figure 1) and even fewer implemented at industrial scale, mainly because membrane applications face some constraints, such as the high cost related to the industrial scale-up and membrane fouling [7].

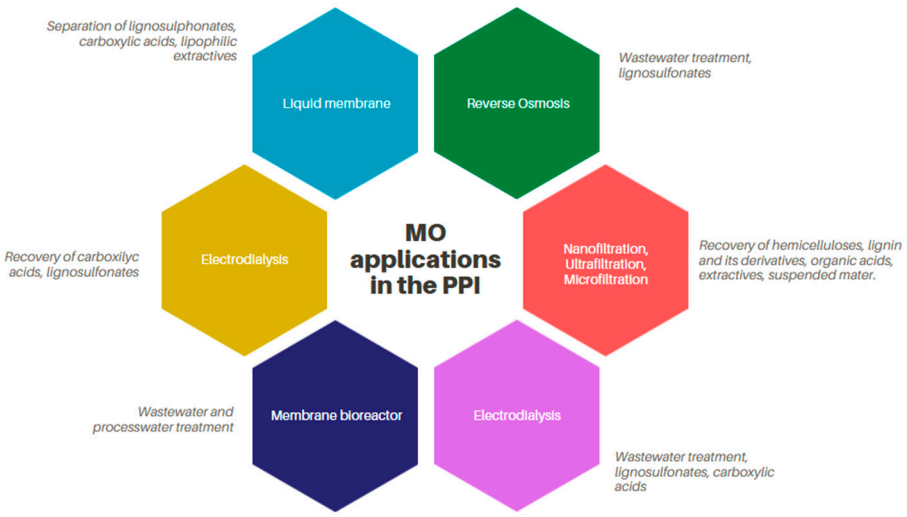

Figure 1. Research of MO applications in the PPI.

In the last decades, research has focused mainly on increasing the technical and economic feasibility and efficiency of MO to promote a shift toward integrated biorefineries in order to

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minimize waste production and maximize the value of available biomass and chemicals. Just by 2015, 32 patents related to the application of ultrafiltration (UF) or nanofiltration (NF) for the isolation of lignin were filed, most of them dealing with the recovery or purification of lignin from cooking liquors [1].

Depending on the lignin disintegration process during wood pulping, the isolation of lignin, hemicelluloses, and other compounds is already state of the art or is under investigation. Compounds that have been studied, along with their summarized characteristics and MO employed for their isolation, are summarized in Table 1.

Table 1. MO used for added value production in the PPI.

Compound	Reported characteristics	MO
Lignin	particle size range: 0.1-2 µm lignin in wastewater: colloidal sizes molecular weight willed wood lignin: 5,900–23,500 g·mol^{-1} molecular weight hardwood kraft lignin: 3,300-3,900 g·mol^{-1} molecular weight softwood kraft lignin: 6,500-8,000 g·mol^{-1} [9]	UF, MF, NF, UF-NF, Diafiltration [10,20,61,62]
Lignan	< 0.1 µm	NF
Lignosulfonates	anionically charged. water soluble particle size > 2 µm molecular weight: 1,000-140,000 g·mol^{-1}	UF, liquid-membrane [12–15].
Hemicelluloses	particle size > 2 µm molecular weight (from sulfite pulping): 18,900 and 30,000 g·mol^{-1} [16]	UF-NF, MF, MF-UF
Extractives and acids	colloidal < 3kDa particles [10]	MF, NF-UF, UF, liquid-membrane, pervaporation [10,15]

This review summarizes state-of-the-art membrane-based processes and the potential applications thereof in the PPI. Further, reported costs for membrane-based processes in the PPI are presented. Applications of MO in wastewater treatment of PPI effluents are beyond the scope of this paper, as this topic is already nicely summarized and discussed in the literature [2,3].

2. Compounds of interest

2.1. Lignin and lignosulfonates

Lignin accounts for 20-35% of the plant biomass and represents the second most abundant biopolymer of land-based biomass [4], which renders lignin the most important biofuel worldwide. It is built up from monolignols, which are *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol [5]. Annually, more than $5 \cdot 10^7$ tons of lignin are dissolved via chemical cooking [6], and around 85% thereof are disintegrated using the kraft process [4]. Lignosulfonates, on the other hand, are byproducts obtained from the production of wood pulp using sulfite pulping. Both lignin and lignosulfonates can be sold as emulsifiers, dispersants, or as precursors for the synthesis of electrochemically active substances [4,7,8], and lignin is normally used as biofuel in the recovery boiler onsite in PPI.

2.2. Lignan

Lignans, such as matairesinol or pinoresinol, are low molecular weight polyphenols [9] that are-like lignin-responsible for the structural integrity of plant cell walls. They are built from the same

monomers as lignin, but they are dimeric instead of polymeric and, in contrast to lignin, optically active. Due to their associated anticancer and antioxidant activity, lignans are commonly used for pharmaceutical applications; as an example, the price for the lignan hydroxymatauresinol, which is used as nutritional supplement, is reported with 1 € mg^{-1} [10]. Even when high prices can be achieved with this compound, the concentration of lignans as compared to lignin is small and the isolation thereof is complex. [10,11]

2.3. Hemicellulose

Hemicelluloses are heterogeneous, amorphous, polymeric carbohydrates composed of pentoses, like arabinose and xylose, and hexoses, such as mannose, glucose, or galactose [22]. Depending on the wood source the proportion of the sugar changes, but their main constituents are xylan, arabinan, and galactan [12]. In process streams of chemical pulping, they are present in the form of galactoglucomannan, glucomannan and arabinoglucuronoxylan, and glucuronoxylan. Some applications of hemicelluloses include oxygen barrier films for packaging, paper additives, food ingredients, or coatings [13–17]. However, many laboratory products based on hemicellulose have not been scaled up yet due to their low availability [18].

Hemicelluloses can be recovered from each chemical pulping process, but the isolation process of hemicelluloses is complex and not yet state-of-the-art [11,19].Nevertheless, for the viscose process hemicellulose recovery is state-of-the-art due to higher concentrations thereof. Also, from the process water of thermomechanical pulping (TMP) hemicellulose are already recovered today [14].

2.4. Hydroxy carboxylic acids

During kraft or alkaline pulping, a substantial part of hemicelluloses is converted to hydroxy carboxylic acids [12]. The dry solids content of kraft black liquor (BL) is typically 12-18%, from which 10% are hydroxy carboxylic acids [20]. Hydroxy carboxylic acids can be used to produce biodegradable polymers and plastics, cosmetics, and heavy metal chelating agents [12]. However, the isolation of hydroxy carboxylic acids from spent liquor or BL is not state-of-the-art.

2.5. Extractives, turpentine, tall oil

Wood extractives are lipophilic compounds such as fatty acids, resin acids, sterols, steryl esters, and triglycerides [21]. They are present in pulping liquors either in their original forms or in a variation after undergoing hydrolysis or other transformation reactions [12]. Depending on the wood source, these extractives can account for up to 10 wt.% of the wood dry matter [21]. Turpentine, a fluid obtained from the resin of trees made up of terpenes, is a by-product of the kraft process and can be removed via MF or steam or air stripping. Its primary uses are as a solvent and as a source of materials for organic synthesis. Tall oil is obtained during the pulping process, after BL is concentrated and left to settle, leaving a top layer known as “tall oil soap”. Tall oil can be sold as feedstock for special chemicals production [58].

3. Streams studied for compound recovery and treatment

3.1. BL

BL is a byproduct of kraft pulping. The composition of BL varies considerably with the digestion process and the raw material used. Typically, lignin accounts for approximately one third of the mass of BL and the remaining part consists of organic acids, wood extractives, and various inorganic and organic compounds. It is well known that lignin can be separated from BL by acid precipitation, which is used by the state-of-the-art processes LignoBoost, LignoForce, and WestVaco process [7,22,23]. As a first step of these processes, carbon dioxide is used as acidifying agent. Then, a precipitation step follows using sulfuric acid. At this point, precipitated lignin agglomerates have a molecular weight of 1700-4500 g mol^{-1} [24,25]. Afterwards, membrane filtration can be applied to separate the lignin.

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Lignin recovery has been implemented by different companies. West Fraser Company in Canada uses the LignoForce technology, whereas Domtar Corporation uses the LignoBoost technology and produces roughly 25,000 tons of lignin per year. SunCarbon AB, founded in 2014 in Sweden [26], has a pilot plant with an integrated three-step process: membrane separation, hydrothermal treatment and purification, and process integration to recover lignin from BL [27,28]. The membrane pilot plant with a production capacity of 1.5 kg lignin h^{-1} was built to scale up the patented SunCarbon process and has been in operation at the kraft mill since 2016 [28].

Besides lignin, the extraction of organic acids has been studied by Mänttäri et al. [20]. They combined MO with acidification and cooling crystallization for the simultaneous recovery of lignin and organic acids. By combining acid precipitation and UF, they removed 75% of the lignin present in a sample of BL. The organic acids in the permeate were then purified by acidification, crystallization, and NF in diafiltration mode. The final acid concentration was of 20 g L^{-1}. [33]

Maitz et al. investigated electrodialysis to recover both, carboxylic acids and NaOH. The results were promising; however, the energy demand was too high for economic implementation [29].

3.2. Sulfite spent liquor (SSL)

Lignosulfonates are mostly recovered by the Howard process. This process is commercially operated since 1981 at Borregaard Industries Ltd located in Sarpsborg, Norway [22]. The process consists of the addition of lime to the spent liquor to precipitate calcium lignosulfonates at a pH of 8.5, followed by a UF step using membranes with a MWCO of 20 kDa [1,30–32]. This pre-concentrated stream can be used to convert lignosulfonates at least partially to vanillin [32].

Alternatively, electrolysis, the Pekilo process, and reverse osmosis are membrane separation techniques suggested for separating lignosulfonates from spent sulfite liquor. In electrolysis, magnesium sulfite from the spent liquor is desalinized and demineralized to produce lignosulfonates. In the Pekilo process, hemicelluloses are fermented and ultra-filtered to obtain lignosulfonates. However, none of these methods have been commercialized yet, mainly due to their high operational costs [22].

3.3. TMP water

Process water from TMP processes is rich in hemicelluloses, lignin, lignin carbohydrate complexes, and lipophilic and phenolic extractives [10,18]. The low concentrations of these components in the process water – not more than 1-3 g L^{-1} [10] – render their isolation challenging [33]. However, the potential for TMP process water valorization is high given the high flow rate of several hundred cubic meters per hour during pulp processing. Additionally, the mild conditions of TMP maintain the native structure of the wood components, which suggests them as suitable candidates for other fine processes, such as the depolymerization into bulk and fine aromatic and phenolic chemicals [10].

Studies of MO for the isolation of compounds present in the TMP process water include the recovery of hemicelluloses [18,34] and the recovery of lignin and lignans [10]. Thuvander et al. focused on the valorization of hemicellulose, especially galactoglucomannan. In their study, the process water was pre-filtered with a 100 µm membrane for the removal of particles and fines, followed by a MF unit with 3 mm flow channels and a crossflow velocity of 3 m s^{-1}. Finally, the permeate was filtered with a UF unit with a molecular cutoff (MWCO) of 10 kDa. [18] The cost estimate of this continuous, multistage membrane process for galactoglucomannan recovery was 1,160 € per ton of hemicelluloses produced [35]. Reported market prices of galactoglucomannan are around 800 USD per ton, hence, the process remains unfeasible to date.

Villain-Gambier et al. used a NF membrane to retain lignin and lignans from TMP process water in a pilot plant study. The TMP process water was pre-treated with a flotation step to remove lipophilic matter, followed by a clarification step with a 150 kDa membrane to remove suspended mater. After these pre-treatment steps, a membrane of 1 kDa was used to retain lignin, followed by a membrane with a MWCO of 300 Da to retain lignans. The retention of lignin in the 1 kDa membrane was 39% of the initial lignin, whereas the retention of lignin and lignan in the 300 Da membrane was

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29 and 70%, respectively. The permeate from this membrane was re-introduced into the process, consequently saving freshwater consumption. The techno-economic evaluation showed that a selling price including production of around 10 € per kg was acceptable for the lignin and lignan extracts; lignin extract with a concentration of 27.4 g L^{-1} from the 1 kDa retentate and lignan-rich extract with a concentration of 7.4 g L^{-1} from the 300 Da retentate were obtained when the plant capacity was 10 $m^3 h^{-1}$. A pilot plant with capacity of 60 $m^3 h^{-1}$ can produce 12 tons of lignin and 825 kg of lignans per month. [10]

In another study, the fractionation of TMP process water into lignin, hemicellulose, extractives, suspended matter, and water was performed using a cascade of MF, UF, and NF membranes. Each ton of produced pulp produced about 10 kg of suspended matter, more than 0.3 kg of extractives, 11 kg of hemicelluloses, and 8 kg of lignin in the retentates of a drum filtration. Besides the recovery of valuable compounds, it was determined that approximately 40% of the filtrated process water had the conditions to be recovered as fresh water [34].

4. Challenges for MO implementation for industrial scale-up

Main challenges for the implementation of MO at industrial scale are membrane fouling, selectivity, and competitive costs for making the recovery of compounds economically feasible for scale-up.

4.1. Fouling

Foulants and foulant mechanisms for different types of membranes have been extensively studied [21,22,36,37]. Fouling types, fouling mechanisms, and main foulants in membrane processes applied to process streams in the PPI are presented in Table 2. Selecting an appropriate membrane material minimizes adsorptive fouling, while pore plugging can be controlled by using a membrane with a suitable MWCO [38]. Polyacrylonitrile, polysulfones, polyethersulfone, polyamide-imide, and polyether-imide membranes have been shown to be severely affected by adsorptive fouling from pressates coming from semichemical mechanical pulp mill; they showed a loss of 60-80% of their pure water permeability. In contrast, hydrophilic membranes[39] and regenerated cellulose and thin film composite membranes [38] exhibit a lower fouling potential. Some methods that have been studied for minimizing and/or preventing fouling in membranes include flotation as a pre-treatment step [40], the optimization of the operating temperature and crossflow velocity [41], and the modification of membranes (e.g. with Praestol 859 or Pluronic F108) to increase the membrane fouling resistance [42]. Membrane cleaning with non-ionic detergents has also been proposed [43].

Table 2. Fouling types, fouling mechanisms, and main foulants in membrane processes for compound valorization. Based on [35,49,50].

Process	Membrane type	Fouling type	Mechanism	Main foulant
Lignin recovery	MF, UF, NF	Organic	Cake/gel layer, pore blocking, adsorption	Lignin, extractives
Hemicelluloses recovery	MF, UF, NF	Organic	Cake/gel layer	Hemicelluloses
Extractive recovery	UF	Organic	Adsorption	Dissolved and colloidal lipophilic extractives, sterols

4.2. Selectivity

Besides fouling, the overlap in particle size of compounds of interest, such as lignosulfonates and hemicelluloses, in PPI process streams makes their isolation challenging [36]. Thus, membrane selectivity can be critical for efficient separation of pulp compounds. The selection and preparation of membranes for certain applications have been thoroughly investigated and is well documented. Hydrophilic membranes have been proven to have a lower affinity for lignin, resulting in lower

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retention and, hence, lower fouling, as shown in the study of Al-Rudainy et al. [52]. Inorganic membranes have a high mechanical, chemical, and thermal stability, a long service life, a comparatively low membrane resistance, and a high filtration performance against organic membranes [57]. However, they cannot stand the extreme conditions of temperature and pH value, which are commonly present for example in BL. Protective coating materials that allow in-situ regeneration of these membranes have been proposed as an alternative. Ceramic membranes have a higher hydrophilicity as compared to other inorganic membranes and, therefore, achieve higher fluxes of BL. However, ceramic membranes have a lower lignin retention [21,25] and higher capital costs [58] in comparison with to polymeric membranes. To reduce costs by lowering energy consumption, air sparging has been proven to be effective for increasing hemicellulose retention from wheat bran in UF membranes; a transfer to streams from the PPI may be possible but has not been reported yet. [54].

The viability of other non-commercially scaled up MO include supported liquid membrane extraction and permeation. Liquid membrane permeation with supported membranes has demonstrated to be a potential future isolation technology for the treatment of process streams from the PPI, particularly for the extraction of lignosulfonates [12]. As support layers, cellulose [12] and polyvinylidene fluoride have been studied [13] with tri-*n*-octylamine (TOA) used as a reactive extraction agent [13,14]. The extraction efficiency of lignosulfonates isolation with this method was reported between 85 and 92% [14,15]. Ke Xian et al. [13] extracted lignosulphonates from an aqueous solution using a polycylidene membrane of 0.45 μm, kerosene as solvent, and NaOH as stripping agent. Leiviska et al. [10] characterized pulp and paper mill wastewater fractions regarding extractives, lignin, and suspended solids by using MF and UF membranes. From their studies it was discovered that most of the lignin present in PPI wastewater is in the colloidal form and in the <3 kDa particle range size. They further stated that wood extractives have an almost equal distribution in the range of 8 μm and 3 kDa and could therefore be extracted with a MF membrane of 8 μm.

Patil et al. [59] performed a scale-up study of a hollow fiber supported liquid membrane (HFSLM) for the extraction of carboxylic acids and developed a mathematical model for their transport behavior. They compared the extraction performance using tri-*n*-butyl phosphate (TBP), TOA, and tri-*n*-octyl phosphine (TOPO) as extractants and concluded that almost 99% of the carboxylic acids can be extracted using 1% TOPO as an extractant; this proposes a generalized methodology for the HFSLM extraction of carboxylic acids. Kessy et al. [60] demonstrated the technical feasibility of the isolation of lipophilic extractives from the sulfite pulping process after the oxygen bleaching stage by performing a liquid-liquid extraction followed by a HFSLM. Liquid-liquid extraction was carried out using hexane and hexane-ethyl acetate as solvent. The extract was dried, weighted, and afterwards dissolved with acetone for derivatization with methanolic HCl addition. After pH adjustment, a two phase HFSLM extraction was performed using propylene hollow fibers impregnated with a mixture of 1-octanol and undecane. The lipophilic extractives obtained were mainly fatty acids, identified as their methyl esters, sterols, and steroid hydrocarbons.

4.3. Costs

Previously mentioned challenges influence operation costs that are currently high for industrial implementation of MO. Cost estimates for membrane plants in pulp and paper mills are rare in scientific journals [32], but Table 3 summarizes the literature dealing with cost estimation with respect to MO in the PPI.

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Table 3. Reported costs for different stream applications and membrane types *TMC water with a concentration of 2.35 g L^{-1} hemicelluloses.

Process	Application	OPEX k€·$year^{-1}$	Production Rate	Cost/product	Ref.
NF ceramic 1 kDa	Lignin from TMC process water	92.8	1.049 ton retentate·$year^{-1}$ (23% lignin); capacity: 8 m^3·$year^{-1}$	17 000 €·ton^{-1}	[24]
NF polymeric 300 Da	Lignan from TMC process water		0.697 ton retentate·$year^{-1}$ (2% lignan)	17 000 €·ton^{-1}	
UF (ceramic) NF (ceramic)	Lignin from BL	2.8	8,300 ton lignin solution $year^{-1}$	430 €·ton^{-1}	[25]
UF (ceramic) NF (polymeric)		3.0	30,000 ton lignin solution $year^{-1}$	130 € ton^{-1}	
NF (ceramic)		3.6	41,000 ton lignin solution $year^{-1}$	68 € ton^{-1}	
NF (polymeric)		2.8	68,000 ton lignin solution $year^{-1}$	46 € ton^{-1} lignin in solution (230 g L^{-1})	
UF-RO 80% water recovery	Lignin from spent liquor (AlkOx process; reuse of purified water)	51	10,000 m^3 treated liquor $year^{-1}$	521-1,175 € ton^{-1}	[8]
UF-RO, without water recovery		55	10,000 m^3 treated liquor $year^{-1}$	539-616 € ton^{-1}	
UF	Galactoglucomman from spent sulfite liquor	1.06	2.75 GGM h^{-1}	48.23 € ton^{-1}	[49]
MF-UF	Galactoglucomman from TMC process water	713 € ton^{-1}	180 m^3 of process TMC water h^{-1}*	1,160 € ton^{-1} GGM in solution (47 g L^{-1})	[32]

5. Conclusion

Membrane operations can be used to extract high-value products, such as lignin, hemicelluloses, and extractives from process streams of the pulp and paper industry, including black liquor, sulfite spent liquor, and thermomechanical pulping water. A combination of more than one membrane technique is usually necessary to obtain a purified or concentrated fraction of interest. Main challenges for industrial implementation of MO are fouling, selectivity, and costs, but some industries have already overcome these challenges by combining other separation technologies, which demonstrate a high potential in scaling MO to industrial applications with economic feasibility.

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