Review Paper

A Review of Membrane Technologies for Integrated Forest Biorefinery

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Article info

Highlights

• Membrane technologies for value-added chemicals recovery and bioenergy production in IFBR are reviewed
• Challenges and opportunities of membrane technologies in IFBR are discussed
• Membrane fouling and its control in IFBR are highlighted
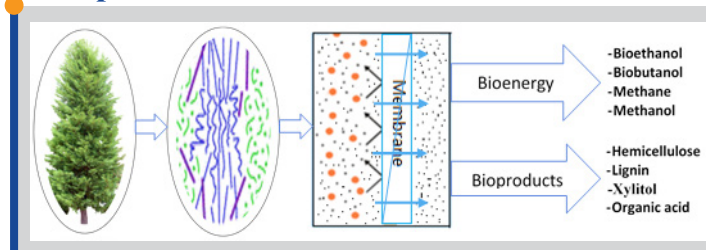
Graphical abstract

Abstract

More recently, the concept of integrated forest biorefinery (IFBR) has received much attention as a promising solution for the struggling forest industry in North America and Europe to overcome its difficult financial period and competes globally. This new business paradigm offers a broad range of potentially attractive products, from bioenergy to value-added green organic chemicals in addition to traditional pulp and paper products. However, it also implies adoption of different types of appropriate separation technologies. Recent advancements in membrane technologies and their valuable applications have resulted in numerous breakthroughs in IFBR. The review of the implementation of membrane technologies for the separation of the value-added chemicals in the integrated forest biorefinery could contribute to the knowledge required for the large-scale adoption of membrane technologies in the forest industry. This paper aims to present a state-of-the-art review on the applications and the recent advancements of membrane technologies in IFBR, and their capacities to produce value-added chemicals and bioenergy. The emphasis is given to the focus areas of IFBR, particularly: the recovery of value-added chemicals, black liquor concentration, product recovery from Kraft evaporator condensates, tall oil recovery, inorganic and inorganic compounds recovery, fermentation inhibitors removal, enzyme recovery, biobutanol and bioethanol production and recovery. The paper also discusses the challenges and opportunities of this new business paradigm of forest industries.

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1. Introduction

Forests and forest products industries are one of the most important industries in North America and Europe. However, more recently they are facing reduced profit margins and a globally competitive market because of the new shift from newsprint to electronic media, increasing competition from low-cost countries, restricted environmental laws, and high energy, and water consumption. These issues have resulted in plant closures, layoffs, and mergers. Accordingly, pulp and paper companies have begun looking for new opportunities to improve revenue streams and profitability. Therefore, the notion of repurposing pulp and paper mills into an integrated forest biorefinery (IFBR) was created [1,2]. Implementing IFBR would improve the profitability and competitiveness of a stagnant pulp and paper industry by diversifying the industry's products and generating new revenues.

The biorefinery concept is similar to today's petroleum refinery, which generates different fuels and oil products. However, compared to the oil refinery, biorefinery products are environmentally friendly (non-toxic, biodegradable, reusable, and recyclable). *Biorefining*, defined by the International Energy Agency (Biorefinery, task 42), is the sustainable processing of biomass into a spectrum of marketable food & feed, products, and energy [3]. Biorefinery processes diverse bio-based feedstocks into a wide spectrum of products and biofuels.

IFBR is precisely required to process forest biomass materials into a spectrum of biofuel and bioproducts, similar to the operation of conventional petroleum refineries while maintaining cellulosic fibers for pulp and paper production [4]. It intends to implement biorefinery units into an existing pulping mill called receptor Kraft. The IFBR has multiple production platforms (e.g., cellulose, hemicelluloses, lignin, and extractives) that can be used in an integrated manner for the manufacturing of a wide range of potentially attractive products, from biofuels to value-added chemicals, as summarized in Figure 1.

In implementing IFBR, highly developed separation technologies that are cost efficient and environmentally responsible, are needed. Recent advancements in membrane technologies and their practical applications have resulted in numerous breakthroughs in IFBR. Membrane technologies have the potential to be a promising avenue of research and innovation for such applications because of their capabilities to offer excellent fractionation and separation, short processing steps, reduced chemicals utilization and considerable energy saving [5].

This paper discusses the applications and the recent development of membrane technologies related to IFBR and their capacity to produce value-added chemicals from forest biomass and wastes. The emphasis is given to the focus areas of IFBR, particularly: the recovery of value-added chemicals,

black liquor concentration, product recovery from Kraft evaporator condensates, tall oil recovery, inorganic and organic compounds recovery, fermentation inhibitors removal, enzyme recovery, and bioethanol and butanol production and recovery. This paper also discusses the advantages and limitations of membrane technologies for IFBR applications.

2. Membrane separation processes for IFBR

In the last few years, membrane filtration has been widely considered and implemented because it works simply and efficiently. Membrane separation processes allow the passage of one component more readily than the other because of the differences in physical and/or chemical characteristics of the membrane and the permeating components. Most membranes fall into one of two broad categories: microporous membranes and solution-diffusion membranes (as illustrated in Table 1). Membrane processes can be classified further as symmetrical or asymmetrical membranes.

Membrane separation processes, such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverses osmosis (RO), pervaporation (PV), membrane distillation (MD), and diafiltration (DF) have special values in bioenergy and biomaterials production [5]. MF process is of great interest in the solid particles removal and large molecules separation. It does not develop significant osmotic pressures like the other membrane processes. In the arena of IFBR, UF has been utilized to concentrate and purify hemicellulose solutions with different molecular weight distributions, whereas NF has been used for the lignin recovery from prehydrolysate solutions and black liquor (BL). PV and MD are commonly used for dehydration and separation of organic compounds mixtures, while DF is usually used as downstream processing step for product concentration and purification.

Polymeric membranes, which utilize polysulfone (PS), polyethersulfone (PES), polyvinylidene fluoride (PVDF), regenerated cellulose (RC), polytetrafluoroethylene (PTFE), and fluoropolymers (FP), are the dominant membranes used for hemicellulose recovery. Whereas, ceramic membranes are the primary membranes used for lignin recovery from BL due to BL harsh conditions. Many configurations of membrane modules, such as tubular, flat sheet/plate-and-frame, spiral wound, and hollow fiber, have been used in the forest biorefinery. In IFBR, membrane separation processes are applied as a means of separation, recovery, purification, and dehydration, although they also have many other applications beyond the scope of this review.
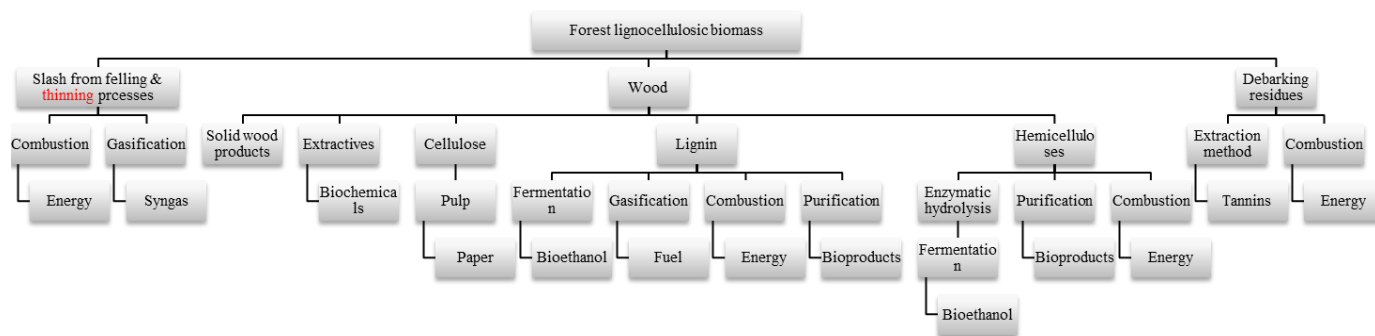
Fig. 1. Simplified chart for the potential products from integrated forest biorefinery.

Table 1
Comparison between the main membrane separations processes related to IFBR modified from [5].

Membrane	Microfiltration (MF)	Ultrafiltration (UF)	Nanofiltration (NF)	Reverse Osmosis (RO)	Pervaporation (PV)	Membrane Distillation (MD)
Driving force	Pressure < 2 bar	Pressure 1-10 bar	Pressure 5-35 bar	Pressure 15-150 bar	Partial vapor Pressure	Vapor pressure difference
Thickness (μm)	10-150 micron	150-250 micron	150 micron	150 micron	~0.1 to few (Top layer)	20–100
Separation principle	Sieving mechanism	Sieving mechanism	Solution-diffusion	Solution-diffusion	Solution-diffusion	Vapor–liquid equilibrium
Membrane structure	Symmetric porous	Asymmetric porous	Composite	Composite	Homogeneous or composite	Symmetric or asymmetric porous
Pore size (nm)	~50–10,000	~1–100	< 2	0.1-1	Nonporous (dense)	~200–1000
Module Configuration	Flat sheet/plate-and-frame, tubular, hollow fiber	Flat sheet/plate-and-frame, tubular, spiral wound, hollow fiber, capillary	Flat sheet/plate-and-frame, tubular, spiral wound	Flat sheet Tubular Spiral wound Hollow fiber	Flat sheet/plate-and-frame, tubular, hollow fiber	Flat sheet/plate-and-frame, tubular, capillary
Membrane material	Polymeric, ceramic	Polymeric, ceramic	Polymeric	Organic polymers (cellulosic & polyamide derivatives)	Polymeric, ceramic, organic–inorganic	Hydrophobic polymer
Applications	Lignin and hemicelluloses recovery and enzyme recovery	Lignin and hemicelluloses recovery, enzyme recovery	Lignin and hemicelluloses recovery and fermentation inhibitors removal	Lignin and hemicelluloses recovery and fermentation inhibitors removal	Bioethanol recovery	Bioethanol recovery

3. Recovery of value-added chemicals in IFBR

Lignocellulosic biomass consists of four major components: cellulose, hemicellulose, lignin, and extractives. Proportions of these components vary depending on the biomass materials [6]. The relative ratio of cellulose and lignin is one of the important factors determining the suitability of plant species for any processing program. Biorefinery takes advantage of these different components and their intermediates, therefore maximizing the values derived from them.

In pulp and paper mills, cellulose is mainly devoted to the production of pulp and paper instead of bioenergy and biochemical, while the fate of hemicelluloses and lignins are depolymerized, de-branched, and solubilized in the cooking liquor. These components represent about half of the woody material [5]. Hemicellulose and Lignin can be recovered as value-added materials. Reportedly, many applications exist for lignin and hemicellulose, ranging from upgraded biofuels to high-value specialized chemicals [7,8]. Thus, these amounts of hemicellulose and lignin can be better used to increase the revenue margin of pulp and paper industry, as summarized in Figure 1.

3.1. Hemicelluloses recovery

Hemicelluloses represent one of the most abundant renewable resources on the earth. They belong to a group of complex polysaccharides which are formed through biosynthetic paths different from that of cellulose. Hemicelluloses are commonly divided into four groups of structurally different oligomer types: xyloglucans, mannans, xylans, glucomannans, and β-(1→3, 1→4)-glucans [9]. The composition and structure of hemicellulose vary considerably depending on the plant species. The molecular weight distribution of hemicelluloses varies widely, depending on the raw materials, and hemicellulose has a much lower molecular weight than cellulose. Like cellulose, hemicelluloses function as supporting material in the cell wall.

During the pulping, hemicelluloses and lignin are extracted from wood chips and partially end up in the black or prehydrolysis liquor. The fate of the hemicellulose is traditionally, and unfortunately, limited to discharge in wastewater streams for aerobic/anaerobic biological treatment [10]. Preferably, it can be burned in the mill's recovery boiler as BL to regenerate energy. Since the heat value that can be generated of hemicelluloses (13.6 MJ/kg) is nearly half of that of lignin ((26.9 MJ/kg)), using hemicelluloses as a fuel source is unjustifiable [2].

Recently, many applications for hemicellulosic materials have emerged, including the production of hydrogels [11] and the fabrication of oxygen barrier film for food packaging [12]. Also, it can be used as a source of sugar that can be fermented to ethanol [13] or utilized as an emulsion stabilizer in food and feed [14]. Figure 2 illustrates some uses of hemicellulose. Moreover, hemicelluloses are used as a raw material for the production of furfural, hydroxymethylfurfural (HMF), and lactic acid [15]. On the other hand, hemicelluloses oligomers are highly bioactive and can be used as growth hormones for trees.

Hemicelluloses recovery would be beneficial to pulp mills, not only to increase profitability and competitiveness, but also to reduce the organic loading to the wastewater treatment facility and minimize overloading to the bottleneck recovery boiler. However, highly developed separation technologies that are cost efficient and environmentally friendly are needed for achieving these potential benefits. Isolation of hemicelluloses from different raw materials sources has been studied since the 1950s. However, more ultimate and profitable separation methods, which prevent hemicelluloses degradation and maximize the value derived from hemicellulose, are lacking. Membrane technologies has appeared as a promising separation method for hemicellulose isolation and purification from different raw materials without degradation. This review discusses MF,

UF, NF, and DF for hemicellulose recovery and purification.

3.1.1. Microfiltration (MF)

MF is a membrane separation process that can be used to separate particles or biological entities in the range of ~ 0.05 μm to 10.0 μm from fluids by passage through a microporous membrane filter. Many studies were conducted to examine the suitability of MF to remove particles and suspended matter from the process water originating from the pulp and paper industry, as summarized in Table 2. MF effectively removed all the suspended matter. However, hemicelluloses are partly retained.

Persson et al. [16] extracted hemicelluloses from process water of the production of Masonite using a method involving three steps: removal of high molecular species by MF, pre-concentration of hemicelluloses by UF, and reduction of the salts concentration and monosaccharides by DF. Their results show that MF could efficiently remove high molar mass compounds. The total dry solid content (TDS) was 0.6 wt% in the primary process water, 0.35 wt% in the permeate, and 5.2 wt% in the retentate. Andersson et al. [17] confirmed that particles and suspended matters in the process water could be removed by MF. In their study, turbidity decreased from 960 nephelometric turbidity units (NTU) in the process water to 4 NTU in the permeate. Moreover, Hasan et al. [18] reported that colloidal and particle removal, using MF, is feasible and can significantly reduce turbidity when they examined the separation of sugar maple wood extracts by ceramic membrane of two different pore sizes: 0.2 μm and 0.01 μm.

Krawczyk and Jönsson [14] investigated the influence of membrane pore size (0.2, 0.4 and 0.8μm), cross-flow velocity, and back pulsing on membrane performance during the MF of thermomechanical pulping (TMP) process water. The results revealed the challenges of recovering the pure water flux of the 0.4 and 0.8μm membranes. However, increasing cross-flow velocity and back pulsing had a positive effect on the flux, but only a minor influence on the retention. Also, MF followed by UF was found to be a suitable combination, providing a concentrated and purified hemicellulose fraction [19,20]. MF has shown high capabilities to clarify the process water and successfully remove all suspended matters. However, there is a need for feasibility studies to evaluate the cost-effectiveness of currently applied MF in the separation and purification of hemicelluloses.
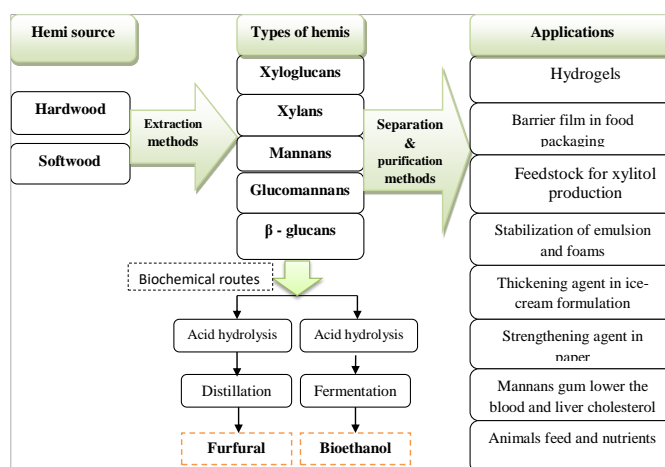
Fig. 2. Sources and types of hemicelluloses with some of their uses in industry.

Table 2
Summary of MF membrane process for hemicelluloses recovery.

Raw material	Characteristics of membrane			Operating conditions						Performance		Reference
	Pore size	Material	Configuration	Scale	VR[c]	Hemicellulose conc. (g/L)	Temp (°C)	TMP (bar)	Cross flow velocity	Flux (L·m⁻²·h⁻¹)	Hemi rejection (%)	
Spruce softwood process water	0.2, 0.4, 0.8 μm	Ceramic	Tubular	Lab scale	–	1.04/0.05/0.12	80	0.5	4 m/s	60 - 350	>50	[14]
Sugar maple wood extracts	0.2 /0.01 μm	Ceramic	–[b]	Lab scale	–	–	20	1.5-2	1.3, 2, 2.6 m/s	–	–	[18]
Spruce wood process water	0.2 μm	Ceramic	Tubular	Lab scale	~0.98	0.8	60	0.7	5m/s	60 - 260	80	[19]
Spruce wood process water	0.2 μm	PTFE[a]	flat sheet/plate-and-frame	Lab scale	–	1-1.5	20 - 25	4	8.5 L/min	–	–	[21]
Spruce wood process water	0.2 μm	Ceramic	Tubular	Lab scale	0.98	1.16	80	0.7	4 m/s	80-380	55-90	[21]

[a] PTFE = polytetrafluoroethylene
[b] Indicates value not reported or not available.
[c] Volume Reduction (VR) is the ratio between the volume of the permeate and the initial volume of the feed

3.1.2. Ultrafiltration (UF)

UF is a membrane process that operates on a physical sieving separation process. It is best used to retain macromolecules. The range of molecules sizes that can be retained is from 0.001 μm to 0.1 μm. The UF process requires low trans-membrane pressure to operate, and driving pressure is usually between 1 and 10 bars. Currently, the UF membrane is widely used for various applications because of its high throughput, low operation cost, excellent selectivity, and requires no chemicals additives, thereby minimizing the extent of denaturation and degradation of biological products.

In the pulp and paper industry, UF membrane is an effective method for the treatment of pulp and paper effluent. It removes most of the polluting substances, consisting of high molecular mass compounds, efficiently [22] and recycles valuable materials [13,21,23]. Koivula et al. [24] stated that recovery, purification, concentration, and fractionation of hemicelluloses from wood hydrolysates are most attractive characteristics of UF membrane.

Hemicellulose isolation from process streams of forest industry using UF

membrane has been investigated intensively by many researchers [10,16, 17,20,21,25,26]. Table 3 summarized the results of recent studies. Persson et al. [21] investigated four filtrations and membrane filtration process – namely, drum filtration, MF, UF, and NF – to fractionate the process water from a TMP mill. The permeate from the MF stage was ultrafiltered to concentrate and purify the hemicelluloses. They concluded that UF recovered about 95% of the hemicelluloses. Persson and Jönsson, [25] isolated galactoglucomannan (GGM) from a TMP mill process water using UF membrane. They suggested that, to retain the hemicelluloses, a UF membrane with a molecular weight cut-off between 1 and 10 kDa should be used.

A comparable study was conducted by Al Manasrah et al. [27]. They recovered GGM from wood hydrolysate using regenerated cellulose UF membranes with different molecular weight cut-off values 5 kDa, 10 kDa, and 30 kDa. 5 kDa membrane achieved 88% GGM retention, 63% purity, and 70% recovery rate at a VR of 86%, whereas, cut-off values 10 and 30 kDa have partly separated GGM. However, Persson et al. [16,20] achieved 80% purity when separated hemicelluloses TMP process water using hydrophilic UF membranes. Another study on the recovery of hemicellulose was reported by Jun et al. [28], who extracted hemicellulose from aspen chips before kraft pulping utilizing kraft white liquor by UF. They were able to recover xylan at levels of up to 48 g kg^{-1} of dry chips.

Other studies compared UF with their counterparts. For example, Liu et al. [29] compared the performance of UF and NF for hemicelluloses concentration. The results of this study showed that NF gave much better rejection rates on organic compounds than UF. In the same way, Ajao et al. [30] conducted experiments to screen and select suitable organic membranes among three membranes separation processes – RO, NF, and UF – to concentrate and detoxify Kraft prehydrolysate. The three membranes demonstrated high sugar retentions compared to inhibitor removal. They were, however, not effective for the removal of the phenolic compounds.

During hemicellulose isolation, several studies have proved that a hydrophobic membrane has a higher fouling tendency than a hydrophilic membrane [10,16,20,24], while most of the foulants, exhibited in the pulp and paper effluents, are of phenolic and hydrophobic nature. However, pretreatment methods, such as pH adjustment, ion-exchange resin, use of MF, and activated carbon (AC) adsorption had positive impacts on the filtration capability of UF membrane [24,29]. Accordingly, to avoid fouling, high operational cost, and membrane lifetime shortening, the most suitable membrane and pretreatment method should be applied. Also, from these results, it was demonstrated that effective pretreatment method not only decreases membrane fouling but also enhances the efficiency of membrane cleaning.

Table 3
Summary of UF membrane process for hemicelluloses recovery.

| Raw material | Characteristics of membrane | | | Operating conditions | | | | | | | Performance | | Reference |
	MWCO (kDa)	Material[a]	Configuration	Scale	VR[c]	Hemi conc. (g/L)	pH	Temp. (°C)	TMP (bar)	Cross flow velocity	Flux (L·m−2·h−1)	Hemi rejection (%)	
Spruce wood process water	5/10	PS/PS	Spiral wound	Lab scale	0, 0.70/ 0.97	14/53.5	–[b]	60	3/5	20/21.6 L/min	32 - 170	70–96	[19]
Spruce wood process water	5	PES	Spiral wound	Lab scale	0.99	0.83	–	80	6	25 L/min	10-135	93-99	[21]
Birch hydrolysate and Spruce hydrolysate	5/10	PS/RC	–	Lab scale	0.66	–	7 - 8	60/55	3/5.5	1.5m/s	3 – 55/30 – 179/ 20 - 190	61–76	[24]
Spruce wood process water	10	PVDF	Spiral wound	Lab scale	0.75-0.99	0.5-0.9	–	60	0.5-2.5	20 L/min	20-160	72-94	[25]
Spruce wood process water	1	PVDF	Spiral wound	Lab scale	0-0.95	0.5-0.9	–	60	4-10	10L/min	<105	<90	[25]
Spruce wood process water	5	PS	Spiral wound	Lab scale	–	0.7	–	75	2-6	20 L/min	40-90	<90	[25]
spruce sawdust extract liquor	30/10/5	RC	flat sheet/plate-and-frame	Lab scale	0.86	4.7	–	65	1/3/3.5	2 m/s	~ 107 - 245	88	[27]
aspen wood chips extracted liquor	10	PS	–	Lab scale	–	–	13.98	70 - 90	3.1-3.45		–	–	[28]

[a] RC = regenerated cellulose, PS = polysulfone, PES = polyethersulfone, PVDF = polyvinylidene fluoride.
[b] – indicates value not reported or not available.
[c] Volume Reduction (VR) is the ratio between the volume of the permeate and the initial volume of the feed.

3.1.3. Nanofiltration (NF)

NF has been implemented effectively in a wide range of applications, such as the removal of organic contaminants from the aqueous solutions [31] and partial fractionation and concentration of the sugars [32]. NF has been used widely for a long time, and while its industrial application has been limited to moderate pH for sometimes [33]. More recently, NF membranes for a broad range of pH have become commercially available.

In the forest industry, NF of effluents, from the alkaline extraction stage, has been investigated extensively using both polymeric and ceramic membranes [21,26,33]. Table 4 summarizes the results of recent studies. Schlesinger et al. [33] investigated the performance of five polymeric NF and tight UF membranes during the separation of hemicellulosic materials from process liquors containing 200 g/L sodium hydroxide. The experimental data showed that hemicellulose is almost quantitatively retained at molar masses above 1,000 g/mol. Also, Liu et al. [29] compared the performance of UF and NF membranes during hemicellulose concentration. Their results indicated that NF gave much better rejection rates on organic compounds than UF. Furthermore, Ajao et al. [34] evaluated the performance of six organic NF

membranes with different MWCOs and polymer materials to examine their ability to concentrate hemicellulosic sugars from prehydrolysate solution. 200 Da membrane was superior compared with others membranes' cut-offs and achieved 99% sugars retention. Sjoman et al. [32] carried out another NF study on hemicelluloses recovery to recover d-xylose in the permeate from a hemicelluloses hydrolyzate stream. According to the results, NF showed a promising ability in recovering xylose from hemicellulose hydrolyzate permeate.

Other reported applications include the effects of fouling on the performance of NF membrane separation process. Shen et al. [35] used a combined process, involving activated carbon adsorption, ion exchange resin treatment, and membrane concentration, to concentrate dissolved organic compounds from prehydrolysis liquor (PHL). Similarly, Ahsan et al. [36] also employed activated carbon to reduce the fouling of NF and RO during the recovery and concentration of sugar and acetic acid from PHL. Pretreatment of pulp and paper wastewater, prior to filtration, could efficiently reduce the membrane fouling. Also, membranes with a high contact angle were found to have worse fouling during filtrations of paper mill process water at constant

pressure compared with membranes with a low contact angle. High fouling was also observed in the filtrations made at an acidic pH solution, as compared to a neutral pH. Additionally, the retention of organic substances was significantly better at a neutral pH and the hydrophilicity of the membrane increased with the increase in pH.

NF has been used in a wide range of prehydrolysate solutions. It showed good performance regarding pure permeate product and low energy consumption. However, the fouling phenomenon is one of the main shortcomings facing NF's commercialization. Therefore, treatment of PHL, prior to the NF step, might be an effective way to improve filterability of the NF membrane process. Also, future research should include pilot scale experiments to enable a detailed economic analysis of the membrane system in a biorefinery process as few studies have examined the feasibility of using NF membranes for the filtration of paper mill process water.

Table 4
Summary of NF membrane process for hemicelluloses recovery.

Raw material	Characteristics of membrane			Operating conditions							Performance		Ref.
	MWCO (kDa)	Material	Configuration	Scale	VR^b	Hemi conc. (g/L)	pH	Temp (°C)	TMP (bar)	Cross flow velocity	Flux (L·m^{-2}·h^{-1})	Hemi rejection (%)	
Spruce wood process water	1	–^a	Spiral wound	Lab scale	0.5-0.76	0.07	–	50	20	18 L/min	63/27	100	[21]
Hardwood black liquor (permeate of UF)	1	–	Tubular	Lab scale	0.7	2.5	–	60	25	4 m/s	110	–	[26]
Aspen/ Maple wood prehydrolysate	0.2	Polyamide/ Cellulose acetate blend	flat sheet/plate-and-frame	Lab scale	–	–	–	40	21/35	0.45/0.66 m/s	12	99	[30]
Hemicellulose hydrolysates	0.15/0.3	Polysulfone	–	Lab scale	–	–	–	40/50 /60	20/25/ 30/35	–	36.4 – 180.6	78-82/ 86-88	[32]
Aspen/ Maple wood prehydrolysate	0.15/3.5	polyamide	flat sheet/plate-and-frame	Lab scale	–	–	2.8/3. 5	30/40	5.5/21	0.4/0.5 m/s	14	84 -92	[34]
Maple, Poplar and Birch prehydrolysis liquor	0.15/0.3	polyamide	–	Lab scale	0.5	31/196	4.3	–	34.5	–	–	74/99	[36]
Maple, Poplar and Birch prehydrolysis liquor	–	polysulfone	–	Lab scale	0.3	172	–	–	34.5	–	190 – 31.6	–	[37]

^a – indicates value not reported or not available.
^b Volume Reduction (VR) is the ratio between the volume of the permeate and the initial volume of the feed.

3.1.4. Diafiltration (DF)

DF is a technique that selectively utilizes permeable (porous) materials to separate the components of solutions and suspensions based on their molecular size. Recent technological advances in membrane technologies and system design have created a new opportunity for efficient DF of various organic polymers and inorganic chemicals. However, the success of a DF for performing fractionation and concentration processes is largely associated with the selection of an appropriate membrane.

In general, DF is commonly used as downstream processing steps for product concentration and purification. For example, Andersson et al. [17] used DF to recover hemicelluloses from process water of a TMP mill using spruce. They found that the purity of hemicellulose was increased from 57 to 77% after DF when they compared the UF retentate before and after DF. Also, González-Muñoz et al. [38] assessed the performance of DF as a method for purification of oligosaccharides obtained by auto-hydrolysis of Pinus pinaster wood. Continuous DF has been observed to result in an increased weight percent of substituted oligosaccharides, from 79.2% up to 94.7%. Further, the selective removal of monosaccharides rose from 4.3 up to 17.8 as a substituted oligosaccharides to monosaccharides ratio.

Al Manasrah et al. [27] also reported that DF can achieve a partial removal of xylan and a complete removal of monosaccharides from the GGM rich concentrate. González-Muñoz et al. [39] studied the fractionation of extracted hemicellulosic saccharides from Pinus pinaster wood by a multistep membrane process. The solution from the hydrothermal process was subjected to consecutive steps of DF using membranes of 0.3, 1, 3, 5, and 10 kDa. This work resulted in streams containing poly- and oligosaccharides (POHS) of different molecular mass distribution with decreased contents of monosaccharides.

The DF approach is suitable for obtaining a product with a high purity, depending on the molecules of interest and process conditions. Thus, selecting the most compatible membrane processes for overall effectiveness is important.

3.2. Lignin recovery

Lignin is a complex natural amorphous polymer. It acts as the essential glue that gives plants their structural integrity and holds the fibers of polysaccharide together. The structure of lignin changes according to the biomass source and the isolation technique. In general, softwoods contain more lignin (25–35%) than hardwoods (20–25%) [40]. Lignin consists of three hydroxycinnamoyl alcohol monomers (C9), differing in their degree of methoxylation: p-coumaryl, coniferyl, and sinapyl alcohols [41]. The molecular weight of kraft lignin extracted from the black liquor range from 1000–2000 Da [8].

In the forest products industry, lignin is usually isolated from other components of wood chips (delignification) through the application of different extraction methods. These extraction methods result in various types of lignin with different characteristics (spent liquor), as showed in Figure 3. This pulping liquor cannot be utilized in pulp production because of its inferior quality, but is typically concentrated and then fired in a recovery boiler for the generation of steam and production of inorganic chemicals [42].

Compared to hemicellulose, lignin also offers several opportunities for IFBR to enhance their revenue streams and operation because it contributes as much as 30% of the weight and 40% of the energy content of lignocellulosic biomass. Besides being burned to produce energy in recovery boilers [43], lignin can also be used for different applications. For example, Kraft lignins have been utilized to produce binders, resins, carriers for fertilizers and pesticides, thermoplastic polymers, asphalt, lead storage batteries, and activated carbon [44]. Also, they can be used as a chelating agent for the removal of heavy metals from industrial wastewater, or as a dispersant in cement and gypsum blends [5]. Some examples of lignin applications in industry are shown in Figure 3.

However, the exploitation of these lignins as an intermediate chemical feedstock is difficult because of their complicated structure. They require depolymerization and refining to appropriate forms that can then serve as the building blocks for chemical syntheses [31]. Several possible techniques for the removal of lignin from the industrial residue stream have been tested. The most common applied methods for the extraction of lignin are precipitation and filtration [45]. However, the differential precipitation of the liquor gradually decreases the pH of the solution, which is a clear disadvantage for this method. Also, colloids formation during the precipitation process complicates subsequent filtration and separation steps, resulting in a relatively low purity of the lignin obtained. As effective separation technologies, membrane filtration can be tailored to the required degree of purification
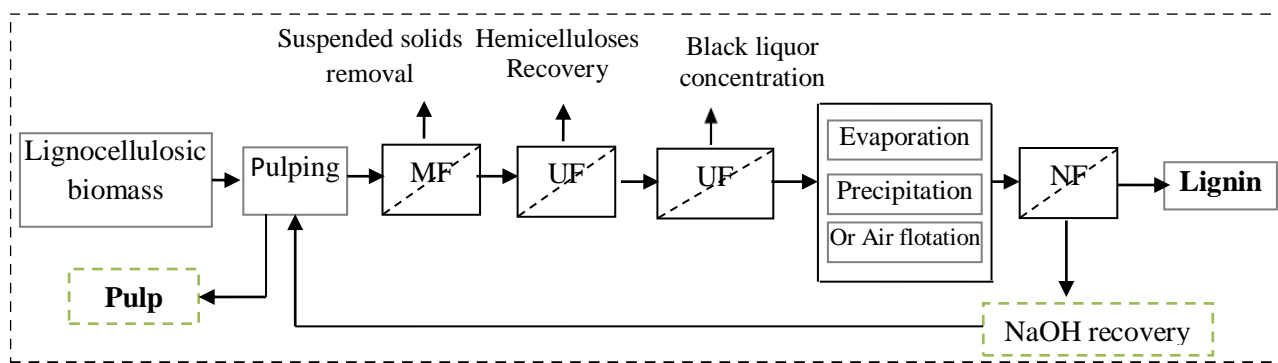
compared to traditional separation methods.

Fig. 3. Sources and types of lignins with some of their applications in industry.

Membrane processes have been applied since the late sixties, but most of the applications have focused on the treatment of bleach plant effluent and fractionation of spent sulfite liquor [26]. More recently, much effort has been spent, and many in-depth investigations have been carried out, to reduce the organic load to the recovery boiler. Consequently, a wide range of pressure-driven liquid phase membrane separation processes, including MF, UF, NF, RO, or a combination of them, has been studied. UF and NF membranes were the most common types among them. This can be attributed to the size of the lignin molecules. UF and NF have been applied at both lab- and pilot-scale studies.

Many studies investigated the applications of ceramic UF membranes to isolate lignin from cooking liquors [8,26,46-48]. Table 5 summarizes the results of recent studies. Wallberg and Jonsson [46] and Toledano et al. [47] investigated the performance of UF membranes for lignin isolation from black liquor (BL) solutions. It was found that UF membranes were an effective method to fractionate lignin. However, Holmqvist et al. [48] found that membrane flux for treating hardwood cooking liquor was much higher, and the retention was much lower compared to that for treating softwood liquor.

Likewise, some studies examined the use of polymeric UF membranes for lignin recovery [8,26]. The results of these studies indicated that the extraction of lignin from kraft cooking liquor, taken directly from a continuous digester without adjustment of pH and temperature, is possible. On the other hand, NF membranes were also applied to separate the dissolved lignin from pulp and paper mills BL. As shown in Table 5, both ceramic and polymeric NF membranes were studied. Arkell et al. [45] reported that polymeric NF membranes with a MWCO of 1 kDa had the best performance when compared to the other membranes.

Alternatively, several studies investigated hybrid membrane systems that apply combinations of UF with NF to treat BLs. Sjodahl et al. [49] and Dafinov et al. [50] reported that NF and UF were technically feasible ways to remove the organic materials from kraft pulping BLs and could achieve a higher flux in a batch process. Furthermore, Jonsson et al. [26] studied the performance of hybrid UF/NF and evaporation/UF processes for lignin extraction from BLs and cooking liquor. UF/NF process achieved a higher product concentration and purity compared to evaporation/UF process. Most of these studies have reported that there are certain ranges of the molecular masses that have a negative impact on filtration capacity. It is recommended that, to decrease membrane fouling, the focus should be not only on the highest removal of lignin and hemicellulose, but also on the sizes of hemicelluloses and lignin molecules.

Polymeric and Ceramic membranes for lignin recovery and purification

were the focus of the majority of the reported studies. Ceramic membranes have been shown to possess better performance over polymeric membranes [45]. Compared to polymeric membranes, ceramic membranes can withstand BLs without pH and temperature adjustment because of their high thermal and chemical stability. Moreover, ceramic membranes are slower to foul and can be recovered utilizing more extreme membrane performance recovery systems that polymeric membranes are not able to handle. Although the ceramic membranes exhibit a higher capital cost compared to polymeric membranes, they are capable of achieving a high productivity as a result of their inherent hydrophilicity, which leads to reduced organic fouling.

The performance of membrane technologies also depends on the application of appropriate module design and configurations. There are two main types of modules used in BL treatment: plate and frame module and tubular module. The plate and frame module is the simplest configuration, comprising two end plates, a flat sheet membrane, and spacers; whereas in the tubular module configuration, the membrane is often cast on the inside of a tubular support, the feed will be pumped through the tube, and the permeate will be collected on the outer surface of the tube into a shell which could hold one or many tubes packed in a bundle.

The feasibility of membrane technology for lignin recovery from BL has been widely studied. Jonsson et al. [26] studied UF and a hybrid UF/NF process of cooking liquor and BL. The production cost of UF of extracted BL and the hybrid UF/NF process was € 33 per ton of lignin produced. Holmqvist et al. [48] conducted a cost estimate of lignin fuel extraction from BL. The cost was approximately € 20 per MWh of the calorific value of the lignin fuel. Also, Jönsson and Wallberg [51] estimated recovery costs of hardwood lignin by a ceramic UF membrane with a MWCO of 15 kDa from two process streams in a Kraft pulp mill processing 200 m³/h pulping liquor. Lignin was concentrated to 100 g/L and the estimated cost was about € 60 per ton of lignin. This cost could be further reduced if high membrane fluxes could be achieved.

Both UF and NF showed a high performance in the removal of hemicelluloses and lignin from BLs. However, some issues need further investigation. Since each molecular weight of the lignin has designated applications, the remaining question is whether the quality of purified lignin fulfills the demands for high-value-added products. Also, to date, most of the studies have been conducted on a lab-scale, with a few pilot- and full-scale applications. Long-term feasibility studies at pilot-scale and full-scale applications are needed to offer a starting point for further optimization of separation processes in lignin recovery. Figure 4 shows a proposed technical path for hemicelluloses and lignin recovery and purification from pulp and paper effluents.

Fig. 4. Separation and recovery of hemicelluloses and lignins from product streams.

Table 5
Summary of UF and NF membrane processes for lignin recovery.

| Raw material | Classification | Characteristics of membrane | | | Operating conditions | | | | | | | Performance | | Ref. |
		MWCO (kDa)	Material	Configuration	Scale	VR[b]	Lignin conc. (g/L)	pH	Temp (°C)	TMP (bar)	Cross flow velocity	Flux (L·m⁻²·h⁻¹)	Lignin Rejection (%)	
Hardwood kraft black liquor (permeate of UF)	NF	1	–[a]	Tubular	Lab	0.7	54	–	60	25	4 m/s	110	80	[26]
Softwood kraft black liquor	UF	20	Al₂O₃/TiO₂	Tubular	–	-	57.6	13	90	2	5 m/s	–	–	[45]
Softwood kraft black liquor	NF	1	TiO₂	Tubular	–	0.85	252	13	90	2 - 20	4-2 m/s	159	~78	[45]
Softwood kraft black liquor	NF	0.2/0.6/ 1	–	Tubular	–	0.70	282	13	70	5 - 35	4-2 m/s	81	~90	[45]
Hardwood black liquor	NF	1	ZrO₂	–	Lab	–	48.8	–	25	2-6	1.5m/s	1-5	67.4	[49]
Black liquor	NF	1	TiO₂	Tubular	Lab	–	–	12	30	3-7	2.1m/s	12-22	–	[50]
Birch wood chips extract	UF	5	Polysulphone	flat sheet	Lab	0.66	2.2 – 4.4	–	60	5.5	1.5 m/s	15 - 120	–	[52]
Woody spent liquor	NF/UF	1/3	TiO₂ and ZrO₂	flat sheet/ Tubular	Lab	–	16-24	–	25	5	2 m/s	30-139	75-94	[53]
Spruce wood pressurized hot water extract	UF	5/1	TiO₂ and ZrO₃	–	Pilot	–	–	–	40	2.6/2. 2	1.7m/s	–	–	[54]
Olive tree clippings Black liquor	UF	300/150/ 15/5	Ceramic	Tubular	Lab	–	–	–	–	–	–	–	–	[55]
Spent sulphite liquors (SSL)	UF	1/5/15	Ceramic TiO₂	–	Pilot	0.78 /0.4 5/ 0.15	44.25 / 39.57/ 40.67	3.3	20	1.8 - 2	8 m/s	55.45/ 5.77/ 6.00	45.67/ 65.38/ 41.69	[56]

[a] – indicates value not reported or not available.
[b] Volume Reduction (VR) is the ratio between the volume of the permeate and the initial volume of the feed

3.3. Wood extractives recovery

Extractives substances can be defined as lipophilic compounds that are soluble in various neutral organic solvents [57]. These compounds include simple sugars, turpentine, resin acids, fatty acids, waxes, and complex phenolic compounds, as shown in Table 6. Composition and content of these extractives are quite variable depending on the plant species [57]. Wood extractives are valuable compounds, which could be utilized as preservatives in food or raw materials for pharmaceutical and chemical industry [58]. Another new application for wood extractives is used as biocides. However, during the pulping processing, the majority of the wood extractives would be dissolved in the BL and either burnt to produce energy or discharged in wastewater.

Different methods have been investigated to separate wood extractives from BL. One of the possible alternatives for separation of wood extractives

is membrane separation processes [57]. Membrane-based techniques are known to offer a high level of purification coupled with a relatively low level of energy consumption. However, only a few studies were conducted for the use of the membrane technology in the removal of wood extractives, because membrane fouling hinders the wide adoption of this technology.

Leiviska et al. [60] characterized wastewater (influent and effluent) from integrated kraft pulp and paper mill by MF (8, 3, 0.45 and 0.22 μm) and UF (100, 50, 30 and 3 kDa) membranes, based on different size fractions. It was found that the sieved influent contained about 14.3 mg/L of wood extractives, of which 12.8 mg/L were resin and fatty acids and 1.5 mg/L sterols. The sieved effluent contained 1.7 mg/L of wood extractives, of which 1.45 mg/L were resin and fatty acids and 0.26 mg/L sterols. Leiviska et al. [60] also reported that MF with a large pore size (8 μm) was able to remove 30–50% of wood extractives.

Table 6
Classification of the common wood extractives (Compiled from [57, 59]).

Types	Components	Types	Components
Lipid extractive components	Aliphatics and alicyclic: ▪ Fatty acids	**Carbohydrates**	▪ Arabinose
	▪ Fats (fatty acid esters of glycerol)		▪ Galactose
	▪ Fatty alcohols		▪ Glucose
	▪ Waxes (esters of other alcohols)		▪ Xylose
	▪ Suberin (polyester)		▪ Raffinose
	▪ Terpenoids: ▪ Monoterpenes (turpentine)		▪ Starch
	▪ Diterpenes		▪ Pectic material
	▪ Triterpenes ▪ (including resin acids and steroids)		
Phenolic extractive components	▪ Simple Phenolics	**Other compounds**	▪ Cyclitols
	▪ Stilbenes		▪ Tropolones
	▪ Flavonoids		▪ Amino acids
	▪ Isoflavones		▪ Alkaloids
	▪ Condensed tannins		▪ Coumarins
	▪ Hydrolyzable tannins		▪ Quinones
	▪ Lignans		▪ protein

In another study, Puro et al. [58] achieved 90% extractives retention from two chemo thermomechanical (CTMP) pulp mill process waters using one regenerated cellulose (RC) UF membrane and two polyethersulphones (PES) UF membranes. Kilulya et al. [61] revealed that the utilization of an ionic liquid, in the extraction of lipophilic wood extractives, coupled with liquid membrane extraction systems, offered a possible separation method. Pinto [62] tested different NF membranes and UF membranes with a lower molecular weight cut-off for the concentration of polyphenolic compounds (gallic, tannic acids and maltose) and carbohydrate from an ethanolic extract of *Eucalyptus globulus* bark. All the tested membranes exhibited selective retention of polyphenolic compounds.

4. Black liquor concentration

Kraft pulp mills have utilized BLs as an energy source since the 1930s. Weak black liquor (WBL) is typically 15% dry solids and 85% water. It is usually concentrated to 65 - 80% by multi-effect evaporators and burned in a recovery boiler for the energy production. This technique consumes much energy during the evaporation of the water in the large steam-heated multiple-effect evaporators. Membrane filtration has been proposed as possible techniques to reduce this amount of water prior to evaporation. Pre-concentration of BL streams by membrane processes reduces power consumption rate in the evaporation stages.

However, unlike conventional membrane separation processes for water purification/desalination applications – the membranes required for concentrating BL must withstand the high pH (>12), high temperature (80-90°C), and different fouling species in BL. Technically, ceramic membranes appear to be an appropriate choice for this task. Liu et al. [63] studied BL concentration conditions using UF ceramic membrane technology. They concluded that BL could be concentrated up to 4-6 times by UF membrane. However, ceramic membranes are characterized by higher capital costs. In contrast, polymeric membranes are available at reasonable prices, but without pretreatment, are not withstand the harsh natures of the BL. To overcome these problem, the U.S. Department of Energy developed sacrificial protective coating materials that can be regenerated in-situ to enable high-performance membranes. They believe that this layer will prevent foulants in the WBL from adhering to the membranes, while also giving protection from BL harsh conditions [64]. Also, New Logic International developed "Vibratory Shear Enhanced Process" (VSEP™) for the treatment of BL streams without causing the fouling problems exhibited by conventional membrane systems. VSEP can be used with polymer MC, UF, NF and RO membranes [65]. This technology applies vibration technique to reduce fouling, and it has been studied in the pulp and paper industry for applications in black liquor concentration, paper mill effluent, paper coating effluent, whitewater treatment, and paperboard mill effluent [65].

5. Products recovery from Kraft evaporator condensates

5.1. Methanol and TRS recovery

Kraft pulping condensates are rich in methanol and totally reduced sulfur (TRS) compounds. Kraft pulp mills have the potential to produce around 15 kg of bio-methanol per ton of pulp from their evaporator condensates, depending on the type of wood and the pulping conditions [66]. During the BL evaporation to an adequate level of dry solids suitable for the combustion in the recovery boiler or a dedicated incinerator, the liquor releases volatile materials, such as sulfur compounds, terpenes, and methanol. These volatile compounds must be removed, either because they have economic value or because they cause pollution problems if discharged directly to the environment. For instance, recovery of methanol would become beneficial by reducing the cost of purchasing methanol that pulp mills use in the production of chlorine dioxide or as a reducing agent in the manufacture of bleach. Furthermore, TRS compounds can be utilized effectively as a reducing agent during the manufacturing of chlorine dioxide as well [67,68].

Many technologies have been suggested, evaluated, and applied for methanol and TRS recovery. These methods are based either on desorption or decomposition and are associated with high capital and operating costs. Currently, the majority of kraft pulp mills are using the air stripping technique to separate TRS compounds or the steam stripping method to isolate both methanol and TRS from evaporator condensates. Air stripping needs tall and costly columns and may cause operational problems in the form of foaming, flooding, or channeling. Steam stripping is characterized by high capital and operating costs because of living steam utilization in most cases. Among the advanced treatment processes, membrane technology has been also tested as shown below. Table 7 summarizes the patent information of membrane technology for methanol and TRS recovery. Jemaa et al. [67], Blume and Baker [69], and Savage and Piroozmand [70] developed methods and apparatuses for the treatment of kraft pulp mills' condensate for TRS and methanol removal using membrane technology.

At pilot and mill demonstration trials, using a hollow fiber contactor (HFC) technology, Jemaa et al. [67] efficiently removed TRS compounds with as high as a 99% removal efficiency and with negligible methanol losses from kraft and sulfite mill evaporator condensates. Methanol was also recovered from kraft mill condensates, but at a lower rate compared with TRS removal. The authors [67] stated that placing a hollow fiber contactor ahead of a steam stripper in the pulping mill may produce relatively pure methanol suitable for different purposes. Blume and Baker [69] used pervaporation composite membranes coated with silicone rubber to remove methanol from black liquor evaporator condensate. In this experiment methanol concentration enriched up to 15 times and a permeate flux of about 0.4 L/m²·h was achieved. Peter and Farshad [70] treated a clean evaporator condensate by RO membrane. They concluded that the treatment of clean evaporator condensate by RO offers a simple, economical, and efficient treatment process over biological treatment and steam stripping techniques.

Table 7
Characteristics of membranes applied for methanol and TRS compounds recovery from black liquor condensate.

Membrane	US Pat. No. 8,349,130 B2 [67]	US Pat. No. 4,952,751 [68]	US Pat. No. 6,110,376 [70]
Membrane type	Hollow fiber contactors	Pervaporation (PV)	Reverse osmosis (RO)
Driving force	Vapor pressure difference	Partial vapor Pressure 0.27 bar	Pressure 27.57 bar
Thickness (μm)	–	1 micron	5 micron
Module configuration	hollow fiber	spiral-wound	Spiral-wound
Membrane material	polypropylene	Silicone rubber	polyamide
Separation principle	Distribution coefficient	Solution-diffusion	Solution-diffusion

5.2. Turpentine removal

In the kraft process, turpentine is an important by-product which can be recovered from evaporator condensate as a saleable product or to burn as a fuel. It is also an inhibitor compound that can impede biofuel processing efficiency [71]. Many processes are known for the removal of terpenes, steam or air stripping is the technology commonly used to treat this condensate. Among these methods, membrane filtration process was also applied for treating kraft evaporator condensate. Minami et al. [71] studied the thermophilic anaerobic digestion of evaporator condensate obtained from a Kraft pulp mill production process. They examined a microfiltration (MF) membrane made of Teflon for terpene oils removal. Teflon membrane was selected because of its resistibility. The MF membrane was an effective method for the removal of terpene oil and the authors achieved about 90% removal of these oily substances. Alsuliman [72] examined the performance of Membrane bioreactors in the treatment of real kraft pulp mill evaporator condensate under different operational conditions (high temperature, short solids retention time, and low hydraulic retention time) and turpentine shock loads. The results of this study indicated that the biological removal of the main contaminants in evaporator condensate was feasible. However, turpentine shock loads exerted a significant impact on the overall removal kinetics of the main contaminants in evaporator condensate.

6. Tall oil recovery

In the pulping process, particularly kraft pulping of pine, spruce, and birch trees, tall oil soap is a major by-product. When the BL is concentrated and left to settle, the top layer of it is known as "tall oil soap." A typical composition of the tall oil is about 49% resin acids, 32% fatty acids, and 19% unsaponifiable [73]. Tall oil is a valuable by-product and can be recovered from spent BL and sold as a feedstock for special chemicals production [73]. Also, it can be toxic if discharged into the biological wastewater treatment system.

Therefore, the recovery of the tall oil is not only necessary to increase mill revenue streams, but also to decrease the toxicity of pulp mill effluents. A commonly used method for recovering the tall oil from concentrated liquor is flotation. However, through this process, a significant amount of tall oil may be lost as waste or, in best cases, burned for its heat value and not recovered for its much higher tall oil value. Membrane technology may contribute to the improvement of this method and reduce those losses. Under this context, Fremont [74] developed a process for enhancing the recovery of tall oil soap from BL. This process consists of two zones. In the first zone, the tall oil soap is collected on the surface of the BL and is skimmed from the tank. In the second zone, the remaining BL phase is subjected to a UF unit (Abcor HFJ and HFD membranes) with a MWCO of about 10kDa to concentrate the residual tall oil soap. This concentrate is recycled to the skim tank (first zone) to allow the tall oil soap to agglomerate. The tall oil soap is skimmed off while the permeate is disposed of. The author concluded that a continuous UF of the skim tank effluents could recover up to 55% more tall oil per ton of pine pulp produced.

7. Inorganic and organic compounds recovery

7.1. Inorganic compounds recovery

BL from the pulp and paper mills, referred to as "spent cooking liquor," contains different compounds of degradation products of lignin and wood carbohydrates and numerous high-value inorganic chemicals which are used during the pulping process. These inorganic compounds can be recovered, and the active cooking chemicals (white liquor) can be reused in the cooking cycle. Many methods were investigated for the separation of inorganic compounds from BL. Application of membrane processes is one such option which can recover inorganic chemicals and minimize the load on multi-stages evaporator system with no significant loss of inorganic compounds.

Mansour et al. [75] studied the separation of alkali from silica-rich BL with cellophane membrane dialysis. They concluded that less concentration and higher volume of the BL increase the efficiency of the dialysis. Also, a higher dialysis efficiency could be obtained at a higher temperature and shorter time. Moreover, the vibration of the BL during the dialysis process increased the effect of the surface area and reduced membrane fouling. In another study, the recovery of inorganic compounds, from the discharge water of the pulp and paper industry, was investigated by Mänttäri et al. [23]. In this study, the instantaneous chloride retention using a NF membrane varied between 26% and 10%. However, the retention of inorganic carbon was 60% to 70%. From these studies, it can be concluded that the membrane technology could be used to recover the alkaline chemicals from the process wastewater of pulp and paper mills.

7.2. Organic compounds recovery

7.2.1. Organic acids recovery

Spent Liquors from the kraft pulping process represent an unexploited source of various valuable organic compounds. The recovery of these organic compounds has rarely been studied for the reason that separating them from BL is challenging due to their low concentrations and the presence of inorganic compounds. Membrane technology has been introduced as a new approach for the separation and purification of these organic compounds. Figure 5 shows a proposed process for carboxylic acids production from BL.

Niemi et al. [76] studied the separation and fractionation of organic and inorganic compounds by membrane separation and crystallization under different operating conditions. Their outcomes demonstrated that a combination of membrane separation and crystallization is a productive strategy for recovering and purifying the valuable organic compounds in the BL. A similar study was carried out by Mänttäri et al. [77]. They studied the recovery and purification of organic acids from BL in two separation steps: UF for lignin removal from organic acids and NF for the organic acids purification after acidification. Their results indicated that UF, with a 1 kDa membrane, removed 75% of the lignin and that the total acid concentration in the permeate stream was 1.4 fold compared to the original BL. The purity of the organic acid from NF, after the acidification and cooling crystallization stages, was about 80% at the highest. Because of the Donnan exclusion and electro-neutrality principles, it was acid molecules permeated the membrane faster than water molecules. Also, Hellstén et al. [78] investigated the recovery and purification of hydroxyl acids from soda BL without neutralization, using UF, size-exclusion chromatography, ion-exchange, adsorption, and evaporation. They reported that a reduction of 99% in lignin content of the organic acid fraction was achieved and mixtures of hydroxyl acids at a high purity were produced. The typical purities of hydroxyl acids separated from softwood and hardwood black liquors were 81% and 63% on the mass basis, respectively.

7.2.2. Xylitol recovery

Xylitol is a natural sugar found in most plant materials. Currently, it can be commercially produced by either chemical reduction or microbial fermentation of xylose present in the spent sulfite liquor (SSL) and pre-hydrolysis liquor (PHL). Xylitol production is important because of its applicability as a diabetic sweetener (insulin is not needed to regulate its metabolism) [79]. According to Rafiqul and Mimi [80], the xylitol market is rising fast and is estimated to reach over US$ 340 million/year and is priced at US$ 6–7 per kg. However, xylitol recovery and purification is still the most challenge step in the xylitol production process.

Xylitol can be separated and purified by chromatographic methods because of the low product concentration. However, it is a very expensive method. An alternative membrane separation approach was proposed because

of the potential energy savings and higher purity. Affleck [81] found that a 10 kDa molecular weight cutoff of polysulfone membrane is the most efficient membrane among 11 membranes tested for the separation and recovery of xylitol from a fermentation broth. Reportedly, the membrane allowed 82.2 to 90.3% of xylitol in the fermentation broth to pass through the membrane while retaining 49.2 to 53.6% of impurities such as peptides and oligopeptides. The collected permeate from the 10 kDa membrane was crystallized and then analyzed by HPLC for xylitol and impurities. The results showed a high xylitol purity up to 90.3%.
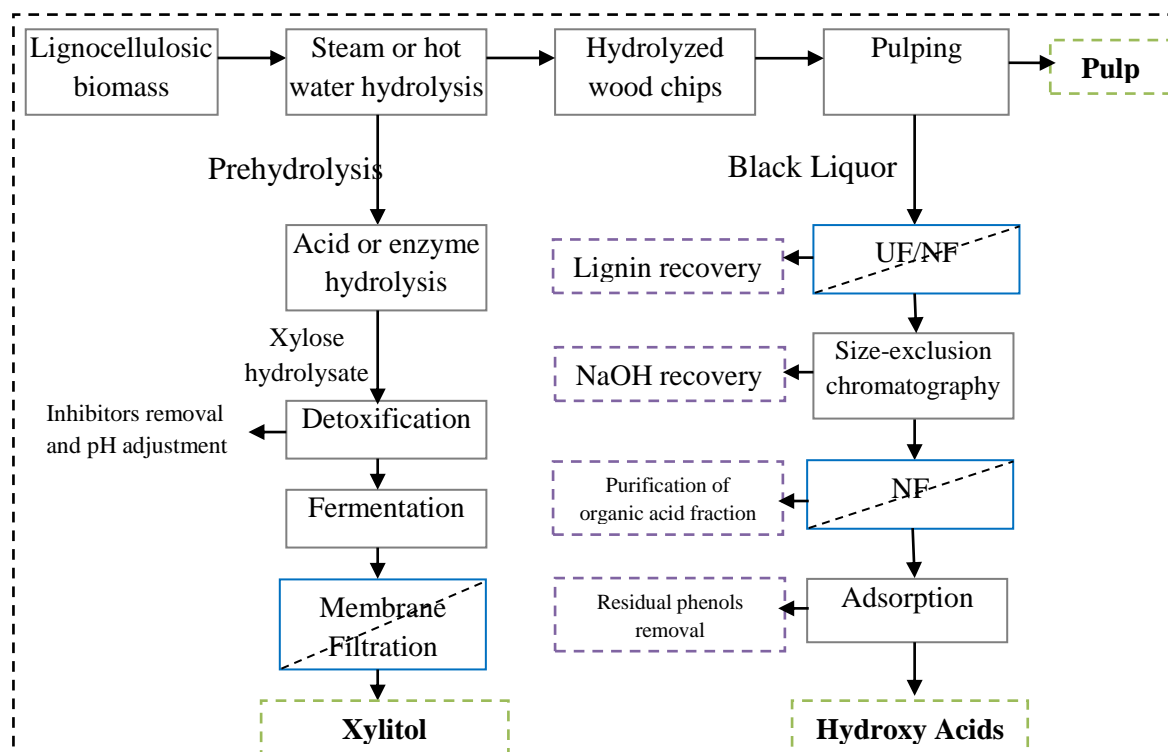
Fig. 5. Proposed process for xylitol production from prehydrolysis liquor and carboxylic acids production from black liquor.

8. Second generation biofuel production

Recently, biofuel production from lignocellulosic biomass has received increased interest because of environmental pollution issues, depletion of global petroleum resources, and continuing price increase of crude oil. Production of the second-generation biofuels, based on forest biomass, could be beneficial to IFBR since it would add value to IFBR revenue streams as by-products. This review addresses the applications of membrane technologies for bioethanol and biobutanol production and recovery.

8.1. Bioethanol production and recovery

8.1.1. Fermentation inhibitors removal
The production of lignocellulosic-based biofuels is a challenging process because of the complicated nature of the raw materials. For this reason, harsh treatments, e.g., with chemicals and/or high temperatures, are needed to degrade lignocellulose to fermentable sugars. During the hydrolysis of these materials, a large group of compounds that are inhibitory to the fermentable microorganisms is formed or released [5]. In general, there are three main common types of fermentation inhibitors produced during biomass conversion: (1) weak acids (acetic, formic and levulinic acid), (2) furans (furfural and hydroxymethylfurfural (HMF)) (3) phenolic compounds (vanillin, phenol, and p-hydroxybenzoic acid). The types and concentrations of these inhibitors are determined by the pretreatment techniques, fermented feedstocks, and biomass sources [82].

The literature has applied and discussed a variety of detoxification methods for overcoming the inhibitors problems, including extraction, treatment with lime, zeolites adsorption, or using activated carbon [83,84]. However, most of these methods are accompanied by some disadvantages, such as high processing costs, the creation of additional waste, and/or losing sugars [83,84]. Thus, the development of effective pretreatment strategies to isolate these inhibitors from the forest biomass hydrolyzates is needed. In most cases, pretreatment optimization is the best way to prevent the formation of many of these compounds. Membrane separation technology seems a

capable candidate for this application. Accordingly, UF, NF, and RO processes have been examined for tackling these problems.

Han et al. [85] used adsorptive membranes and anion exchange resin for acetic acid removal from wood hydrolyzate. They concluded that membranes exhibited higher capacity and separation than ion exchange resins. Liu et al. [86] reported that acetic acid, methanol, furfural, hydroxymethylfurfural, and formic acid could preferentially be removed to the permeates side if a NF membrane is used. Also, Choi et al. [87] and Weng et al. [88] tested NF membranes at different pH levels for acetic acid removal. They found that pH affects the separation performance of acetic acid and that the rejection rate of acetic acid is increased with increasing pH.

Qi et al. [89] investigated the removal of furfural by NF membranes. Furfural rejection rate decreased when the temperature and pH increased. However, permeation flux was increased for all membranes. Afonso [90] assessed NF and RO for the concentration of acetic acid and furfural from the condensate of eucalyptus spent sulfite liquor. They reported that NF and RO demonstrated high retentions for both acetic acid and furfural. However, Zhou et al. [91] compared the NF and RO membranes' performance for acetic acid separation under different operating conditions. The experimental results proved that RO membranes are much more efficient than NF membranes for retaining monosaccharides and decreasing the concentration of acetic acid. Different results were reported by Gautam and Menkhaus [92] when testing the efficiency of RO and NF for fermentation inhibitors removal. In this study, NF showed very promising results: sugars concentrated to more than 2.5 fold in the retentate and simultaneously separated more than 50% of the inhibitory components into permeate. Furthermore, Ajao et al. [30] studied the feasibility of NF membrane for a simultaneous concentration of acetic acid and sugars in the prehydrolysate solution from a Kraft dissolving pulp mill. The results of this study indicated that an NF membrane, with a MWCO of 200 Da, is capable of achieving about 99% sugar retention.

NF and RO membranes exhibited excellent efficiency in the removal of fermentation inhibitors and sugars concentration. However, the efficiency markedly depends on the operating conditions, such as feed concentration, feed pH, solute concentration, pressure, and temperature.

8.1.2. Enzyme recovery

Enzymes are used for hydrolysis during the process of converting lignocellulosic materials to bioethanol or biobutanol. Enzymes are expensive and represent approximately 20% of the total ethanol production cost. Much of the enzymes used remain active after hydrolysis; their recycling could be considerably beneficial to IFBR for decreasing its operating expenses. Figure 6 demonstrates one of the possible ways to separate and recover cellulase enzyme.

Enzyme recovery during ethanol production process can be achieved by the use of sedimentation process, followed by MF or UF. In the sedimentation step, the larger particles are removed to avoid the blocking of the tubing or membrane filter in the later filtration step [93]. In this step, suspended solids larger than 0.2 µm in diameter are removed by MF, but the cellulase enzyme (mol wt. = 60~90 kDa) passes through to the permeate side. Then, in the UF step, these enzymes are retained by the membrane while the water, sugars, ethanol, and other small molecules pass through the membrane for further processing. UF, with the pore size between 0.001 and 0.1 µm, is considered to be the most appropriate membrane for enzyme fractionation [94]. The retained cellulase may finally be reused for further hydrolysis. The proposed separation strategy may be used either after simultaneous saccharification and fermentation or between the hydrolysis and fermentation steps. For the latter, lignocellulosic particles and cellulase enzyme would be retained in the hydrolysis reactor while sugars pass through the membranes to the fermentation vessel.
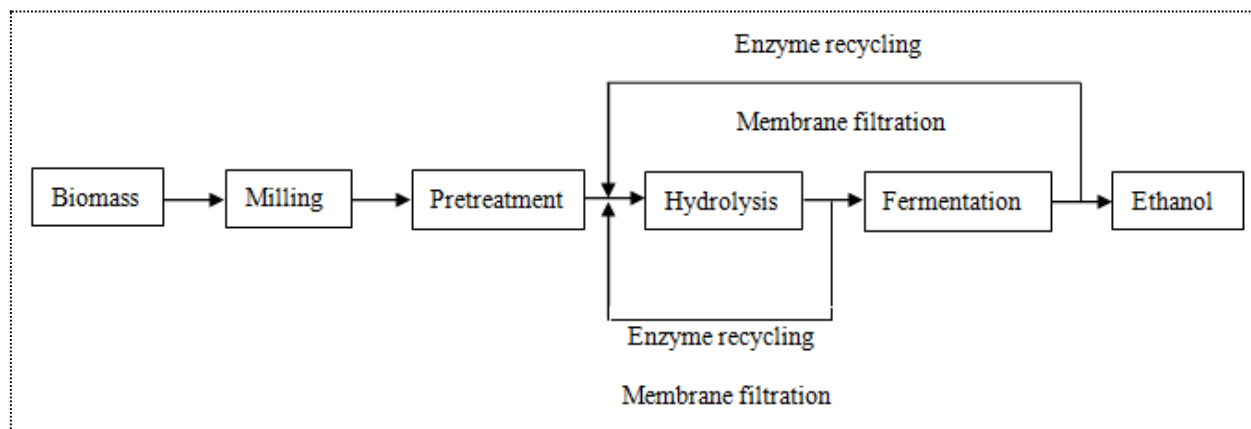
Fig. 6. Enzyme recovery during ethanol production process.

In literature, several studies investigated the technologies suitable for the separation and reuse of cellulase enzymes during the enzymatic saccharification of pretreated biomass. Knutsen and Davis [95] reported that, when they used UF with 50 kDa of polyethersulfone, the most suited enzyme separation method was a filter with relatively large pores in the range of 20-25 µm. This separation process retained residual solids while passed reaction products, such as glucose and cellobiose, formed a sugar stream for many end applications. Their results also indicated that a simple solid/liquid separation, using a large-pore vacuum filtration unit, is a viable method for recovering significant quantities of active cellulase enzymes bound to the solid substrate and that these enzymes may be reused by simply mixing a new substrate with the spent hydrolysate. Szélpál et al. [96] conducted a laboratory study with the hydrolysate made from sugar-beet pulp in a 2 L fermentation unit at 26 °C and pH 4 and with two types of membranes (polyethersulfone membrane with a cut-off value of 5 kDa and thin-film membrane with a cut-off of 4 kDa). Their results showed that 2% of used cellobiase enzymes could be recovered by membrane separation under appropriate operating conditions. In another study, Abels et al. [97] studied glucose recovery from enzymatic hydrolysis of ionic liquid pretreated cellulose using UF, NF, and electrodialysis (ED). UF process was used to remove residual particulates and enzymes which existed in the hydrolysate after enzymatic conversion of cellulose to glucose. They achieved a permeate yield of 60%. By further filtration, the enzymes could be recovered for reusing in the following enzymatic hydrolysis.

8.1.3. Membrane bioreactor (MBR) for bioethanol production

Membrane bioreactors (MBRs) have been widely used in wastewater treatment to achieve superior quality water. Recently, they have also been applied in biorefining and bioenergy production [98]. The most commonly used techniques of fermentation systems for fuel bioethanol production are batch, continuous, fed-batch, and semi-continuous processes. However, the conventional batch fermentation processes have low volumetric productivities (2–2.5 g ethanol/L/h) and are time-consuming because of the low concentration of cells, end-product inhibition, and substrate utilization [99]. Adoption of MBR technology may significantly contribute to make fuel ethanol and biogas production from lignocellulosic materials more commercially viable and productive [100]. MBR makes the process continuous and increases the cell concentration by recycling them back to the fermenter while also providing a high permeate quality.

MBRs are a combination of two fundamental processes: biological reactor systems and membrane separation. Membranes can be configured externally to the bioreactor (side-stream (sMBR)) or submerged in the bioreactor (immersed (iMBR)). There are two ways of operating membrane filtration: cross-flow and dead-end operations. Many membrane modules have been tested in MBRs for ethanol and biogas production processes such tubular, hollow fiber, plate-and-frame, and spiral wound membrane reactors [100].

The hybrid pervaporation (PV) - bioreactor process, with different configurations, is considered a promising method for bioethanol production. Accordingly, many researchers have investigated the performance of Hybrid PV-bioreactor process using different membranes, cultures, and configurations for continuous ethanol production and mixtures separation. Ding et al. [101] constructed a continuous closed circulating system for ethanol fermentation via coupling PV with a cell-immobilized bed fermenter using a composite PDMS membrane. They obtained an ethanol productivity of 9.6 g L^{-1} h^{-1}. The average ethanol concentration in the permeate was 23.1 wt. %. Chen et al. [102] examined ethanol production by *Saccharomyces cerevisiae* in a continuous and closed circulating fermentation (CCCF) system, using a polydimethylsiloxane (PDMS) PV membrane bioreactor. They reported that long-term continuous operation of the CCCF system was viable and promising. The volumetric ethanol productivity was 1.39 g L^{-1} h^{-1} in the third cycle, with ethanol yield rate of 0.13 h^{-1}. A comparable study was also carried out by Fan et al. [103] considering a kinetic model of continuous ethanol production in a closed circulating process of PV MBR using *Saccharomyces cerevisiae* to describe the cell growth and ethanol production. In this experiment, a volumetric ethanol productivity of 609.8 g/L in the first run and 750.1 g/L in the second run were obtained. Also, Chen et al. [104] investigated continuous acetone, butanol, and ethanol (ABE) fermentation and gas production under slightly higher pressure in an MBR. A comparable fermentation ability was observed between slightly pressurized operation and atmospheric pressure operation.

Many studies have examined the effect of operating conditions on the performance of the membrane PV for bioethanol production. Jiraratananon et al. [105] tested composite hydrophilic PV membranes processes for dehydration performance of ethanol–water mixtures. Results of the study revealed that operating the PV system at low permeate pressure can increase both flux and separation factor. Dobrak et al. [106] studied the influence of ethanol concentrations in the feed and temperature on PDMS membranes performance for the removal of ethanol from ethanol/water mixtures. They

noticed that an increase of the temperature was associated with a larger increase of ethanol flux in comparison to water flux and that the membrane selectivity was largely dependent on the feed concentration.

Schmidt et al. [107] found polyacetylene membrane poly [(1-trimethylsilyl)-l-propyne] (PTMSP) has a distinct advantage over conventional PDMS membranes for ethanol removal. The flux with PTMSP was about three-fold higher, and the concentration factor was about twice higher than the flux and concentration achieved with PDMS under similar conditions [107]. Ylitervo et al. [98], when studying the performance of an *s*MBR for the ethanol yield and productivity at different dilution rates of toxic wood hydrolyzate, affirmed that the yeast in the *s*MBR is capable of fermenting the wood hydrolyzate, even at high dilution rates. In a similar experiment, Ylitervo et al. [108] reported no significant differences in the acetic acid tolerance of the yeast cultivated at a high enzyme concentration when testing the effect of high acetic acid concentrations of lignocellulosic raw materials on continuous ethanol production with an MBR.

A few studies investigated the feasibility of the hybrid fermentation–PV process for bioethanol production [84,109,110]. The results from these studies showed that the total ethanol production cost of the conventional fermentation processes was slightly lower than the hybrid fermentation–PV process because of the high costs of membrane. The hybrid PV-bioreactor process showed a high capacity to increase ethanol or butanol productivity by recycling yeast cells back to the fermenter system. The hybrid PV-bioreactor system was also very efficient regarding selectivity, cost, and energy saving as compared to the traditional batch or continuous processes. However, economic analysis of bioethanol/biobutanol production from lignocellulosic biomass materials is needed to examine the use of the PV process regarding high bioethanol or butanol productivity and low energy consumption.

8.1.4. Bioethanol recovery and dehydration

Among the variety of potential co-products from the IFBR, bioethanol production is gaining considerable attention because of the economic downturn and competition facing the pulp and paper industry. Also, the utilization of bioethanol, as an alternative renewable bio-fuel, has substantial environmental benefits in the long run because it could greatly decrease net greenhouse gas (GHG) emissions [13]. However, bioethanol production from lignocellulosic biomass is complex and involves many processing steps, including pretreatment, hydrolysis, fermentation, and recovery.

The processes of converting lignocellulosic materials into bioethanol have been widely investigated in the past decade. A diverse range of separation technologies has been applied for recovery and dehydration of bioethanol, including distillation (ordinary, azeotropic, and extractive), liquid–liquid extraction, molecular sieve adsorption, and some complex hybrid separation methods [13]. However, ethanol forms azeotrope at 95.6% by weight or 97.2% by volume of water at a temperature of 78.15 °C [13]. This phenomenon makes the complete separation of ethanol and water by the above-mentioned distillation means impossible. Selective adsorption is a promising alternative to distillation for bioethanol dehydration, but water is very strongly sorbed and high temperatures and/or low pressures are required to regenerate them [111]. However, PV membranes showed promising results in dehydration of alcohol–water mixtures, and they have been commercialized since 1982 [105]. Copolymerization, blending, and crosslinking techniques have been shown to improve PV capacity, and hydrophilic membranes such as chitosan (CS) and polyvinyl alcohol (PVA) are suitable for dehydration purpose [105]. PV can be an efficient method to overcome azeotrope problem in distillation and obtaining fuel grade ethanol because they are highly selective and cost-effective. This review discusses the use of membrane PV and membrane distillation (MD) for water/ethanol mixtures separation.

8.1.4.1. Membrane distillation (MD)

MD is a thermally driven process appropriate for applications in which water is the large component in the feed solution that needs to be treated [112]. Based on the adopted condensation methods, the MD systems can be divided into four types of configurations: direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), sweeping gas membrane distillation (SGMD), and vacuum membrane distillation (VMD) [113]. A large variety of membrane modules has been designed and tested in MD systems, including a flat sheet, hollow fiber, capillary, and tubular. However, majority of laboratory scale modules are intended for use with flat sheet membranes.

Several studies have tested the viability of MD as a method for dilute ethanol separation from water. Udriot et al. [114] reported that the continuous extraction of ethanol by MD enhanced ethanol productivity by 87% (from 0.99 to 1.85 g/L/h) when cultivating an anaerobic batch of *Kluyveromyces fragilis* on a complex medium containing glucose100g/L. Calibo et al. [115] examined SGMD for ethanol removal from an 8wt. % ethanol–water solution

using a tubular PTFE striping module. They reported that a long time operation, using the PTFE module, was feasible and that a slight improvement of the ethanol separation performance of the PTFE module was observed.

Lewandowicz et al. [99] tested the MD process for ethanol recovery using an experimental system consisting of a bioreactor, equipped with a capillary MF unit. It was found that MD, coupled with a bioreactor, was a straightforward method for biofuel industry in maximizing the volumetric productivity and reducing the production costs. Furthermore, Barancewicz and Gryta [116] investigated ethanol production in a bioreactor with an integrated MD module using a hydrophobic capillary polypropylene membrane. They observed that ethanol and acetic acid were selectively removed from the fermentation broth by the MD process and that the retention of inorganic solutes was about 100 %. Adoption of MD, coupled with a bioreactor, can tackle the shortcomings of conventional batch production.

8.1.4.2. Pervaporation (PV)

PV (permeation and evaporation) is a process that uses a non-porous membrane, made of swollen homogeneous polymers, to separate mixtures of liquids by partial vaporization [117]. The separation mechanism of the pervaporation membrane is based on the sorption, diffusion, and desorption of the target component through the membrane [118,119]. The key advantage of this process, in comparison with the other techniques, is that the selectivity can be maximized independently by choosing the right membrane material.

Numerous studies were performed to test the application of PV processes in bioethanol production. Table 8 summarizes the results of recent research. Polymeric membranes are commonly used for PV ethanol recovery because of their low cost of fabrication. They are applied at both lab- and pilot-scale studies. A wide range of materials have been used, such as cup ammonium regenerated cellulose (CRC), poly (amide sulfonamide) (PASA), sodium alginate (SA), poly (phenylene oxide) (PPO), and chitosan (CS). Polymeric PV membranes demonstrated higher fluxes and selectivity for the ethanol/water azeotrope [5].

Inorganic PV membranes, made from inorganic materials (zeolites and silicalite-1), were investigated by many researchers because of their superiority to polymeric materials in thermal and mechanical stability [5]. For instance, Nomura et al. [120] investigated the transport mechanism of ethanol/water mixtures by PV through silicalite membrane. They found that the presence of ethanol in the feed had a significant impact on the degree of water permeation. Total permeate flux progressively increased with an increase in feed ethanol concentration. Ikegami et al. [121] studied the use of silicalite membranes, coated with a hydrophobic material (silicone rubber), to stabilize the production of highly concentrated ethanol in the fermentation/PV process. They reported that coating a naked silicalite membrane with the silicone rubber to maintain a constant ethanol concentration in permeate during the fermentation/PV process was useful.

In other studies, Nomura et al. [122] examined the selective extraction of ethanol from ethanol fermentation broth through a silicalite zeolite membrane. The silicalite zeolite membrane showed a high ethanol selectivity during PV of the fermentation broth. Sato et al. [123] synthesized industrial-scale zeolite NaY membranes in two types of a porous aluminum tube of monolayer support and asymmetric support, using vapor permeation (VP) and pervaporation (PV) apparatuses. The ethanol permeability was 1.1×10^{-7} mol m^{-2} s^{-1} Pa^{-1} in vapor permeation (VP) mode and 7.2×10^{-8} mol m^{-2} s^{-1} Pa^{-1} in pervaporation (PV) mode at 130 °C and 570 kPa. Although inorganic PV membranes are superior in some qualities over the polymeric PV membranes, the complexity of inorganic PV membrane fabrication and its reduced feasibility are two main shortcomings that limit its broad applications.

On the other hand, some studies have focused on the selectivity of PV membranes during separation of ethanol/water mixtures. Thongsukmak and Sirkar [124] studied a supported liquid membrane of trioctylamine in PV using coated porous hollow fibers to remove acetone, ethanol, and butanol from their dilute aqueous solutions. They observed that selectiveness and fluxes increased considerably as the temperature of the feed solution was increased. In another study, Thongsukmak and Sirkar [125] used extractive PV to separate ethanol from its dilute aqueous solutions. The addition of a small amount of n-butanol into the solution containing 5–10 wt. % ethanol improved the separation performance of extractive PV using Tri-n-octylamine as the liquid membrane with coated porous hollow fibers. The selectivity of ethanol improved significantly from 38 to 113 at 54 °C for the feed containing ~10 wt. % ethanol when 2.5 wt. % n-butanol was added to the feed. Although PV is a promising solution for the separation of ethanol from the fermentation broth, additional investigations are needed to improve their efficiency regarding developing a highly ethanol-selective membrane and increasing the permeate flux.

Some other studies tested the feasibility of using membrane PV for ethanol dehydration. For example, Tsuyumoto et al. [126] constructed a pilot-

scale plant, equipped with hollow-fiber membranes in a module form, to evaluate the economic aspects of membrane PV for ethanol dehydration. The total cost of membrane PV method for a full-scale plant in which 94.9 wt. % aqueous ethanol dehydrated to 99.8 wt. % at 70 °C at a rate of 150 m³/day was evaluated to be $21–26/ton, approximately 1/3 – 1/4 of that for azeotropic distillation. Also, O'Brien et al. [127] reported that if the

performance of PV membranes could be improved to provide a flux of 150 g m⁻² h⁻¹ and a separation factor of 10.3 for ethanol to water, the PV for ethanol recovery from fermentation broths could be cost-effective. In conclusion, PV has many advantages, including energy saving and an absence of thermal and chemical stresses on fermentation broth, for ethanol separation from water and thus is a promising technology.

Table 8
Literature review (> 2015) of applying pervaporation membrane process for bioethanol recovery.

Feed source	Membrane type	Membrane material	Feed ethanol content (wt %)	Scale	Pressure (pa)	Temp (°C)	Separation factor	Total Flux (Kg·m⁻²·h⁻¹)	Ref.
Model solution	Supported H-ZSM-5 membranes	High-silica MFI zeolite membrane	5–10	–[c]	–	30 -70	4 - 7	2 – 14	[128]
Model solution	Metal–organic frameworks (MOFs)	MIL-53/PDMS[a] hybrid	5	Lab scale	100	30 - 80	11.1	1.667 – 5.467	[129]
Model solution	Composite membrane	Silicalite-1/PDMS	5	Lab scale	50	60	14.7	12	[130]
Model solution	Organophilic	PDMS)	5	Lab scale	~200	60	12.5	1.186 – 0. 807	[131]
Model solution	Organophilic	mixed matrix copolymer	5	Lab scale	–	30	16	0.34	[132]
Model solution	Isomorphously Membrane	B-ZSM-11 zeolite	5	Lab scale	–	60	35.0	1.51	[133]
Model solution	Hybrid process	PERVAP 4060/ Pervatech PDMS/ silica filled-PTMSP[b]	6	Lab scale	–	50	9/ 5.03 /6.52	0.557/0. 926/2.667	[134]
Model solution	Modified membrane	Fe-ZSM-5 membranes	5	Lab scale	133	50	–	0.49 – 2.73	[135]
Lignocellulosic hydrolysates	Composite membrane	silicalite-1/PDMS/PAN	2	Lab scale	266.64	35	–	0.130	[136]
Model solution	Hybrid membranes	PDMS/silicalite-1	5	Lab scale	400	50	23.8/23/23.9	0.170/0.223/0.245	[137]
Synthetic materials + *Saccharomyces cerevisiae*	Composite membrane	PDMS	10	Lab scale	–	30	8.6–11.7/ 8– 11.6	0.3962–0.6637/ 0. 3324–0.5481	[138]
Synthetic materials + *C. acetobutylicum* JB200	Composite membrane	CNTs-PDMS MMM	1.4/6 g/L	Lab scale	–	37	–	0.655	[139]

[a] PDMS = polydimethylsiloxane
[b] PTMSP = Poly[1-(trimethylsilyl)-1-propyne].
[c] – Indicates value not reported or not available.

8.2. Biobutanol recovery

Biobutanol is considered a potential biofuel and may replace gasoline in the future. Compared to ethanol, butanol is characterized by lower vapor pressure, higher energy content, and sufficient blending ability with gasoline. Also, it has low hygroscopicity and high compatibility compared with the most current combustion engines [140]. Biobutanol can also be used as a solvent for a wide variety of chemical and textile processes. Table 9 summarizes the results of recent studies on the use of the pervaporation membrane process for butanol recovery.

Production of butanol, as the second generation biofuel via bioconversion route of lignocellulosic materials, relies on the application of *Clostridia species*. Its production method, via fermentation, is similar to that of ethanol production: enzymatic hydrolysis of polysaccharides to monosaccharides followed by fermentation [141]. The application of the fermentation process, using *Clostridia sp.*, led to the ABE production of approximately 15–25 g/L with a yield of 0.25–0.4g ABE/g sugar [142]. The fermentation of glucose to biobutanol can be carried out in a batch or continuous process.

The profitability of biobutanol production via fermentation method is high, however, this depending on bioconversion efficiency and product purity [143] because there are phenolic compounds of cellulosic materials that inhibit the butanol fermentation process [141]. Secondly, the existence of butanol at a concentration rate higher than 7.4 g/l, decreases the cell growth [144]. Also, biobutanol production is characterized by high recovery costs as a result of low butanol concentration and the issue of butanol/water azeotrope.

For overcoming the high cost associated with butanol recovery from the fermentation broth, many approaches have been investigated including

adsorption, perstraction, gas stripping, ionic liquids, liquid-liquid extraction, flash fermentation, reverse osmosis (RO), aqueous two-phase separation, supercritical extraction, and pervaporation (PV) [142,143]. Among these methods, membrane filtration showed a high capability regarding energy efficiency and product quality. Also, it has no harmful consequences on the fermentable microorganisms. In this review, only PV and RO membrane-based separation technologies are discussed.

8.2.1. Pervaporation (PV)

In the biobutanol production process, PV is an efficient separation technology, not only for butanol recovery from the fermentation broth but also for dehydration of butanol from low-water content solutions. Many studies have been conducted on the recovery of butanol from the fermentation broth or a model solution. Both hydrophobic polymeric membranes and polymeric composite membranes were investigated concerning performance and efficiency.

Hydrophobic polymeric membranes for butanol recovery were studied by many researchers [145-147]. Table 9 summarizes the results of recent research on pervaporation membrane process for butanol recovery. Marszalek et al. [148] evaluated the performance of two PV membrane PERVAP 4060 commercial membranes and ionic liquid (IL-PDMS) membranes for butanol concentration from fermentation broths. As compared to the PERVAP 4060 membranes, IL-PDMS membrane showed a higher butanol selectivity but a lower flux rate because of additional layer resistance. In another study, using IL liquid-based PV membranes, Heitmann et al. [149] noticed that a higher affinity of the IL to butanol increases the permeability of the membrane more

than three times and fluxes increased with an increase in the IL content in the membrane.

Xue et al. [150] studied the performance of the zeolite-mixed polydimethylsiloxane (PDMS) membranes to recover butanol from acetone–butanol–ethanol (ABE) fermentation system and butanol/water binary solution. Integration of zeolite-mixed PDMS membrane with (ABE) fermentation demonstrated an excellent capacity for butanol recovery with a high purity. The butanol concentration in permeate was 334.6 g/L at 80 °C.

To overcome nanoparticle agglomeration during hybrid membrane formation, Fan et al. [151] developed nano-disperse ZIF-8/PDMS hybrid membranes for biobutanol recovery by directly dispersing a nascent ZIF-8 suspension in a PDMS solution without further centrifuging and drying. For the separation of 5.0 wt% n-butanol–water solution at a temperature of 80 °C, the prepared ZIF-8/PDMS membrane displayed a high separation factor (52.81) and a high flux (2800.5 $gm^{-2}h^{-1}$). Butanol can also be effectively separated, from either ABE model solutions or fermentation broths, using silicalite–silicone composite PV membranes. Ikegami et al. [152] achieved a concentration of more than 80% (w/w) butanol when they studied the separation of clostridia ABE fermentation broths using silicone rubber-coated silicalite-1 PV membranes. According to the literature, the PTMSP membrane has excellent performance, concerning the permeate flux and separation factor, in both butanol and ethanol recovery because of its highly hydrophobic properties, good thermal, chemical, and mechanical stability. However, further studies on the feasibility of incorporating the PV technology with the fermentation process for simultaneous production and recovery of butanol from the fermentation broth are needed.

8.2.2. Reverse osmosis (RO)

RO has been tested in butanol concentration and recovery during a continuous butanol production. Garcia et al. [153] examined RO polyamide membranes for the concentration of dilute solvent butanol-acetone fermentations. The results showed that RO membranes exhibited rejection rates as high as 98%. Also, Diltz et al. [154] reported a rejection rate greater than 99% for butanol, and other organic compounds, at a pressure of 5.5 MPa when studying an RO membrane for organic model compounds recovery from fermentation broths.

Ito et al. [155] invented a patented butanol production process. Part of the process used RO technology to concentrate the fermentation broth. This invention consists of three steps: first, a butanol-containing solution is filtered through a NF membrane. Then the permeate of the NF membrane is concentrated through a RO membrane for a two-phase separation of a butanol phase (a non-permeated liquid) and an aqueous phase (permeate does not contain butanol). Finally, butanol is separated from the butanol phase by distillation. They concluded that to concentrate butanol by RO efficiently, a pressure between 0.5 and 7 Mpa is appropriate for separation because the membrane permeation flux will be high and the possibility of damaging the membrane is small. Butanol concentration by RO was not less than the butanol saturation solubility of 8 wt%. Since RO membrane is carried out under a high pressure and this represents part of the butanol production costs, there is a need for a feasibility study to test the effectiveness of RO in butanol concentration.

In the biobutanol and bioethanol production processes, most studies have focused on the use of model solutions (ethanol/water and butanol/water mixtures) or synthetic materials plus microorganism as feed sources. Therefore, the transformation of synthetic solutions to the real pulp and paper wastewater and forest-based materials is required.

9. Challenges and opportunities

9.1. Challenges

9.1.1. Membrane-related challenges

Because of the composition of forest industry process streams and effluents, membrane fouling is the most important issue affecting the broad applications of membrane separation technology in the IFBR area. Membrane fouling would worsen membrane performance and shorten membrane life. Also, membrane integrity is another important issue because membrane integrity and testing protocols are still under development. Among other aspects that limit the widespread adoption of membrane filtration in IFBR are the high cost of membrane replacement, concentration polarization, and energy consumption. Membrane replacement represents the major operating cost and membrane life expectancy varies with process operating conditions. This review addresses membrane fouling in details and the core foulant materials behind it in pulp and paper process water and offers some possible solutions. Also, concentration polarization effect is discussed.

Fouling phenomenon and control

In recent years, membrane separation processes have received much attention from lab-scale studies to wide applications in industrial operations. However, in the pulp and paper industry, fouling is the most determining factor affecting the broad applications of membrane filtration because of the complexity and high fouling tendency of wood hydrolysates [24,167]. The wood hydrolysate effluents contain various substances such as carbohydrates, extractives, and lignins. Based on particle sizes, the pulp and paper mill effluents categorized into three groups: suspended solids (size >2 μm), colloidal substances (0.1-2 μm) and dissolved substances (< 0.1 μm) [168]. The main difference between the types of membrane fouling is the nature of the particles that cause the fouling. During pulp and paper process wastewater filtration, organic and inorganic were the most dominant mechanisms of membrane fouling.

The constituents that cause membrane fouling during the filtration of pulp and paper process water were investigated by relatively few studies. Nystrom et al. [169] reported that resin, fatty acids and to some extent lignans were the main wood extractives that caused membrane fouling during the filtration of pulp and paper mill wastewaters. Also, Maartens et al. [22] treated pulp and paper effluent by UF and observed that foulants present in the effluent were of a phenolic nature. Puro et al. [58] studied the fouling of extractives of two process wastewater originated from a pulping process using a mixture of hardwood and softwood and softwood alone by UF. They found that fatty and resin acids were the most abundant foulant materials in the membranes; however, they also noticed that sterols contributed remarkably to the fouling of RC membrane although their amount in the process wastewaters was low. In general, detailed information about the nature of foulants is lack, due to the complexity of constitutes in pulp and paper wastewaters and limited studies of membrane fouling in IFBR.

Based on the attachment of particles to the membrane surface, membrane fouling can be clasiffied into reversible and irreversible fouling. Chen et al. [170] characterized membrane foulants in a fine paper mill effluent filtration by a polyethersulfone (PES) UF membrane. Their results indicated that the reversible membrane foulants accounted for 85.52% of the total foulants and mainly came from retention aids, drainage aids, and wet strength resins, whereas the irreversible adsorptive foulants accounted for 14.48% and mostly originated from sizing agents and coating chemicals.

In biorefining and bioenergy production, great progresses have been made in understanding the connections between the membrane types, foulants, and the operating conditions [22,58,165]. Puro et al. [58] reported that polyethersulfone (PES) has greater fouling tendency than regenerated cellulose (RC) membranes. According to Puro et al. [171] surface roughness has a positive effect on membrane fouling in pulp and paper mill applications. It was also found that a membrane with a rougher surface has more fouling tendency than a membrane with a smoother surface. Also, compared to tighter membranes, looser membranes are more sensitive to fouling during pulp mills effluent filtration. On the other hand, Maartens et al. [22] and Nystrom et al. [169] indicated that the hydrophilicity of the membranes has a major role in the membrane fouling reduction during pulp and paper effluents filtration.

However, membrane fouling characterization in pulp and paper mill effluents filtration using analytical methods, such as atennual total reflectance Fourier transform infrared spectroscopy (ATRFTIR), scanning electron microscope (SEM), energy dispersive spectrometry (EDS), and contact angle and zeta potential measurements, are very limited [172,173]. Carlsson et al. [172] used a surface spectroscopic method for membranes fouling study in pulp mill effluent treatment. They noticed that fatty acids were the dominant foulant materials in the membranes rather than resin acids. Kallioinen et al. [173] analyzed organic foulants by ATR-FTIR during the filtration of groundwood mill circulation water. Fatty and resin acids and cellulosic species were the major foulant materials. Puro et al. [168] studied organic foulants in membranes fouled by pulp and paper mill effluent using solid-liquid extraction and further identified foulants with gas chromatography (GC). They found that fatty and resin acids and some traces of lignans fouled the membranes in the filtration of groundwood mill circulation water. However, the hydrophobic membranes were more severely affected by these acids and lignans than the hydrophilic membranes.

Many strategies have been developed to mitigate membrane fouling, including physical or chemical cleaning, membrane surface modification, optimization of membrane and biomass characteristics. Pretreatment methods gained increasing popularity in membrane technology. Effects of the pretreatment methods on membrane fouling are briefly described in Table 10. Ko and Fan [174] added laccase, prior to filtration of pulp and paper wastewater, and concluded that a laccase pretreatment and membrane process is a good combination for treating the pulp and paper effluents. However, inactivated laccase addition caused further flux reduction. Persson and Jönsson [25] reported that pretreatment of forest industry effluents by activated carbon before filtration had positive impacts on permeate flux

improvement and membrane fouling reduction. However, pretreatment methods have to be tailored separately, due to the fact that each individual pulp and paper effluent has different characteristics, depending on the pulping process such as thermomechanical (TMP) or chemithermomechanical pulp (CTMP) or the raw material used in the pulp manufacturing. Membrane fouling could be reduced if the process operating conditions could be optimized.

Among fouling control and prevention strategies, chemical cleaning remains the favored method for real industrial applications. Cleaning agents such as detergents, acids or alkalis are often used to clean fouled membranes. However, the chemical cleaning sometimes damages the membrane materials and causes secondary pollution. Another problem associated with chemical cleaning is that cleaning often modifies membrane characteristics that are critical to filtration such as membrane hydrophobicity and charge. Alternatively, ultrasound has also been used as a method for cleaning, but studies on ultrasonic membrane cleaning are limited. Also, the enhancement of membrane shear-rates has been considered one of the most efficient ways for fouling control.

Fouling phenomena, during the application of membrane technology in IFBR, represents a significant impediment to the adoption of this technology on a large scale. Fouling leads to a decrease in filtration capacity, an increase in the number of membrane cleanings required, and a reduction in membrane lifetime, consequently leading to higher operating and membrane replacement cost. Therefore, for the vast implementation of membrane technology in IFBR, much research and development effort are needed for the development of effective membrane fouling control strategies.

Table 9
Summary (>2012) of pervaporation membrane process for butanol recovery.

Membrane	Feed butanol content (wt %)	Operating mode	TMP (pa)	Temp (°C)	Separation factor	Butanol concentration (wt %)	Culture and media	Flux (Kg·m^{-2}·h^{-1})	Reference
PDMS composite	6.3–11.7	Continuous	1990	35	–	–	Synthetic materials + *C. acetobutylicum*	0.014 – 0.016	[145]
PDMS (4060)	5.9	Continuous/ fed-batch	1000	37	–	16.7	Synthetic materials + *C. acetobutylicum*	>0.4	[146]
PDMS composite	0.58–1.8	Continuous	1230	37	6 – 33	60.4–131.6	Synthetic materials + *C. acetobutylicum*	0.561– 0.621	[147]
IL-PDMS/PDMS 4060	0.25 –3	Batch	3000	50	–	–	Model solution (n-butanol/water)	1.295/1.63	[148]
Zeolite-mixed PDMS	1.5	Fed-batch	–	37/80	33	60	*C. acetobutylicum* ATCC 55025	0.016/0.096	[150]
Silicalite-1 membrane	1.1	Batch	400	45	–	1.1	Synthetic materials + *C. saccharoperbutyl acetonicum*	0.04 – 0.02	[150]
Nanodisperse ZIF-8/PDMS	5	Batch	200	30 - 80	53	–	Model solution (n-butanol/water)	2.8005	[156]
PDMS/ceramic	6.2	Fed-batch		37	–	–	Synthetic materials + *C. acetobutylicum*	0.005 – 0.0271	[157]
PhTMS/PDMS/ ceramic	1–5	–	<300	20 - 40	10–30	5	Model solution (butanol/water)	0.2 – 0.9	[158]
PEBA polymeric	0.8–1.2	Batch	5333–6666	37	–	–	Synthetic materials + *C. acetobutylicum*	0.09 – 0.161	[159]
PEBA ionic liquid-based polymeric	5	–	1000	37	11.57	55	Model solution (butanol/water)	0.56	[160]
PEBA/ZIF-71 (MMMs)	1	Batch	<400	37	18.8	18.6	Synthetic materials + *C. acetobutylicum*	0.520	[161]
Organic–inorganic hybrid silica (HybSi®)	5	Batch	–	30/60/90	10.5 - 11.7	12/31/42	Model solution (n-butanol/water)	0.450 –1.40	[162]
ZSM-5/PEBA Composite	2.5	Batch	320	35	30	4.25	Model solution (n-butanol/water)	0.390	[163]
PDMS/PAN	–^{a}	–	–	42	21–26/ 22–29/ 5–7	–	Model solution (n-butanol/water)	1.390	[164]
PDMS/hollow fiber ceramic	1	Continuous	–	40	42.9	–	Model solution (n-butanol/water)	1.282	[165]
PDMS/hollow fiber ceramic	1	Continuous	–	40	22.2	–	Model solution (n-butanol/water)	1.000	[166]

^{c} – Indicates value not reported or not available.

Concentration polarization and control

Concentration polarization is a phenomenon causing a permeate flux (J) decline during the filtration process. It occurs due to solute being retained on the membrane surface and the solvent passing the membrane. In contrast to membrane fouling, concentration polarization is a reversible phenomenon. The optimum way of decreasing concentration polarization effect is reducing the deposition that takes place on top of the membrane by shear forces at the membrane surface [66]. Also, increasing the cross-flow velocity is considered as the most direct technique to minimize concentration polarization effect during lignin recovery [26], and inhibitor removal [88].

9.1.2. IFBR-related challenges with corresponding applied solutions

The main IFBR-related membrane separation challenges are represented in the separation of harsh nature black liquor, fermentation inhibitors removal, hemicelluloses extraction prior mixing with BL, and tackling the issue of the azeotrope of butanol or ethanol/water mixtures.

Inhibitors removal

The bioconversion of lignocellulosic biomass usually involves hydrolysis of cellulose and hemicellulose to monosugars, followed by fermentation of the monosugars into the desired products. During the hydrolysis of this material, a large group of compounds that are inhibitory to the fermentable microorganisms is formed or released. They must be removed from the hydrolyzate prior to fermentation. Based on this review, NF and RO membranes exhibited excellent efficiency in overcoming this problem. Also, the integration of ABE fermentation with a membrane separation can effectively eliminate fermentation inhibitor compounds and thus could make bioethanol or biobutanol production more economically viable. For example, hydrophobic pervaporation with PDMS composite membrane coupled to the fermentor is regarded as a promising technology in terms of inhibitor removal and the permeate enrichment. In addition, boiling, ion exchange resins (IER), and over-liming have been proposed as alternative methods to reduce the concentration of inhibitors in the literature. However, anion exchange

membrane exhibited better separation performance in terms of throughput and product loss compared to IER.

Hemicellulose extraction prior to pulping

Although the prehydrolysis step of the Kraft dissolving pulp production process perfectly fits into the IFBR concept, the extraction of hemicelluloses, before the pulping, is still a remaining challenge needs to be addressed. In the production of dissolving pulps, many pretreatment methods have been investigated. However, developing a pretreatment process that solubilizes hemicellulose sugars, while maintaining the fiber integrity, is desirable. Placing UF membranes after preextraction step can help greatly in the optimization of the pretreatment process because the UF membranes have the ability to recover hemicelluloses dissolved in PHL effectively. Therefore, integrated pretreatment process can provide feedstock for bioethanol or chemicals production, thus increasing the total revenue stream for the pulp and paper mills. Another consideration for hemicelluloses extraction prior to pulping is about alkaline pretreatment process. This technique usually produces hemicelluloses with smaller molecular weights, compared to other pretreatments such as hot water pretreatment and autohydrolysis. In this case, NF is found to be an effective method for hemicelluloses recovery from hydrolyzates than UF.

Table 10
Results of wood-based hydrolysates pretreatment methods on membrane fouling control.

Raw material	Pretreatment Method	Results
Masonite process stream/Birch and spruce sawdust hydrolysate	pH adjustment	Lowering the pH from 4.5 to 3 led to less fouling of RC membrane, but a lower flux of the composite fluoropolymer membrane [10]. pH (7–8) had a minor influence on the filtration capacity of RC UF membrane [24]. pH adjustment to 10 significantly reduced UF membrane fouling [167]. Filtration at neutral pH associated with reduced fouling [176].
Birch and spruce sawdust hydrolysate	Centrifugation at room temperature	No significant influence on the filtration capacity was noticed [24].
PHL	Ion exchange resin	Resulted in significant removal of acetic acid [35]. Increased oligosaccharides purity [74].
Masonite process stream/Birch and spruce hydrolysate/PHL	Activated carbon adsorption	Resulted in higher flux and less fouling of both hydrophilic and hydrophobic membranes [10]. Membrane filterability improved [24,35,36].
Spruce hydrolysate	Hemp adsorption	No significant influence on the foulants adsorption [24].
Birch and spruce sawdust hydrolysate/ Wood auto-hydrolyzate	Oxidation by pulsed corona discharge (PCD)	Significant improvement in the filtration capacity [24]. Its effect on the fouling of the cellulose-based UF membranes was low [175].
PHL/Kraft pulp and paper mill effluent	Laccase addition	Membrane filterability increased [37] Polymerized pollutants removed without significant fouling [174].
Kraft pulp and paper mill effluent	Inactivated laccase addition	Caused further flux reduction [174].
Hemicelluloses hydrolysate from TMP mill	MF	MF with a pore size of 0.1 μm removed colloidal extractives while a high amount of high molecular mass hemicelluloses passed to permeate [177].

Black liquor (BL) concentration

In addition to the above separation challenges, the membranes required for the concentration of the naturally harsh black liquor (BL) of the pulp and paper industry must be able to withstand the high pH and temperature. Technically ceramic membranes seem appropriate choice for this task if its capital cost is reduced. Therefore, the development of more resistant polymeric and cheaper ceramic membranes is needed for treating BL which is characterized by harsh conditions (very alkaline or acidic conditions and high temperatures). Also, there are other successful techniques have applied for BL preconcentration such as vibratory shear enhanced process and sacrificial protective coating materials.

9.2. Opportunities

Figure 7 shows the potential bioproducts from IFBR. Lignocellulosic biomass is suitable for the production of different components including fuels, heat, and power (bioenergy platform) and diverse array of co-products (materials and chemicals platform). In energy platform, the feedstock which is used to produce bioenergy is pretreated using steam explosion. In the pretreatment processes, hemicellulose will be liberated, and lignin is removed which improves the digestibility of hemicellulose in the following hydrolysis process. Hemicellulose is then hydrolyzed to fermentable monosugars, followed by detoxification step for inhibitors removal prior to fermentation processes. Following this, the detoxified hydrolysate slurry is fermented via microorganisms to bioethanol or butanol, depending on the microorganisms used because butanol production from cellulose mainly relies on the use of *clostridia species*. In the subsequent stage, the water/ethanol mixture is separated and purified. Also, during the pretreatment process, acetic acid will be generated from acetate in the wood and furfural and hydroxymethylfurfural (HMF) will be produced from pentose and hexose sugars if pretreatment conditions were severe. The high concentrations of these compounds will inhibit or reduce the microorganism's growth rate in the fermentation step. In contrast, these compounds are valuable chemicals commodity that can be recovered and used in many applications in the field of chemical industry. In bioenergy platform, forest residues can be directly gasified for renewable fuels and energy production after size reduction. Besides heat and power generation, synthesis gas from biomass gasification can be subsequently converted into liquid transportation fuels such as diesel and gasoline. In the other case, forest residues can follow the biochemical route for biofuel production. For example, anaerobic membrane bioreactors (AnMBRs) can be used for anaerobic digestion of pulp and paper sludge and effluents for biogas production with many advantages (reduced bioreactor sizes and superior quality of effluents) [5,178,179,180,181].

Although several challenges persist, the implementation of membrane technology in IFBR offers many opportunities for future wide-scale adoption. Figure 8 illustrates the proposed schematic diagram for the application of membrane processes in IFBR. Bioproducts can be produced via biochemical, or thermochemical conversion routes. In the biochemical conversion biorefinery, membrane processes are applied directly to isolate hemicellulose (UF), lignin (NF), and extractives (RO) after pretreatment step for various co-products production. Also, membrane processes (NF and RO), overliming, and boiling have been extensively used to remove or reduce the concentration of the inhibitors because of their low cost. After inhibitors removal, the detoxified hydrolyzate is fermented. The resulting products are recovered and purified by pervaporation and membrane distillation. Also, MF can be used as a pretreatment method to minimize membrane fouling and enhance the ethanol productivity. In addition, UF and NF are also applied for enzyme recovery from the fermentation step. Furthermore, NF and RO membranes are used for the removal of acetic acid and furfural. Also, it has found that hot water pretreatment process produces less inhibitory compounds (weak acids and furans) compared to steam explosion method.

Figure 9 shows proposed process for bioethanol production via fermentation integrated with PV unit. The system consists of a feed tank, membrane units, cold traps or condenser, and vacuum pump. Pumps are used to add the medium from feed tank to the fermentor (pump 1) and to transfer fermentation broth from the fermentor over the pervaporation modules (pump 2). The feed solution is also circulated through the membrane module by a pump (pump3) to the feed tank, while the pressure difference is acting as a driving force for the system for the product separation. The produced PV permeate will be condensed over a given period in the cold traps or condenser.

Figure 10 shows a hybrid system for direct membranes applications, and AnMBR process set up for forest industry process streams and effluents treatment for biogas production. For value-added recovery, three-stage filtration employing microfiltration to remove large contaminants (suspended matter and colloidal extractives) followed by UF to concentrate and purify the

hemicelluloses from low molecular mass contaminants. Next, NF is used to recover lignin from UF effluent. In the subsequent stage, the permeate of NF membrane is treated by AnMBR with a membrane module for contaminants removal and biogas and clear permeate production. The produced biogas (CO_2, CH_4, N_2, & H_2) can be further fractionated by membrane processes for energy recovery, while the clear produced permeate can be reused in the mill. In AnSMBR, besides biogas sparging, additional shear can be applied by circulating sludge to control membrane fouling.
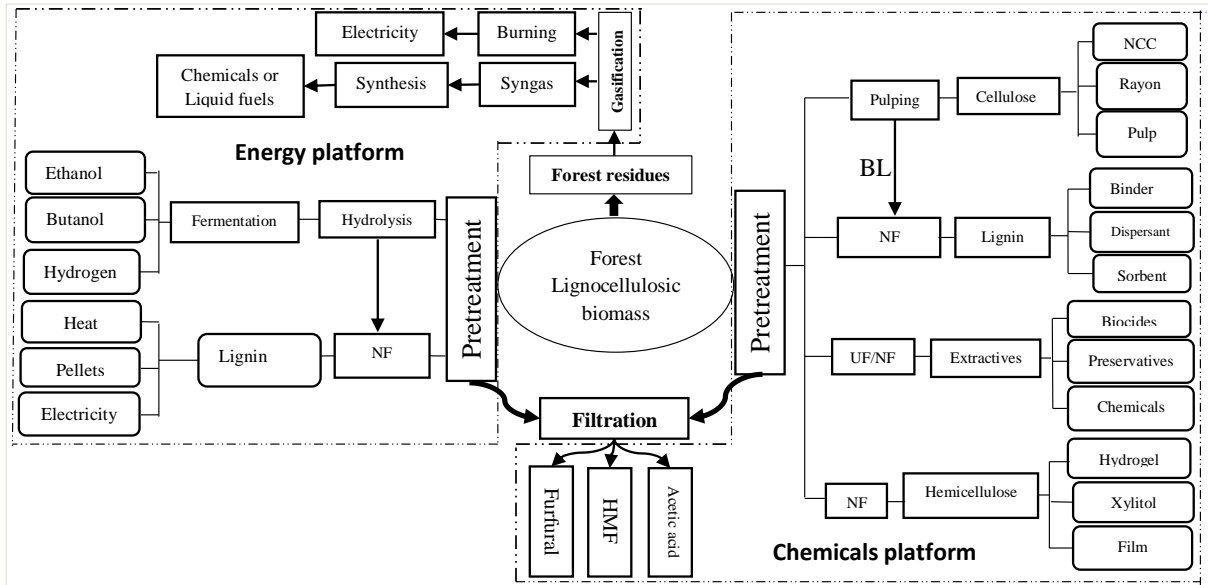
Fig. 7. Simplified process block diagram of the possible bio-products from IFBR.
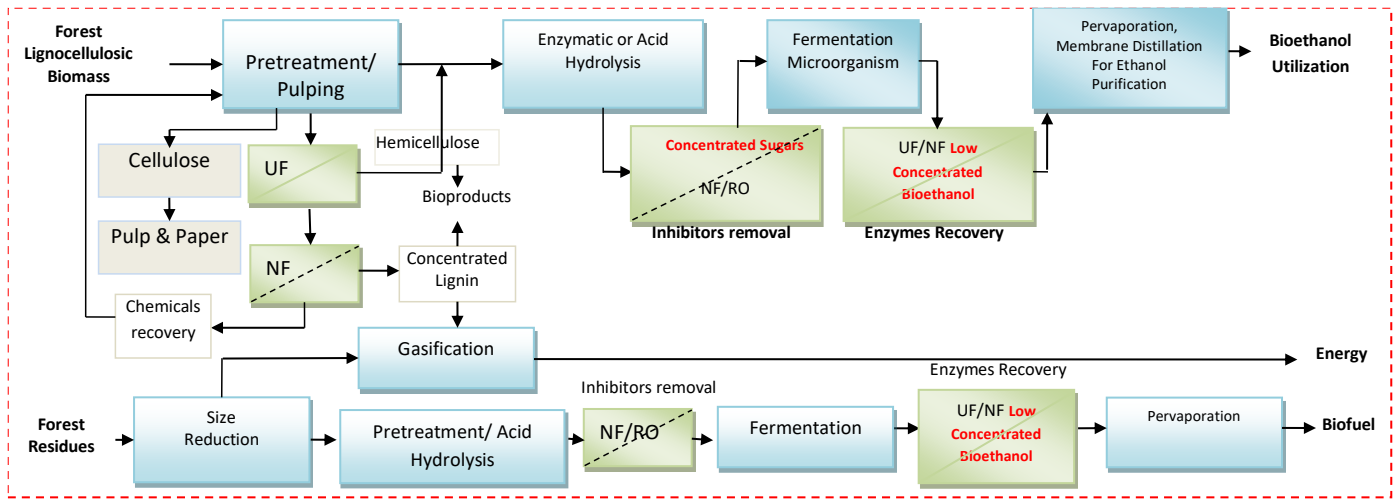
Fig. 8. Proposed schematic diagram for the application of membrane processes in integrated forest biorefinery.
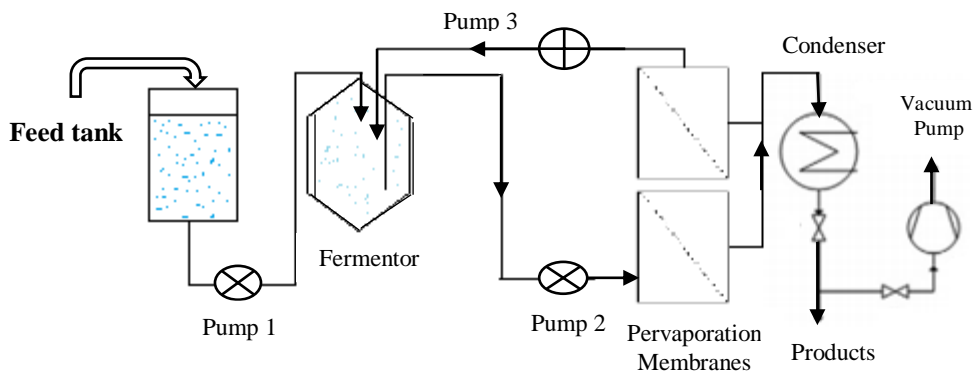
Fig. 9. Proposed hybrid system for bioethanol production via fermentation integrated with PV unit.
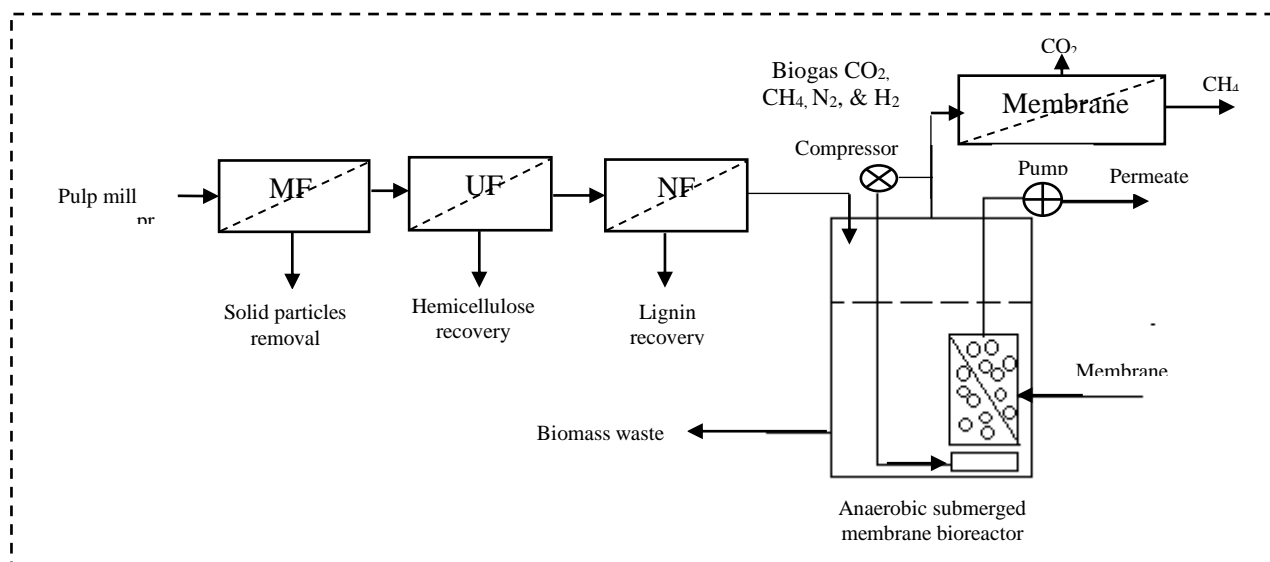
Fig. 10. Proposed hybrid membrane process for forest industry process streams and effluents treatment.

10. Conclusions

The information presented in this review shows that membrane separation is an efficient and cost-effective technology for IFBR. Compared to the conventional separation technologies, membrane technologies offer excellent fractionation and separation capacity, low chemical consumption, and reduced energy and water requirements. Also, along with their easy operation and scale-up, membrane separation processes can be integrated with the existing operating units. This review found that MF possesses a high capacity to clarify the process water and successfully remove all suspended matter. Both UF and NF membrane separation processes are the ideal methods for recovering and purifying hemicelluloses and lignin from forest industry side stream, while NF and RO membranes have a high potential in the fermentation inhibitors removal and sugars concentration.

Ceramic membranes provide a high separation capacity, but they are expensive. Compared to ceramic membranes, polymeric membranes are reasonably priced but are not able to bear the relatively harsh physical and chemical properties of black liquor. So, the development of cheaper ceramic and more resistant polymeric membranes would make the applications of membrane technologies an attractive alternative in pulp and paper mill. Membrane PV has been shown to tackle the issue of the azeotrope of ethanol or butanol/water mixtures successfully. Integration of ABE fermentation with a membrane filtration can effectively eliminate product inhibition and thus could make bioethanol or biobutanol production more viable. However, the hybrid PV-bioreactor process demonstrated great potential and showed proper performance in the bioethanol production because of the high yeast concentration inside the reactor in addition to its low-cost and energy-saving.

Despite the success of membrane technology in IFBR, some challenges persist, such as membrane fouling because of the composition of forest industry process streams and effluents. Therefore, applying appropriate pretreatment methods to the feed water, employing appropriate physical or chemical cleaning protocols, and chemically or biochemically modifying the mixed liquor are needed to control membrane fouling and clogging. We thought that further researches should focus on the fabricating of novel membrane materials to meet the requirements in IFBR. Also, the transition from lab scale- and pilot-scale studies to industrial operations is still a remaining challenge in IFBR. Overall, membrane separations are promising technologies for IFBR.

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