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To cite this article: Nikita S. Kevlich, Meisha L. Shofner & Sankar Nair (2017) Membranes for Kraft black liquor concentration and chemical recovery: Current progress, challenges, and opportunities, Separation Science and Technology, 52:6, 1070-1094, DOI: 10.1080/01496395.2017.1279180

To link to this article: http://dx.doi.org/10.1080/01496395.2017.1279180
Membranes for Kraft black liquor concentration and chemical recovery: Current progress, challenges, and opportunities

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ABSTRACT

Membranes can significantly reduce energy consumption during concentration of black liquor (BL) in the Kraft papermaking process, but the harsh conditions (pH $\sim$12, 80°C–95°C, $\sim$15 wt% solids) make this challenging. We elucidate challenges and opportunities for membranes in BL applications. We critically review membrane materials, processes, and operational modes investigated in the literature. Future advances will involve fabrication of higher-rejecting (≥95% lignin and inorganics), BL-resistant, NF, and RO membranes. Opportunities exist for molecular sieving and electrically driven membranes to recover other valuable chemicals such as carboxylic acids. We also discuss the economics of BL concentration with a single-stage membrane process.

INTRODUCTION

The production of forest-based products such as paper involves highly energy-intensive pulping processes. The Kraft process (Fig. 1) is the dominant pulping process, in which NaOH and Na\textsubscript{2}S are used as the primary pulping chemicals (known as cooking liquor or white liquor).\textsuperscript{[1]} In this process, wood chips and the pulping chemicals are mixed in a pressurized, heated digester to break up the lignin that holds the wood fibers together and remove the pulp, which is rich in cellulose and used for paper production. The waste stream from this process is known as black liquor (BL). The BL stream that exits the digester is called weak BL (WBL) and is at a typical temperature of 80°C–95°C, high pH $\sim$12) and about 15% total solids ($\sim$175 kg/m\textsuperscript{3} solutes).\textsuperscript{[2, 3]} It contains a number of inorganic and organic compounds; the most important of which are the pulping chemicals, degraded lignin (used primarily to generate energy), and carboxylic acids (significantly degraded hemicelluloses, which could be used for higher-value products). The weak BL stream is then concentrated in multiple-effect evaporators to strong BL (SBL) that contains about 75%–80% total solids ($\sim$875–933 kg/m\textsuperscript{3} solutes).\textsuperscript{[2, 3]} This concentrated slurry can be combusted to generate steam, and the resultant inorganic smelt is dissolved and causticized to recover the pulping chemicals, which are sent back to the digester.\textsuperscript{[4–6]}

With more than 500 million tons/year of BL generated worldwide and almost 173 trillion kl/year (0.2 Quads/year) of energy used for BL concentration in the US alone, the processing of BL is an important industrial and environmental issue.\textsuperscript{[7]} Membranes are a potential alternative for the energy-efficient concentration of BL and for recovering valuable organic and inorganic components.\textsuperscript{[8]} Because of the high fouling potential and high viscosity of concentrated BL, a complete replacement of the entire evaporation process with membranes is unlikely.\textsuperscript{[8]} However, even partial concentration (up to about 30%–40% total solids) would result in a major reduction in energy usage. Membranes also have advantages over alternate approaches for lignin removal that rely upon inducing its precipitation via acidification or non-membrane electrochemical techniques.\textsuperscript{[9, 10]} One relevant example of the acid precipitation technique is the LignoBoost process developed by Innventia and Chalmers University of Technology, which has been scaled up in two plants. This process focuses on lignin recovery post-precipitation with CO\textsubscript{2} by utilizing membrane filtration and resuspension of the filtrate cake to achieve high purity and high recovery of lignin with a low ash content ($\sim$1 wt%).\textsuperscript{[11, 12]} However, techno-economic comparisons of the acidification or non-membrane electrochemical techniques support the general conclusion that while acidification processes can achieve a
high degree of lignin removal, they may also involve high costs of acidifying chemicals, electrical energy, anti-corrosion, and process safety measures. In light of these drawbacks, membrane processes—mainly pressure driven such as nanofiltration or reverse osmosis, but also potentially electrodialysis and forward osmosis processes—offer the potential of a lower-cost, easily scalable process in existing pulp mills to directly concentrate BL as well as to separate valuable organic and inorganic compounds.

Although BL concentration with membranes is an important technological challenge, the literature on this topic has not yet been organized in the context of a detailed review and critique of the state of the art. There are two main purposes of the present review article. Firstly, we overview and understand the current state of the art in membrane science and engineering for BL concentration and related applications. Secondly, we identify the key challenges related to membrane materials, membrane processing, development of structure–performance relationships, and operational requirements that must be addressed in order to obtain membranes that are viable for BL treatment. In addition to the ubiquitous challenge of achieving high membrane flux and good selectivity for desired components, a number of important issues exist in relation to the long-term stability of membranes under harsh operating conditions (especially pH ~12 and temperature 80°C–95°C), the complex composition of BL, and its fouling characteristics. To address the above two objectives, this article is structured as follows. We begin with a discussion of the key compositional characteristics and physicochemical properties of BL and outline the general membrane characteristics and materials that have been used. We then present a consideration of the membrane characteristics as a function of membrane type and operating configurations. The effects of fouling are also investigated. We conclude with a discussion of the economics of different BL concentration membrane configurations.

### Composition and physicochemical properties of black liquor

BL composition depends significantly on the pulping process and on the type of biomass feedstock used. Common wood sources include softwoods (such as pine), hardwoods (such as eucalyptus), and fibrous plants (such as bamboo). The dry solids content in BL can be represented either as the total dissolved solids (TDS) or as the total solids (TS). TS include both the dissolved solids and the suspended solids that exist as particles or colloids in BL, such as lignin. Tables 1 and 2 summarize key information relevant to the discussion in this section. The main inorganics (Table 1) include NaOH, Na₂S, Na₂CO₃, Na₂SO₄, Na₂S₂O₃, NaCl, and SiO₂ (if non-wood BL), with most of the sodium present in BL bound to the phenolic hydroxyl groups in lignin. Table 2 summarizes the typical relative amounts, concentrations, and weight-average molecular weights (Mₚ) of the three major organic components in BL. The most abundant organic component in BL is the degraded lignin, which exists in BL as colloidal macromolecules that have a high degree of cross-linking. Recovered lignin is valuable because in addition to its

### Table 1. Main inorganic solutes in Kraft black liquor.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(% TDS Basis)</th>
<th>kg/m³</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂CO₃</td>
<td>6.6–12.3</td>
<td>2.05–3.5</td>
<td>[3, 20–26]</td>
</tr>
<tr>
<td>NaOH</td>
<td>1.3–2.4</td>
<td>0.14–40</td>
<td>[3, 21–23, 25, 27, 28]</td>
</tr>
<tr>
<td>Na₂S₂O₃</td>
<td>0.5–4.1</td>
<td>4.7–5.8</td>
<td>[21–23, 29]</td>
</tr>
<tr>
<td>Na₂S</td>
<td>–</td>
<td>0.88–1.11</td>
<td>[3, 25, 26]</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>0.9–8.3</td>
<td>–</td>
<td>[20–24]</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.5</td>
<td>–</td>
<td>[31]</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.2–0.7 (wood)</td>
<td>–</td>
<td>[24, 30]</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1–30 (grasses)</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>

### Table 2. Main types of organic species in Kraft black liquor and some typical ranges.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mₚ (Da)</th>
<th>Wt% dry solids</th>
<th>Conc. kg/m³</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slightly degraded</td>
<td>Up to 6,000–18,900</td>
<td>0.1–9</td>
<td>0.1–30</td>
<td>[9, 15, 20, 27, 32, 39, 45, 46, 48, 50–53]</td>
</tr>
<tr>
<td>Hemicelluloses</td>
<td>on order of 10²</td>
<td>25–35</td>
<td>26–47</td>
<td>[31, 47, 48]</td>
</tr>
<tr>
<td>Significantly degraded</td>
<td>Hemicelluloses</td>
<td>(carboxylic acids)</td>
<td>on order of 10²</td>
<td>0.3–6.7</td>
</tr>
<tr>
<td>Extractives</td>
<td>on order of 10¹</td>
<td>0.3–6.7</td>
<td>0.5–2.1</td>
<td>14–33</td>
</tr>
<tr>
<td>Inorganics</td>
<td>on order of 10¹</td>
<td>0.3–6.7</td>
<td>0.5–2.1</td>
<td>14–33</td>
</tr>
</tbody>
</table>
ability to produce energy from the combustion, lignin has many component species, which can be used in place of petroleum-derived molecules as building blocks for higher-value chemicals. The most common current commercial uses of lignin are as dispersants, as binders, and in steam/power production.\(^{[14,52,58]}\)

The phenolic hydroxyl and carboxyl functional groups in lignin help to stabilize it in BL (e.g., as in Eq. (1)):\(^{[2,24]}\)

\[
R - OH + NaOH \rightarrow R - ONa + H_2O
\]  

(1)

Because BL is highly alkaline, the hydroxyl groups dissociate at higher pH, making the usually hydrophobic lignin more hydrophilic with a negative surface charge.\(^{[34]}\)

If a hydrophilic membrane is used, lignin could interact strongly with the membrane surface and decrease the water flux.\(^{[54]}\) At pH above 12.5, enough phenolic groups have become ionized to enable lignin to take a more compact and spherical particle shape, thus making it easier to handle in feed streams.\(^{[1,2]}\) Even though the \(M_w\) of lignin in BL can vary widely (with extremes <1 and >50 kDa), the \(M_w\) is usually 0.8–9.9 kDa (Table 2), and the polydispersity index is 3.6–4.5, with lignin in softwood BLs generally having a higher \(M_w\) than lignin in hardwood BLs.\(^{[1,4,38,39]}\)

In addition to lignin, the other main organic compounds in BL are hemicelluloses (including their broken-down products in the form of carboxylic acids) and wood extractives. The kinds and amounts of hemicelluloses differ between different wood species. For example, the main hemicellulose in hardwood is glucuronoxylan, while it is galactoglucomannan in softwoods.\(^{[23]}\) Although the \(M_w\) of hemicelluloses vary in BL because of varied amounts of degradation based on different cooking conditions and biomass species, hemicelluloses also tend to entangle, taking up more volume/molecule than lignin, generally making them easier to remove during filtration.\(^{[1,51]}\)

Table 2 shows some typical ranges of hemicellulose properties in Kraft BL. Hardwood xylans have a greater resistance to degradation than their softwood counterparts; hence, softwood hemicelluloses tend to be more degraded and thus have lower \(M_w\).\(^{[59]}\) Extractives are the much lower \(M_w\) compounds that come from the wood itself and include resins, fats, waxes, oils, proteins, terpenes, and other small organic species.\(^{[15]}\) Extractives could be refined to make biodiesel and hemicelluloses (including the degraded products as carboxylic acids) could be used in hydrogels and as a paper additive among other applications.\(^{[6,52,60,61]}\)

During the concentration (up to 30–40 wt% TS at ~80°C–95°C) and chemical recovery of BL with membranes, BL behaves as a Newtonian fluid, although it can be shear thinning at low enough temperatures and high enough TS concentrations.\(^{[2,26,62]}\)

Figure 2 shows how typical BL viscosity can vary with shear rate, temperature, and total solids. As the BL TS concentration increases, BL viscosity also increases significantly. Higher BL concentrations also result in greater osmotic pressure, which lowers the flux drastically at a given transmembrane pressure differential (TMP).\(^{[14]}\) Nordin et al.\(^{[46]}\) showed that beyond a TS concentration of 31–35 wt%, the pump energy costs substantially increase (e.g., by 400% from 35 to 44 wt% at velocity of 2 m/s) and the permeate flux significantly decreases (e.g., by 86% from 31 to 44 wt%) at 2 m/s (Fig. 3).\(^{[46]}\) Because of the above factors, membrane concentration of BL is practically limited to about 30–40 wt% TS, with further concentration requiring traditional reboilers.

Membranes for BL treatment: General characteristics

The full range of membrane processes has been investigated for BL treatment: microfiltration (MF),\(^{[4,33,63–65]}\) ultrafiltration (UF),\(^{[9,31,33,35,38,41,44,45,54,66]}\) nanofiltration (NF),\(^{[3,9,31,45,54]}\) and reverse osmosis (RO).\(^{[67]}\) With UF studied the most. Table 3 summarizes the approximate range of membrane molecular weight cutoff (MWCO) values, pore sizes, and transmembrane pressures (TMPs) that can be used for BL treatment.\(^{[58,68–73]}\) MF membranes investigated for BL treatment are typically symmetric and have a single layer.\(^{[74]}\) This is in contrast to UF, NF, and RO membranes, which are asymmetric and consist of a thin, active membrane layer on top of a thicker and highly porous support, which provides mechanical strength and stability.\(^{[74]}\) The different types of membrane pores can be functionally characterized by their MWCO values, which correspond to the \(M_w\) of a test species that has a rejection coefficient of about 0.90.\(^{[34,74,75]}\) RO would reject all
inorganic and organic species, NF is capable of almost complete rejection of lignin and hemicellulose (non-carboxylic acids), while UF (and MF) would allow only the largest lignin and hemicelluloses to be rejected while permeating the smaller organics and inorganics. In BL concentration studies, membranes have been operated either in dead-end mode (wherein the direction of fluid-phase flow is perpendicular to the membrane surface) or in cross-flow/tangential-flow mode (in which the direction of fluid flow is parallel to the membrane surface), as shown in Fig. 4. More specifically, BL concentration membranes have been operated in stirred-cell, unstirred-cell, or rotated-cell modules, whereas larger-scale tests have been carried out in flat-sheet, spiral-wound, plate-and-frame, and shell-and-tube (including hollow fiber) modules.

**Figure 3.** (a) Flux trends and (b) energy demands for different cross-flow velocities at a TMP of 300 kP (adapted from Ref.).

**Table 3.** Characteristics of MF, UF, NF, and RO membranes for BL concentration.

<table>
<thead>
<tr>
<th>Membrane Type</th>
<th>Pore size (nm)</th>
<th>MWCO (kDa)</th>
<th>TMP (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MF</td>
<td>20–10,000</td>
<td>100–5000</td>
<td>0.1–0.5</td>
</tr>
<tr>
<td>UF</td>
<td>1–50</td>
<td>15–400</td>
<td>0.1–20</td>
</tr>
<tr>
<td>NF</td>
<td>0.5–4</td>
<td>0.1–20</td>
<td>1–3</td>
</tr>
<tr>
<td>RO</td>
<td>0.2–1.5</td>
<td>&lt;0.8</td>
<td>3–20</td>
</tr>
</tbody>
</table>

**Figure 4.** Membrane permeation setups commonly used in the literature for concentration of black liquor using (a) cross-flow (tubular shown here) or (b) dead-end operational modes (adapted from Refs.).
While most of the BL membrane literature focuses on pressure-driven separation of high-MW components, one may also consider electrodialysis (ED) membranes to directly recover Na\(^+\) ions (in the form of NaOH) from a BL stream while simultaneously removing a portion of the lignin. Generally speaking, ED can remove up to 40%-60% of the dissolved ions.\[^{[88]}\] The amount of energy used is directly proportional to how many ions pass through the membrane.\[^{[73]}\] In the traditional ED process (Fig. 5a), only ions (and not water) pass through the membrane. The polymeric membranes are either anion permeable or cation permeable. At the cathode, reduction occurs and water is converted into OH\(^-\) ions and H\(_2\) gas. At the anode, H\(^+\) ions and O\(_2\) gas are produced. ED systems are typically fabricated as flat-sheet membranes in plate-and-frame modules.\[^{[69]}\] The configuration in Fig. 5b is a recent example showing the removal of sodium and lignin from BL. Na\(^+\) ions from BL pass through the cation-selective membrane to react with OH\(^-\) ions produced from the water reduction on the cathode to achieve 43%-51% sodium recovery.\[^{[10]}\] The reduction in pH due to NaOH removal also results in precipitation of lignin. Salt solutions (NaOH and Na\(_2\)SO\(_4\)) were added to the cathode side to reduce voltage drop, thereby increasing efficiency.\[^{[89]}\] While the generation of large amounts of O\(_2\) and H\(_2\) gases is likely undesirable from operational and safety perspectives, the H\(_2\) could be recovered and sold to help offset the costs of this process.\[^{[90]}\]

More advanced ED techniques can be used, such as those involving bipolar membranes (Fig. 5c). Anion-permeable and cation-permeable membrane pairs are still used, but the two types of polymeric membranes are now laminated together. In between the two membranes, there is an intermediate/junction layer (J-layer) where water is split into H\(^+\) and OH\(^-\) without the generation of any gases. Unlike conventional ED, the presence of water in the J-layer is due to the diffusion of water through the membranes in addition to ion permeation. In conventional ED, the generation of H\(_2\) and O\(_2\) gases uses about half of the electrical energy used for the process. Thus, ED with bipolar membranes can be much less energy intensive. The theoretical amount of energy consumed to maintain the voltage drop near the water splitting voltage of 0.83 V is about 600-700 kWh per ton of NaOH produced.\[^{[91]}\]

**BL membrane flux and rejection: Relevant theory**

In this section, we summarize the currently accepted theoretical description and experimental understanding of the key performance parameters of pressure-driven BL concentration membranes: flux, rejection (selectivity), and fouling behavior (including concentration polarization effects). The TMP is the driving force that pushes the permeate through the membrane pores. The osmotic differential pressure, caused by the presence of different solute concentrations on the feed and permeate sides, opposes permeation. As a result, the flux of the solvent can be written in the well-known form of Eq. (2), where \(J\) is the solvent flux, \(P\) is the membrane permeance (permeability divided by the membrane thickness), \(\Pi\) is the osmotic pressure, \(\Delta P - \sigma \Delta \Pi\) is the net driving force, and \(\sigma\) is the osmotic...
reflection coefficient. A σ value of unity implies complete solute rejection, while a σ value of zero implies that all of the solute passes through the membrane. The osmotic pressure is directly related to the solute concentration. Various correlations exist in the literature, the simplest of which is the linear proportionality of osmotic pressure and solute concentration obtained from the van’t Hoff equation and which is valid for dilute solutions. In more concentrated solutions, the osmotic pressure is often correlated to power-law or polynomial functions of the solute concentrations in which the constant parameters are fitted experimentally. The osmotic reflection coefficient couples the solvent transport to the rejection of the solutes.

\[ J = P \left( \Delta P - \sigma \Delta \Pi \right) \]  

(2)

Because MF and UF are driven by bulk flow, it is also common to express Eq. (2) as Eq. (3), where permeance is rewritten to express the effects of solution viscosity (\( \mu \)) and the membrane’s inherent resistance to flow, \( R_m \). Since σ is ~0 due to the large pore sizes in MF and UF, the osmotic contribution can be neglected. Additional resistances can be added to quantify the effects of factors that decrease steady-state flux (e.g., concentration polarization, \( R_{cp} \)).

\[ J = \frac{\Delta P - \sigma \Delta \Pi}{\mu R_m} \]  

(3)

The BL membrane literature usually reports solute rejection values/percentages or solute rejections as a measure of the membrane selectivity toward (or against) that solute. The “observed (or apparent) rejection” (also called “retention” in some works) is defined as \( R_{obs} = 1 - C_p/C_b \), where \( C_p \) and \( C_b \) denote the permeate and bulk feed concentrations, respectively. Some authors also use the retentate concentration in place of bulk concentration, particularly when reporting rejections in experiments where the retentate concentration significantly changes (e.g., dead-end cells). The “real” or “intrinsic” rejection is \( R_{int} = 1 - C_p/C_m \), where \( C_m \) denotes the actual concentration of the solute near the membrane-feed interface. For solutes with a high osmotic reflection coefficient, \( R_{int} \) is greater than \( R_{obs} \) because the solute concentration at the membrane surface is greater than in the bulk feed due to concentration polarization. A useful relationship between the two rejections, the volumetric flux of the permeate through the membrane (\( J_v \)), and the solute mass-transfer coefficient, \( k \), can be derived that accounts for the backdiffusion of a polarized solute into the bulk feed as shown in Eq. (4). A plot of the right side versus the volumetric flux gives a linear relationship, allowing \( R_{int} \) and \( k \) to be determined.

\[ \ln \left( \frac{1 - R_{obs}}{1 - R_{int}} \right) = \ln \left( \frac{1 - R_{int}}{R_{obs}} \right) + \frac{J_v}{k} \]  

(4)

Bhattacharjee et al. examined models based upon irreversible (non-equilibrium) thermodynamics for predicting solvent and solute fluxes as well as the solute rejection in BL concentration for UF membranes. The Spiegler-Kedem (SK) model (combined with film theory to also solve for \( k \) shown in Eq. (5)) relates the observed solute rejection to the mass transfer coefficient of TDS or TS, solvent volumetric flux, solute permeance (\( P_s \)), and \( \sigma \). The SK model outperformed the KK model significantly under predicted the flux. Similarly, in Fig. 6b, flux over time is plotted at different TMPs. Again, the SK model outperformed the KK model with closer agreement to experimental data. The SK model was also better at predicting the permeate TS concentration based on the TMP. The poorer performance of the KK model is likely due to its coefficients being dependent on concentration itself, while the SK model’s coefficients are not dependent on concentration. This independence would allow better predictions of flux and other properties, which are influenced by concentration.

Membrane materials for BL concentration

Figures 7 and 8 illustrate the important milestones in the history of development or evaluation of membrane materials for BL concentration. Primarily polymeric membranes and ceramic (metal oxide) membranes have been investigated. Tables S1 and S2 (Supporting Information) give an overview of the main types of polymeric and ceramic membranes, respectively, that
have been investigated for MF, UF, and NF, and RO concentration of BL. Some of the key developments are discussed in more detail in this section.

The first important usage of membranes for BL concentration appears to have been made by DDS Corporation in Norway in the 1970s, although sulfide (not Kraft) BL was used. This early work included the application of cellulose acetate RO membranes to concentrate BL from 6 to 12 wt% TS. This trial was followed by another usage of DDS cellulose acetate membranes in 1978 in Quebec, Canada, which achieved concentrations of TS from 12 to 18 wt%. The cellulose acetate RO membranes used in both of the above plants had lifetimes of about 1 year. Additionally, these
membranes required cleaning 2–6 times per week because the TS content of BL clogged the pores and fouled the membranes. About a decade later, Ross et al. studied UF concentration of Kraft BL with 10- and 20-kDa MWCO polysulfone membranes. However, these membranes displayed very low rejection of lignin at industrially realistic pHs of 11.3 and 12.5, likely due to membrane degradation. Also, in 1985, Jönsson et al. reviewed the applications of membranes in the paper industry and found that while UF could concentrate Kraft BL from 17 to 23 wt% BL, the heating value of the retentate and permeates were lower than those of the feed BL, making the concentration not worthwhile unless there was a significant market for lignin. Also, an RO laboratory and pilot-plant study was performed on 1–5 wt% BL, but the flux fluctuated widely as feed temperature and pH varied. The RO membrane (DDS HR 95, material not reported) used was stable for at least 2 months.

Cellulose acetate and polysulfone-based membranes were initially used, likely due to their commercial availability. However, while some of these membranes could provide fairly high rejections (e.g., up to 75% rejection of lignin, though at low pH of 10.2), their major drawback has been long-term stability, likely from degradation in the high pH environment. In recent years, polyethersulfone (PES) membranes have gained prominence because of their higher stability, yet the challenge is still to achieve high rejections of organics and ideally even inorganics. Arkell et al. showed that at 70°C, the latest industrial membranes could achieve 90%–97% lignin rejection, with the 90% rejection membrane having the best performance due to its higher flux. Others have proposed combining carbonation (to precipitate lignin) with UF and/or NF to achieve higher rejections. Nevertheless, it is expected that salt rejections are lower than those of organics because of the smaller Mw and size of the inorganic ions. There is a need for stable membranes that can perform RO to separate not only the organics, but also the inorganic species from water in BL.

A general problem with many polymeric membranes used to date is their short (<1.5 years) lifetime and requirement for frequent cleaning, thereby leading to potentially higher capital and maintenance costs. To address these issues, there has been considerable focus in recent years on inorganic (specifically metal oxide) membranes that are more robust and resistant to the high pH and temperature of BL feeds. Ceramic membranes, such as the commercially available Kerasep membranes (made from Al2O3–TiO2) have a general lifetime of about 6 years in caustic solutions. Ceramic membranes also tend to have higher mechanical strength and have been operated successfully at feed
Typically, these commercially available membranes are Al₂O₃, TiO₂, or ZrO₂ membrane layers on top of ceramic supports. All of these membranes, however, have pore sizes that are too large for NF or RO applications. For example, aluminum oxide membranes synthesized using anodic oxidation can achieve a minimum pore size of ~10 nm, which is not sufficient for good NF or any RO separation.¹⁰¹

Although ceramics are generally considered as better membrane materials than polymer membranes for BL concentration because of their thermal and chemical stability, the membrane cost must also be considered. Ceramic membranes are typically more expensive than polymeric membranes. As an example, Arkell et al.⁹ applied their laboratory-scale results of lignin rejection by both ceramic and polymeric NF membranes to estimate the economics of an industrial-scale process.⁹

The cost of polymeric NF membranes used in their study was only about 10% of the ceramic NF membrane cost. On the other hand, the ceramic membrane had a rated lifetime of 6 years compared to the 1.5 years life of the polymeric membrane. Although the ceramic membrane was more stable, calculations showed that the higher lignin rejection of the polymeric NF and its low purchase cost resulted in it being the most economical BL concentration choice. In comparison with using just the NF polymeric membrane, the ceramic NF membrane was 48% more expensive, and the combination of a ceramic UF and the polymeric NF was 161% more expensive.⁹ These estimates indicate the need for non-polymeric membranes with lower manufacturing costs and better lignin rejection if they are to be competitive with current polymeric membranes.

As mentioned earlier, ED membranes may have potential due to their ability to recover the Na⁺ ions in the form of NaOH. Both conventional and bipolar ED membranes must have both acid and base chemical stability since they are exposed not only to BL but also the concentrated base/acid solutions that result from ion transfer through the membranes as well as any sweep solutions used to minimize the applied voltage. In ED using bipolar polymeric membranes, the acid or base concentrations can be as high as 4 M. Similar to the case of NF membranes, many ED membranes are stable in acids but have stability issues at high pH. Membrane swelling and higher temperatures also pose problems because the ion-selective membrane functional groups can be lost and the membrane may thermally expand.¹⁰² Examples of “stable” membrane materials that have been used for ED at high pHs include polysulfone (PSF) and PES and thus could be useful in BL applications. Also, the commercially available Nafion (e.g., N117,¹⁰ 324¹⁸⁹) (from DuPont, USA) and CMB¹⁰³ (Neosepta, Japan) membranes have been used in ED studies for BL concentration and are generally stable at high pHs. However, the capital cost of such membranes could be prohibitively expensive at the large scales required for BL processing. The energy costs of ED-based processes vis-à-vis pressure-driven membranes are yet to be compared in detail. Unlike the case of NF membranes, there does not currently exist a detailed technoeconomic analysis for the use of ED membranes, or even other types of membranes such as forward osmosis (FO) membranes, for BL processing applications. A technoeconomic analysis of this nature, if found to yield promising results, could increase the available process options and broaden the challenges to be overcome in membrane development.

Separation of BL components

As mentioned previously, the large range of membrane separations (MF, UF, NF, and RO) have been investigated for concentration of BL with both polymeric and ceramic membranes, as detailed in the previous section and in Tables S1 and S2 (Supporting Information). Ceramic-based membranes have pore sizes in the MF/UF range and at best, the high molecular weight end of NF. Consequently, polymeric membranes are still used for NF, sometimes in combination with ceramic UF. Future research is likely to move toward introduction of non-polymeric NF and even RO membranes that could offer the advantages of stability and efficient operation at every molecular weight range. RO would be particularly beneficial since it would allow the full capabilities of separation of BL components. In the published literature, NF is the primary membrane type currently being considered for lignin rejection. The development of better NF and RO membranes would permit not only the almost complete rejection of lignin (and all other organics), but would also allow the separation of free salts, further reducing the energy load and scale formation issues in the downstream evaporators and boilers. Below, we discuss some of the key advances in the literature regarding the separation of each of the major components in BL.

Concentration of lignin

The concentration and removal of lignin from the WBL feed stream (and thus the TS concentration of WBL to SBL) are the most common objectives in the BL separation literature. This involves the use of UF or NF membranes to transport water and other low-Mw BL components into the permeate stream, thus producing...
investigated the effects of membrane pore size on lignin rejection. They used three different tubular α-alumina (Al₂O₃) membranes with pore sizes of 50 nm, 0.2 μm, and 0.8 μm (i.e., UF and MF range). These membranes achieved similar lignin rejections of about 75% (likely due to the feed pH of 11, resulting in larger/aggregated lignin molecules that could be rejected by even the largest pore sizes studied) while also maintaining high long-term fluxes. Interestingly, the flux of the 0.2-μm membrane was the highest (0.2–0.3 m³ h⁻¹ m⁻²) for most of the concentration range), while the 50-nm and 0.8-μm membranes had similar lower fluxes. The reason for this is not known. Also, the 0.2-μm membrane had high long-term fluxes, not experiencing major fouling for up to 35 days. Arkell et al. examined the flux, lignin retention, and overall cost of removing lignin from softwood kraft BL. Specifically, they were interested to examine the results of a UF and NF combination compared to a NF only. The UF membrane was ceramic (Al₂O₃ with a surface layer of TiO₂), while one ceramic (TiO₂) and three polymeric composite membranes were tested for NF. At the same MWCO of 1 kDa, the polymeric NF membrane outperformed the ceramic membrane, achieving lignin retention of 90% compared to 80% with the ceramic membrane (with no UF pretreatment). This was because while the manufacturer’s MWCO ratings were the same, a literature study showed that the NF’s pore size was actually somewhat larger than the polymeric membrane. This ambiguity in the MWCO has been observed before. Causserand et al. showed that the observed rejection (used to determine the MWCO) can vary strongly with the operating conditions (which are rarely specified). For example, the observed rejection decreased from 90% to 40% for a 20-kDa PEG as the flux increased (from increasing the TMP). Interestingly, adding an UF prefiltration step decreased the lignin rejection of the ceramic NF membrane from 80% to 56%, while little change was observed with the polymeric membrane of similar MWCO. Again, this was likely because of the larger pore size (larger molecules were retained by the UF but passed through the ceramic NF more easily than the smaller pore-sized polymeric NF). However, the permeate flux was always higher in the NF membranes after a UF pretreatment, likely from the reduction in fouling species and osmotic pressure.

Several authors have reported the interesting observation of a non-monotonic behavior of lignin rejection as a function of membrane MWCO in MF and UF. For example, the results of Hill et al. on polymeric membranes are shown in Fig. 9a. The rejection value passes through a minimum as a function of MWCO, with a 500-kDa membrane having almost as high rejection coefficient as a 20-kDa membrane. It is also surprising that membranes with very high MWCOs have any lignin rejection at all. This trend is also reported in other works and has been attributed to gel layer formation. Lignin is hypothesized to form a relatively dense, dynamic gel layer either at the membrane surface or within the large pores of high-MWCO membranes, resulting in a lower effective MWCO and an unexpectedly high rejection. For lower-end UF and NF, the trend is more clear, as shown in Fig. 9b, which plots data from Tables S1 and S2 for different types of polymeric and ceramic membranes under known or likely conditions of high (unchanged) pH (if pH has been artificially lowered, lignin tends to get larger and thus will likely show higher rejection values than normal). The pore sizes...
of the membranes were not reported in these studies, but were estimated using a literature correlation and the reported MWCOs.\textsuperscript{[80]} Lignin rejection sharply increased at a critical pore size of $\sim 3.5$ nm ($\sim 15$-kDa MWCO) to achieve a maximum lignin rejection of $\sim 60\%$ and again at $\sim 1.3$ nm ($\sim 1$-kDa MWCO) to achieve $>64\%$ rejection. It is also worth mentioning here that hardwood hemicellulose was easily retained in most UF and NF membranes due to its generally higher $M_w$ than lignin. For example, Jönsson et al.\textsuperscript{[45]} reported greater than $80\%$ retention of hemicellulose even with a $100$-kDa membrane, whereas a lignin retention of $61\%$ was observed with a $4$-kDa membrane.\textsuperscript{[45]} Overall, Arkell et al.\textsuperscript{[9]} reported the highest lignin concentrations (from 74 to $252$ kg/m$^3$ with their $1$-kDa ceramic membrane and from $63$ to $282$ kg/m$^3$ with their $1$-kDa polymeric membrane).\textsuperscript{[9]} Unfortunately, no data on the TS of the retentate were given. Otherwise, the highest published TS concentrations are from Jönsson et al., who concentrated BL from $16$ to $29$ wt\% TS.\textsuperscript{[45]}

\section*{Separation of valuable components and value-added products}

As discussed earlier, BL contains a number of organic species. The main organic species are lignin and hemicellulose/carboxylic acids. Due to the lack of appropriate separation technology, most of the valuable BL components are not industrially usable at the moment. Lignin has several direct uses and potential uses for higher value-added products.\textsuperscript{[104]} Concentrated lignin can be gasified to $H_2$, $CH_4$, and CO for use as energy-efficient and low-carbon fuels.\textsuperscript{[10]} Lignin is non-toxic and has FDA approval for usage in food and packaging.\textsuperscript{[104]} The biggest usage of lignin is in commodity markets while specialty markets have less market share because they require additional processing or modification of lignin.\textsuperscript{[104]} Actual uses in commodity markets include as cement/concrete additives ($\sim 50\%$ of what little lignin is diverted from the recovery boiler goes to this use alone), binders, animal feeds, and viscosity reducers in molasses and oil well drilling muds.\textsuperscript{[18, 27, 33, 52, 104, 105]} Specialty market uses have included production of vanillin, pesticides, oil well cement retarders, gypsum board, dispersants, carbon black, inks, industrial cleaners, micronutrients, and lead acid batteries.\textsuperscript{[14, 18, 27, 33, 34, 38, 52, 54, 58, 104]}

Hemicelluloses and their degraded products as carboxylic acids ($M_w$ as small as $100$ Da) are the second most abundant organic component in BL solids. The heating value of carboxylic acids is lower compared to lignin; thus, greater benefit could potentially be derived if the carboxylic acids were instead used to make higher-value products such as biodegradable polymers.\textsuperscript{[60, 66]} Due to the diversity of carboxylic acids present in black liquor, their wide range of $M_w$s, and lack of effective separation and purification processes, little work has been done to recover them from BL. Two recent articles have proposed using UF followed by other unit operations (Fig. 10) not only to remove and purify lignin but also to recover the valuable carboxylic acids such as hydroxy acids.\textsuperscript{[60, 66]} To accomplish the recovery of hydroxy acids from soda BL, Hellstén et al.\textsuperscript{[60]} demonstrated a separation process combining a $1$-kDa MWCO PES UF membrane, size exclusion chromatography, ion exchange, adsorption, and evaporation (Fig. 10a).\textsuperscript{[60]} UF removed up to $75\%$ of the lignin, with

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure10.png}
\caption{Two separation processes for recovery of hydroxy acids from soda black liquor. SEC is size exclusion chromatography (reproduced with permission from Refs.\textsuperscript{[60, 66]}).} 
\end{figure}
the remainder being removed by an adsorption column. These two unit operations combined resulted in 99% removal of lignin. Alkalis in the UF permeate were removed by size exclusion chromatography and ion exchange. In the final step, evaporation was used to separate volatile acids and water from hydroxy acids. Specifically, hydroxy acid purities of up to 81 wt% and yields of up to 91% could be obtained. The final separation step could potentially be carried out using a hydrophilic NF membrane that permeates water to lower energy costs by reducing the amount of water that needs to be evaporated.

Manttari et al.\[66\] first filtered BL with an UF membrane (1.2-kDa MWCO, 75% lignin rejection) and then used acid precipitation (to remove the rest of the lignin), followed by cooling crystallization, NF filtration (0.15–0.3-kDa MWCO) and adsorption (with vacuum filtration in between steps) to recover and purify hydroxy acids (Fig. 10b).\[66\] In this configuration, the UF stage separated the much smaller hydroxy acids from lignin, concentrating the hydroxy acids in the permeate (since charge effects favored hydroxy acid permeation). However, it affected downstream processes by reducing flux, lignin recovery, and hydroxy acid purity. A NF membrane downstream can be used to separate the hydroxy acids from the remaining inorganic species and water. In addition to size of solutes, charge effects are very important in the membrane filtration steps. At the high pH of the UF stage, lignin and hydroxy acids have negative charges. As the negatively charged lignin was concentrated, the significantly smaller hydroxy acids permeated faster, resulting in permeate concentrations 1.4x that of feed black liquor to maintain feed electroneutrality by the Donnan exclusion principle. However, the NF membrane feed was in acidic conditions wherein the hydroxy acids were protonated, and thus, size alone achieved their separation and concentration from inorganics and water. Without the UF, the hydroxy acid purity increased from 21% in BL to 80% in the NF permeate.\[66\]

The above discussion also suggests that purification of BL components will benefit from the development of more stable UF, NF, and molecular sieving membranes with tunable pore sizes. A multistage membrane process could be envisioned wherein the first one or two stages would separate the lignin and carboxylic acids (without the cost of acidifying chemicals) yet maintaining high fluxes. The final NF (or molecular sieving) membrane stage would concentrate the carboxylic acids by permeating water and inorganics. Ideally, these membranes should be negatively charged to favor lignin retention and the Donnan exclusion principle would still apply to maintain feed electroneutrality, thereby first helping carboxylic acids permeate in the initial two stages but then favoring inorganics permeation in the final NF stage to purify and concentrate carboxylic acids.

Under certain conditions (e.g. in hardwood pulping, as mentioned in section on “Composition and Physicochemical Properties of Black Liquor”), some hemicelluloses (like xylan) can remain relatively large and are not significantly degraded into the small carboxylic acids. Xylan is a dominant hemicellulose in hardwood (Mw 6–19 kDa, ~0.1–1.3 wt% in BL), which can be used as a feedstock for production of building-block chemicals like furfural, as a colorant, and as a viscosity reducer in drilling fluids.\[52, 106\] In 2013, the world market for furfural was approximately 300,000 tons per year and is forecast to reach about 650,000 tons by 2020.\[107, 108\] Lake proposed the use of acid precipitation in conjunction with membranes and other unit operations to purify the xylan component in BL for use in furfural synthesis (Fig. 11).\[85\] The process begins by conventional acid precipitation of lignin using CO2, until the pH is reduced to 8.5–9.5. This would remove most of the lignin, which would be retained along with the xylan hemicellulose in membrane separation processes. Furthermore, the reduced pH allows greater flexibility in the choice of membrane materials, since many membrane materials are quite stable at pH 8.5–9.5 but unstable at the high pH (~12) of raw BL. However, as mentioned previously, acidification may have high chemical costs and other supporting costs (e.g., piping and storing pressurized CO2).\[19\] The next step is a tubular UF membrane (MWCO 1.5–2 kDa) process to concentrate the xylan hemicellulose as retentate while allowing most of the water, salts, and low-Mw organics (including any extensively degraded hemicelluloses as carboxylic acids) to permeate. A spiral-wound NF membrane (MWCO 0.15–0.5 kDa) is then used to purify the xylan-rich retentate by completely rejecting xylan while permeating water, salts, and the lowest Mw organics. It is noted that while the NF membrane alone could achieve the desired xylan purity and concentration without UF pretreatment, this may be difficult in practice due to low fluxes and severe fouling. UF pretreatment helps to eliminate most of the undesired fouling components as well as decrease the volume of liquid for processing by the NF unit operation. The concentrated and high-purity hemicellulose solution is then sent to a catalytic reactor wherein xylan is converted to furfural. A final step involves production of pure furfural by its separation from water and xylan. This can be performed by distillation or solvent extraction, but could also potentially be carried out by nanoporous membranes. BL also contains a number of other low-Mw (on order of 0.1 kDa) dissolved organic compounds that appear in the
permeate streams of UF or NF membranes. These low-
M\textsubscript{w} organics include formic and acetic acids, and
extractives such as tall oil and resins.\textsuperscript{[49, 85, 109]} New
membrane technology for separation of dissolved
lower-M\textsubscript{w} BL components from each other may allow
increased usage of these BL components as feedstocks
in a biorefinery scenario (e.g., for the production of
biofuels).

**Separation of BL inorganics from organics**

Conventionally, the inorganic salts present in BL
(Table 1) are recovered as smelt after combustion of
the SBL stream exiting the evaporators (Fig. 1).\textsuperscript{[44]} The
main monovalent ions are primarily sodium (Na\textsuperscript{+}),
with potassium (K\textsuperscript{+}) present in smaller amounts.
Current studies on BL concentration membranes
focus on UF or NF to concentrate lignin and hemicel-
luloses while permeating water and ions. An energy-
efficient membrane process for BL concentration and
inorganics recycling would include a downstream RO
system that permeates water and produces concen-
trated alkaline brine containing the inorganic ions and
dissolved low-M\textsubscript{w} organic solutes. In addition to the
usual requirements of high salt rejection, good water
flux, and fouling resistance, these membranes should be
fabricated from materials capable of withstanding the
high pH of the UF/NF permeate stream. This require-
ment is beyond the capabilities of current polymeric
RO membranes, and there are significant opportunities
and challenges in the development of such membranes.
The monovalent ions tend to be free in the bulk
solution, while the multivalent ions tend to be bound
to lignin or other colloids and hence are found in the
retentate of UF membranes.\textsuperscript{[3, 4, 12, 42]} The total con-
centration of monovalent ions is in the range of 3.1–
42.3 kg/m\textsuperscript{3}. The main multivalent inorganic ions that
have been typically retained are Mg, Mn, Fe, and Ca,
with Mg and Mn typically having higher retentions
(70%–90%\textsuperscript{[44]}) and Fe and Ca having lower retentions
(40%–60%\textsuperscript{[44]}).\textsuperscript{[27, 36, 41–44]} These inorganics make up
only a small portion of the TS in BL. Typical rejections
for multivalent ions have been 80%–100% for Mg,
45%–85% for Mn, 40%–71% for Fe, and 40%–81% for
Ca, while the monovalent inorganics had rejections in
the range of 6%–19% since they are permeated by UF/
NF membranes.\textsuperscript{[27, 42, 44]}

We highlight here the work of De et al.\textsuperscript{[3]} who
used cellulose acetate membranes (1 kDa for UF and
0.5-kDa MWCO for NF) to explore three different
membrane separation strategies to recover inorganics
from BL.\textsuperscript{[3]} Scheme A involved carbonation followed
by UF and NF, Scheme B involved carbonation fol-
lowed by NF, and Scheme C relied solely on NF. In
Scheme A, carbonation lowered the pH of BL to 7.5,
which precipitated the now protonated lignin,
thereby releasing salt ions that were formerly associ-
ated with the negatively charged lignin. The UF and
NF stages would then have permeated mostly water
and inorganics. Scheme B used only a NF membrane
after the carbonation step, while in Scheme C, a
single NF stage directly produced a permeate con-
taining mostly inorganic ions and water from raw BL
without carbonation pretreatment.
Figure 12 shows the TDS rejection, inorganic recovery, and permeate flux in each scheme. The reduction of pH by carbonation should have precipitated most of the organic species, thus leading to high TDS rejections in Schemes A and B. Scheme C (with NF only) has a lower TDS rejection, likely due to the permeation of small organic fragments that carbonation successfully precipitated. Schemes A and B both showed good recovery of inorganics due to the carbonation step which released bound cations from lignin, thus allowing for their recovery in the NF permeate stream while Scheme C showed much lower inorganics recovery since a large fraction of alkali cations remained bound to lignin in the absence of carbonation. The higher permeate flux achieved in Scheme A over Scheme B was likely because the UF membrane removed the higher-$M_w$ TDS components and mitigated fouling/pore blockage in the NF membrane. It is interesting to note that Scheme C had the highest permeate flux, with the NF membrane operating at the same pressure differential in all three schemes. This is likely due to the higher concentrations of feed inorganic salts in Schemes A and B, which would increase the osmotic pressure and thus lower the flux. The increased salt concentrations are likely from both the addition of CO$_2$ from carbonation and the release of inorganic
ions from the lignin when the pH decreased. It should be noted that De et al.[3] did not discuss the economics of carbonation versus membrane permeation. The cost of supplying enough CO₂ to achieve the complete pH reduction on industrial-scale BL feeds is likely higher compared to using membranes (see section on “Economics and Energy Requirements”).

**Water separation**

The forest products sector is water intensive.[110] It would thus be desirable to separate water from BL and recycle it, while recovering the inorganic components as concentrated brine that would place a lower load on the inorganics recycling boiler. To our knowledge, there are no works exploring the production of “pure” water from BL using membranes. The direct production of water from raw BL appears prohibitively challenging for two main reasons. First, the osmotic pressure of WBL (~15 wt% TS) is about 7000 kPa as estimated from the correlation for BL based on TS.[69] This is a high osmotic pressure compared to that encountered in the desalination of seawater (about 2500 kPa[111]) and would likely require significant energy costs for pressurization of the BL feed. Second, the presence of large quantities of organic solids (such as lignin and hemicellulose) and dissolved organic molecules in raw BL will certainly lead to high concentration polarization and fouling effects in RO membranes. Thus, it is more reasonable to consider RO membranes for separation of water from the permeate stream of an efficient NF pretreatment membrane. Therefore, the industrial use of RO membranes for producing water for recycle in BL applications is likely to be contingent on the development and acceptance of NF membranes in the Kraft process. Assuming that the NF membrane can achieve near-complete retention of lignin and most of the other higher-M_w organics while allowing permeation of nearly all monovalent inorganics and some of the other low-M_w organics, the TS content of the NF permeate would likely be lowered to <8 wt% (made up mostly of inorganics and lower-M_w organics), which corresponds to an osmotic pressure of ≤3800 kPa. The pH of this stream would likely be close to the feed pH. This represents a feasible opportunity for the development of inorganic/non-polymeric RO membranes that can produce water suitable for recycle while concentrating the inorganics. It is also noted that the salt rejection requirements for such membranes could be somewhat lower than those of desalination membranes, since this application would not require the RO membrane to produce a water stream of potable quality. Also, there is potential that forward-osmosis membranes, which use a high-osmotic pressure draw solution on the permeate side to remove water from the feed by the osmotic pressure driving force, could be used to help lower the energy costs of inorganic concentration.[112, 113]

Electrochemical membrane techniques such as ED offer another interesting method to produce water from a BL stream, by simultaneously removing the inorganic ions as well as precipitating the lignin. This could be achieved using bipolar ED membranes as illustrated in Fig. 5c. The BL feed solution passes through the center and the inorganic cations (Na⁺) and anions (SO₄²⁻) permeate in opposite directions through the membranes under the applied voltage. However, water splits in the junction layer, and the generated OH⁻ and H⁺ ions react with the inorganic ions. Thus, the process yields three product streams: the ion-depleted BL stream, concentrated aqueous acid (e.g., H₂SO₄), and concentrated aqueous base (e.g., NaOH). The BL product will also be depleted of lignin due to precipitation induced by the pH change and hence yield a much more dilute aqueous stream suitable for other membrane processes such as NF or RO to produce water. For example, Cloutier et al.[69] showed (using both softwood and hardwood BL feeds) that ~75% of lignin could be precipitated and about 80% of the Na⁺ salts converted to NaOH. Two polymeric ionomer membranes (Nafion 324 and R-4010) were tested, with the Nafion membrane having superior performance because of its lower energy consumption. On the other hand, Kumar et al.[48] applied ED after acidification. The addition of acid allowed f ~59% of initial lignin precipitation, and the ED operation further increased the lignin removal to 90% along with 90% sodium recovery and 80% of the carboxylic acids).[48] In a third example, Haddad et al.[114] used bipolar membranes with 20 wt% BL at pH 12.25 to reduce the lignin concentration from 40% to ~30% TS while operating at a somewhat higher temperature of 55°C.[114, 115]

ED membrane techniques may become more feasible if they are used with other unit operations, particularly filtration and/or acidification. One such proposed strategy[116] involves first rejecting most of lignin by UF (thereby concentrating BL from 18 to 33 wt% TS), then performing ED on the 16 wt% TS permeate from the UF membrane (which primarily contains inorganics, carboxylic acids, and residual, low-MW lignin). The latter step could simultaneously remove more than 80% of the inorganic ions, precipitate low-MW lignin, and leave carboxylic acids in solution. These carboxylic acids could then be recovered by other processes,
yielding a purified water stream as a by-product. This process was patented in 1986, at which time the available UF and ED membranes were unreliable. To circumvent the membrane stability issues, a 1991 patent proposed to first remove most of the lignin by acidification to pH 9–10, followed by ED to remove the inorganics. However, with ongoing and future advances in the stability and performance of UF/NF and ED membranes, such a process may become economically feasible.

**Polarization, fouling and flux decline in BL concentration membranes**

One of the disadvantages and challenges of pressure-driven membranes is the significant flux decline over time because of concentration polarization and/or fouling. There are several works describing the flux decline behavior in BL concentration membranes. Dafinov et al.[118] reported that the flux dropped ~ 40% from 0.062 to 0.037 m³ h⁻¹ m⁻² for their 5-kDa ceramic (TiO₂) membrane and ~ 69% from 0.058 to 0.018 m³ h⁻¹ m⁻² for their 15-kDa ceramic (ZrO₂) membrane at 0.5 MPa TMP, within about 100 minutes of operation. This is unexpected, since membranes with higher MWCOs usually have higher fluxes. To explain these results, the authors suggested pore blockage of the membranes by lignin macromolecules (which had sizes similar to the 15-kDa pores). The flux then remained stable, with experimental data measured until almost 10 and 24 hrs for the 5- and 15-kDa membranes, respectively. Wallberg et al.[27] showed that with regular cleaning, ceramic (Al₂O₃–TiO₂) UF membranes maintained flux for over two weeks. As can be expected, it was found that the flux decline is more pronounced as the retentate becomes more concentrated. This is generally depicted in plots of flux versus volume reduction, VR ([feed volume-retentate volume]/feed volume).[14] For example, in one study, the flux declined from 0.12 to 0.02 m³ h⁻¹ m⁻² when VR changed from 0 to 0.9. Liu et al.[33, 63] also described similar behavior using ceramic (α-Al₂O₃) MF and polymeric MF and UF membranes (pore sizes/MWCOs: 0.8, 0.2, and 0.22 μm for MF and 3, 6, 10, 30, and 60 kDa for UF) for lignin removal from wheat straw BL, achieving a lignin retention of 70–80%.[33, 63] The polymeric MF was made of cellulose acetate, and the polymeric UF membranes were made from polyacrylonitrile (PAN), polyaryletherketone (PAEK), or polyethersulfone (PES).[33, 63] Periodic cleaning and the use of high cross-flow velocities (to reduce concentration polarization resistance) enabled high fluxes of 0.15–0.24 m³ h⁻¹ m⁻² to be maintained over more than 40 days of operation. For membranes with MWCO < 10 kDa, resistances from pore plugging and gel layer formation dominated whereas at MWCO >10 kDa, concentration polarization was dominant. The intrinsic membrane resistance was minor. While pore plugging and gel layer formation/surface adsorption probably did occur in both types of membranes, the smaller-pore membranes were likely more affected by these phenomena because even slight pore plugging would have significantly reduced the pore size.

Fouling is also an issue for electrically driven ED membranes. As pH decreases during ED, the lignin tends to aggregate and precipitate on the membrane surfaces and on the electrodes.[114, 119] Lignin is negatively charged and particularly fouls the anode.[10] This effect is more pronounced at higher temperatures, and therefore, ED cannot operate at realistic BL temperatures of ~90°C. As in the case of pressure-driven membranes, fouling by lignin deposition could be addressed by periodic backflushing or electrical pulsing.[114] For example, Cloutier et al.[89] achieved more than 100 hrs of continuous operation using back-flushing and consumed 7000 kWh of energy per ton of caustic (NaOH) produced.[89]

**Economics and energy requirements**

Because of the significant industrial interest in BL concentration by pressure-driven membranes, several techno-economic studies on this subject have been published since the late 1980s. Table 4 summarizes the main findings of these works. In an early work on membrane filtration of BL, Uloth et al.[15, 16] compared economic feasibility of lignin removal by acid precipitation and an unspecified UF membrane material.[15, 16] Acid precipitation performed better than UF, being about half as expensive as UF and having better lignin recovery. UF had at best 54% recovery, while acidification could remove up to 95% of the lignin in BL at pH 4. Additionally, the capital (operating) costs for UF were about 1.7 (2.2) times greater. This is initially surprising, since a large amount of acid must be added to precipitate lignin. However, the membrane replacement cost and steam usage were found to be much higher than the chemical cost of precipitation, hence the greater overall cost. Thus, membrane filtration of BL was considered to be prohibitively expensive in the late 1980s.

Since then, advances in membrane technology have improved the economics of membrane-based BL concentration due to higher water fluxes and solute rejections. Table 4 shows that the economic potential has improved significantly, with the total cost/ton of lignin being much lower than even for acidification in most...
Table 4. Summary of technoeconomic data on membrane-based BL concentration. Cost values calculated in the cited works are adjusted in this work to 2016 US dollars.

<table>
<thead>
<tr>
<th>Reference #</th>
<th>Year</th>
<th>Inlet solids concentration (wt% TS/TDS)</th>
<th>BL feed rate</th>
<th>Feed lignin (kg/m³)</th>
<th>Retentate lignin (kg/m³)</th>
<th>Membrane details</th>
<th>Permeate flux (m³/m² h)</th>
<th>Max lignin rejection (%)</th>
<th>Membrane area (m²)</th>
<th>Membrane lifetime (yrs)</th>
<th>Operating time (hrs/yr)</th>
<th>Capital cost (k$/yr)</th>
<th>Operating cost (k$/yr)</th>
<th>Total cost (k$/yr)</th>
<th>Lignin produced (ton/yr)</th>
<th>Lignin production cost ($/ton lignin)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[15, 16]</td>
<td>1989</td>
<td>32.5</td>
<td>0.00925 tons pulp/s</td>
<td>74 (ceramic NF), 63 (polymeric NF)</td>
<td>90 (UF), 165 (NF)</td>
<td>UF (Al₂O₃-TiO₂, 15 kDa); NF (polymer composite, 1 kDa)</td>
<td>0.070, 0.090</td>
<td>52–60 max</td>
<td>X</td>
<td>1</td>
<td>8000</td>
<td>10,215 (6029 acidification)</td>
<td>539, 1379, 2757</td>
<td>12,407 (7006 acidification)</td>
<td>24,000</td>
<td>517 (292 acidification)</td>
</tr>
<tr>
<td>[45]</td>
<td>2008</td>
<td>17</td>
<td>0.05, 0.056 m³/s</td>
<td>59 (UF), 54 (NF)</td>
<td>74 (ceramic NF), 63 (polymeric NF)</td>
<td>UF (Al₂O₃-TiO₂, 15 kDa); NF (Polymer, 1 kDa)</td>
<td>0.082, 0.110</td>
<td>80 (ceramic NF), 90 (polymeric NF)</td>
<td>X</td>
<td>1.5 (polymeric), 6 (ceramic)</td>
<td>8000</td>
<td>301, 953, 1742</td>
<td>3158, 3384, 3948, 4061</td>
<td>72,000, 78,000, 108,000</td>
<td>11, 30, 41</td>
<td>252, 77, 135, 485</td>
</tr>
<tr>
<td>[9]</td>
<td>2014</td>
<td>~17 wt%</td>
<td>0.028 m³/s</td>
<td>59 (UF), 54 (NF)</td>
<td>252 (ceramic NF), 282 (polymeric NF)</td>
<td>NF (polymer composite, 1 kDa)</td>
<td>0.088, 0.17</td>
<td>X</td>
<td>X</td>
<td>8000</td>
<td>301, 953, 1742</td>
<td>301, 953, 1742</td>
<td>X</td>
<td>301, 953, 1742</td>
<td>72,000, 78,000, 108,000</td>
<td>11, 30, 41</td>
</tr>
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cases. Recent studies have compared the usage of UF and NF combinations versus NF or UF alone, as well as comparisons of polymeric and inorganic membranes for these processes. Jónsson et al.\textsuperscript{[45]} analyzed the economics of removing lignin from various parts of the digesting process.\textsuperscript{[45]} A ceramic (Al\textsubscript{2}O\textsubscript{3−}TiO\textsubscript{2}) membrane (15-kDa MWCO) was used for UF, and a polymeric membrane ( unspecified material) was used for NF (1-kDa MWCO).\textsuperscript{[45]} Three scenarios were considered: (A) treating BL directly from the digester with UF, (B) same as (A) but adding a NF step, and (C) using the traditional evaporators to concentrate BL to 31\% TDS and then sending that stream to UF. Although the cost ($41/ton of lignin; adjusted to 2016 value) of the UF/NF combination (B) was about the same as that of using evaporators followed by UF (C), the UF/NF combination resulted in both the greatest lignin concentration and the greatest purity. UF alone (A) at $30/ton (adjusted to 2016 value) of lignin was the cheapest, but its low lignin rejection (~8.5\%) is not sufficient for industrial use. It is noteworthy that even with inefficient UF membranes, the UF/NF combination was a comparable alternative to the evaporators, thus demonstrating the value of replacing some of the evaporation steps with membranes.

Of final note in Table 4 is the 2014 study by Arkell et al.,\textsuperscript{[9]} which used laboratory-scale NF membranes with best lignin rejection reported to date (~90\% for a polymeric membrane and ~80\% for a ceramic membrane, both with MWCOs of ~1 kDa). The laboratory-scale experimental results were used to estimate the economics of an industrial-scale process with a feed flow rate of 0.028 m\textsuperscript{3}/s and a retentate lignin concentration of 230 kg/m\textsuperscript{3}.\textsuperscript{[9]} Both the polymeric and the ceramic membranes had a MWCO of 1 kDa. Based on their estimates (adjusted to 2016 value), the total cost of removing lignin with polymeric (ceramic) NF membranes only was $52 ($77)/ton of lignin. In comparison, a combination of UF and NF was much more expensive, at $135 ($485)/ton of lignin for the polymeric (ceramic) membranes.\textsuperscript{[9]} It is apparent that regardless of the membrane material, NF alone achieved greater recovery at a much lower capital cost and that the polymeric membrane was considered more economical due to its lower fabrication cost despite its much shorter lifetime (1.5 years compared to 6 years for the ceramic membrane).

In order to obtain a more generalized picture of the effects of permeance and selectivity on the economics of BL concentration membranes, and to relate this analysis to currently available membranes, here we consider a simple mass-balance analysis of a single-stage membrane process assign that both the feed and permeate sides are well-mixed. Figure 13 shows the flow diagram of the input and output streams from this process, and the Supporting Information lists all the equations used to describe the mass balances on this membrane process. The feed is softwood BL whose composition based on a BL analyzed in our laboratory, with the mass fractions of lignin (X\textsubscript{Lp}), salts (X\textsubscript{Sp}), and other organic species (X\textsubscript{Op}) being 0.039, 0.048, and 0.063, respectively. The feed flow rate is 0.032 m\textsuperscript{3}/s and is being concentrated from 15 to 30 wt\% total solids at 85°C. The membrane is operating at a TMP of 3000 kPa, and the osmotic (ΔΠI) term is estimated from a literature correlation using the same reflection coefficient extracted from experimental membrane flux data.\textsuperscript{[9, 69]} For the curves, we assume an ideal membrane with 99\% lignin rejection, 15\% salt rejection, and 57\% rejection of other organic species (an arithmetic average of the lignin and salt rejections, since the other organics are intermediate in size between lignin and inorganic salts). Data from the literature use the given lignin rejections, but assume a 15\% salt rejection and an arithmetic average of the lignin and salt rejections to estimate the other organic species rejection, since that data were not provided. It is assumed that all membranes can be operated at 85°C and 3000 kPa without any fouling and no flux decline. Equations (S1)–(S11) (Supporting Information) are then used to solve for the unknown quantities, which are the retentate and permeate mass flow rates (\(\hat{R}\) and \(\hat{P}\), respectively); the mass rejections of lignin, salts/inorganics, and other organic species in the retentate (X\textsubscript{Lp}, X\textsubscript{Sp}, and X\textsubscript{Op}, respectively) and permeate (X\textsubscript{Lp}, X\textsubscript{Sp}, and X\textsubscript{Op}, respectively), as well as the water mass fraction in the permeate (X\textsubscript{WP}).

Figure 14a shows the calculated membrane area versus permeance for the above membrane process. Figure 14b shows the calculated total levelized membrane cost per year versus permeance for different values of the per-unit-area levelized membrane cost. Levelized cost estimates were based on a period of 7 yrs, consistent with that for the manufacture of pulp and paper and of a waste reduction and resource recovery plant.\textsuperscript{[120]} The levelized membrane cost is obtained as the unit-area cost of the membrane ($/m\textsuperscript{3}$) multiplied by the number of membranes (new and replacement) needed for a 7-yr recovery period and the surface area needed (from Fig. 14a). The number of membranes needed was determined by dividing the recovery period by the rated lifetime of a membrane (1.5 yr for polymers and 6 yr for ceramics). Note that operating costs (e.g., electricity for pressurizing and pumping the feed) are not considered here. The capital cost (including replacement costs due to limited stability in BL) of the membranes is the key issue in their industrial adoption, since it is
reasonable to assume that all the membranes considered here will provide similar energy savings relative to the evaporation processes. The positions of four experimentally studied membranes (three polymeric and one ceramic) from the literature\(^9\) are also shown as open symbols in Figs. 14a–14b. Two of the polymeric

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**Figure 13.** Flow diagram of a single-stage membrane process used to estimate the membrane surface area and costs.

**Figure 14.** (a) Calculated single-stage membrane surface area versus permeance and (b) calculated single-stage membrane levelized yearly cost versus permeance. Experimental literature data (square open symbols) are based upon Ref.\(^9\).
membranes have higher lignin rejections (97% and 93%) and lower permeances, due to their lower MWCOs (0.2 and 0.6 kDa, respectively). The other polymeric membrane and the ceramic membranes have lower lignin rejections (90% and 78%, respectively) and higher permeances due to their higher MWCO (1 kDa).

Figure 14a shows that the state-of-the-art high-rejection membranes have much higher required areas than the desired "ideal case" high-performance single-stage membrane (with the dotted vertical lines denoting the differential between what is currently available and what is desired). In other words, new membranes with higher permeances are needed. The low-rejecting membranes, on the other hand, are close to the optimal membrane area requirements. However, as seen in Fig. 15, these two membranes are estimated to have single-stage lignin recoveries of only 30%–75% and therefore cannot be used in an economical single-stage membrane process. Therefore, increases in lignin rejection are also needed. Clearly, there is no currently available commercial membrane with the required combination of performance characteristics. Similarly, Figure 14b shows that high-rejection membranes are very expensive and require a significant cost reduction to bring them to $50-100/m² cost levels that are common in the case of polymeric gas separation membranes. The currently available low-rejection membranes appear to have lower costs, but are not usable for the reason of low single-stage recovery as mentioned earlier.

Conventional ED technology is, for economic reasons, practically limited to TDS concentrations of ~0.5–15 g/L [69, 121] in applications such as brackish water treatment. BL feed streams have much higher inorganic concentrations (Table 2), and it can therefore be assumed that direct treatment of BL with ED membranes is not feasible. For example, Davy et al. [122] performed an economic estimate on acidification costs compared to ED for lignin precipitation and found that ED was more than 3 times more expensive. Furthermore, ED membranes (both conventional and bipolar) cannot currently operate at typical BL feed temperatures. However, it is possible that electrically driven membranes could be used in combination with pressure-driven membrane. Bipolar membranes have lower energy costs than conventional ED [91] and would probably be used. For example, NF membranes could reject virtually all of the lignin at 90 °C, and the permeate stream could be treated with ED at a lower temperature to achieve NaOH recovery without significant lignin fouling. Given the efficiency limitations of ED, complete inorganic recovery may not be feasible. Hence, the use of a RO/FO membrane could be necessary to separate the low-concentration ED permeate into concentrated brine and purified water.

Overall, the following technoeconomic conclusions can be drawn. If simple concentration of BL to higher TDS content is desired at a lower cost than traditional evaporators, NF appears to be the most desirable option but it requires long-lived membranes that are at least 50% cheaper than the best membranes currently evaluated in the literature. Furthermore, lignin rejections approaching 99% are desirable. There is a significant challenge in developing membranes that satisfy these requirements. Although we do not wish to speculate here regarding details of the composition and fabrication routes of such membranes, a general observation can be made. To lower membrane fabrication costs, low-cost polymers with good stability in BL can still be used as support materials, on which high-performance functional membranes made from new materials could be fabricated using economical and scalable methodologies. If more detailed separation of the TS into different Mw fractions (lignin, other organics like hemicellulose, and inorganics) is desired, then a combination of tunable NF or molecular sieving membranes would be necessary. Neither of the above scenarios addresses the full recovery of inorganics, which would mostly be permeated by the NF membranes. Conventionally, these would still be recovered by combustion of the further concentrated SBL and by evaporation of water from the NF membrane permeate. However, the addition of a RO membrane downstream of the NF membrane could be beneficial in producing purified water and further concentrating the inorganics and low-MW components. In this case, significant challenges also exist in developing robust RO
membranes for inorganics recovery, since the pH of the NF membrane permeate is expected to be essentially the same as that of the BL feed stream. It may also be possible to use ED (likely with bipolar membranes) in conjunction with RO/FO membranes to remove inorganics and carboxylic acids, but the economic viability of this scenario is unclear at present. The third and most conceptually simple scenario is direct RO for raw BL concentration (retaining all suspended and dissolved components and permeating only water). This scenario will likely remain unfeasible in the foreseeable future due to the very high TMPs required for direct RO of raw BL and the prohibitively large amount of fouling that would occur.

**Conclusions**

Significant reductions in cost and carbon emissions from the Kraft process are expected to result from successful development of a BL concentration membrane technology. Additionally, membranes may allow efficient separation of valuable BL components such as low-M<sub>w</sub> organic molecules and inorganic salts. Progress has been made in the development and evaluation of membranes for BL concentration and for separation of its valuable components. Polymeric membranes are challenged in BL applications because of their low lifetimes upon exposure to the harsh BL feed conditions (high pH, relatively high temperature, and many fouling species). Because of their greater stability, non-polymeric (e.g., ceramic) membranes are expected to play a major role in the concentration of black liquor. However, a major challenge exists in improving their rejection and manufacturing costs to decisively improve the economics of membrane-based BL concentration. Furthermore, to achieve the best possible separation (removal of water and ions), NF and RO membranes are also required. These membranes are still largely polymer based, and future research will need to focus on the development of robust, lower-cost NF/RO membranes based upon new materials that are suited for BL applications. While high fluxes are necessary, lignin rejection values (say, 99%) need not be as stringent as those required in desalination NF/RO membranes since it is not sought to produce potable water from BL. The development of membrane technologies driven by electrical power (ED) or concentration gradients (FO) is emerging, but they face significant challenges of stability and cost in BL applications. Overall, the development of viable membrane technologies for BL concentration—departing from classical polymeric or ceramic membranes—is an important need for the forest products industry, leading to significant energy savings and increased opportunities for water and material recycling.

**Acknowledgements**

The authors also thank Steven Lien and Scott Sinquefield (Renewable Bioproducts Institute) and Zhongzhen Wang (Georgia Tech) for valuable discussions and assistance.

**Funding**

The authors acknowledge financial support by the Renewable Bioproducts Institute and the Paper Science & Engineering Fellowship, both at the Georgia Institute of Technology.

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