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Fractionation of Lignin Streams Using Tangential Flow Filtration

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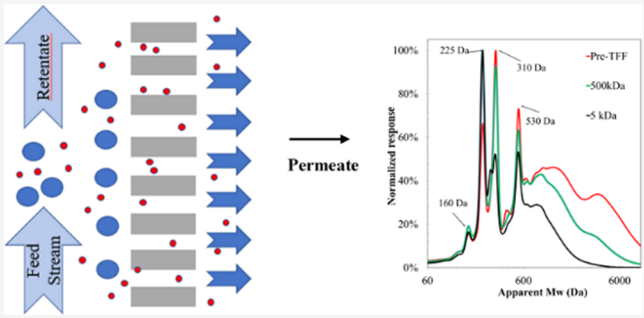
ABSTRACT: Lignin fractionation helps its valorization process and yields high-quality and -value products. In this study, cascading tangential flow filtration (TFF) was employed for the fractionation of lignin molecules. The lignin-rich stream was obtained from the pretreatment process of corn stover using alkali (NaOH) and cholinium lysinate ([Ch][Lys]) as the catalyst. The effect of TFF (microfiltration, ultrafiltration, and nanofiltration) on lignin molecular weight, sugar distribution, viscosity, and lignin functional groups was investigated. In general, the study concluded that the average molecular weight (MW) and polydispersity of the permeate stream decreased with the reduction of the membrane pore size. TFF was effective in separating the low-MW lignin (200−350 Da) from the aqueous stream. Approximately 2% of monomeric lignin and 10−20% of low-molecular-weight lignin were recovered from NaOH- and [Ch][Lys]-extracted streams. Techno-economic analysis (TEA) results show that a high percentage of the low-MW lignin extraction can be achieved via a cascade TFF membrane operating at high transmembrane pressures (TMPs) and cross membrane velocities. Additionally, a high initial concentration of lignin in the liquid stream plays a critical role in the lignin product yield and recovery cost.



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1. INTRODUCTION

The 21st-century lifestyle depends on petroleum-based energy, manufacturing, transportation, and products among other derivatives. However, fossil fuel reserves are depleting, and the unsustainable environmental devastation from burning petroleum has caused irreversible environmental damage to the ecosystem. There has been a growing interest in finding alternatives to petroleum, leveraging clean energy technologies, and converting abundant and renewable biomass into fuels and high value-added products.

Biorefineries are a promising tool poised to break our dependence on petroleum for fuels, chemicals, and materials. These biorefineries take advantage of renewable biomass by breaking it down into its main constituents, cellulose, hemicellulose, and lignin,[1] and further upgrading them to various value-added products.

Most biorefineries and agricultural industries such as the pulp and paper industry burn lignin to supplement their internal energy needs. However, a biorefinery's economic viability and environmental sustainability can be significantly improved if the valorization of lignin is prioritized during the refinement process;[2] using lignin solely to generate energy is short-sighted and inefficient.[3] Research has shown that lignin has far more economic potential when it is converted into valuable chemicals and materials.[3] As the biorefinery industry continues to grow, new processes are needed to facilitate lignin conversion into value-added products. Without such development, the amount of lignin produced will greatly exceed the market demand and will continue to be inefficiently burned, resulting in a misuse of a potential revenue stream.

Lignin is a heterogeneous aromatic biopolymer that provides strength and rigidity to the cell and constitutes 15−40% dry weight of most terrestrial plants.[2,4] Lignin molecules can vary between 1 and 100 kDa within the same sample.[5] Because of this variability, lignin applications are extremely broad; different molecular weight fractions can be used for low-cost carbon fiber, engineering plastics, thermoplastic elastomers, polymeric foams and membranes, board binder, and a variety of fuels and chemicals.[4] Precise fractions of different-molecular-weight lignin molecules are needed for each upstream application to upgrade lignin into these products. Obtaining specific molecular weight fractions is currently difficult because of the lack of an efficient process to separate the different-sized lignin molecules, especially at a large scale.

Compared to traditional processes, such as solvent extraction[6] and precipitation,[7] membrane separation requires no additional agents. It has a relatively lower energy consumption, which can decrease the processing expenditure. No colloids are formed during membrane separation, which leads to higher purity of the

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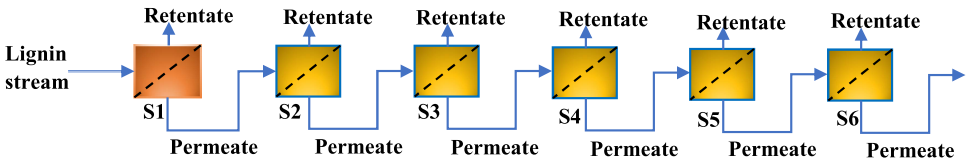
Scheme 1. Layout of the TFF Membrane Cascade



obtained lignin and simplifies the filtration process.[8] Membrane separation was shown to produce high yields (37%) of small phenolic compounds with a reduced polydispersity index.[9] Hussin et al. reported that the chemical and physical properties of the lignin streams were changed through ultrafiltration. Small fragments of lignin structure (MW: less than 5 kDa) provide an excellent antioxidant property and high reactivity.[10] The disadvantage of membrane separation is membrane fouling for the process integrations. Therefore, cascading tangential flow filtration (TFF) is introduced to the lignin fractionation process to reduce the fouling, realize continuous operation, and obtain a narrower polydispersity of lignin stream.[5,11,12] This tangential flow constantly works to clean the membrane's surface and reduce the formation of a cake.

Previous studies mostly focused on applications of ultrafiltration or ultra- and nanofiltration in lignin fractionation using commercial lignin streams such as kraft, soda, or organosolv.[5,11,12] In this work, two cascading TFF systems including microfiltration, ultrafiltration, and nanofiltration were employed to fractionate the lignin-rich streams. The TFF skids used for this study can be easily scaled up to pilot scale; thus, the data is closely relevant to larger-scale applications. In addition, two pretreatment catalysts (alkali and ionic liquid) were compared in parallel to evaluate the impact of lignin extraction efficiency on the downstream recovery cost. A series of analyses such as lignin molecular weight, monomer sugars, polysaccharides, and the rheology properties of the lignin streams from different molecular-weight cutoff membranes were conducted to understand the lignin fractions, optimize the separation process, and determine the future application. Techno-economic analysis (TEA) was also conducted for the membrane separation process to provide a preliminary evaluation of the economic viability of the separation approach.

2. MATERIALS AND METHODS

2.1. Biomass Pretreatment. The corn stover was milled to 3/16″ and air-dried by Idaho National Laboratory (INL). The biomass consists of 33.86% glucan, 15.00% xylan, and 24.96% lignin.[13] The feedstocks were stored in airtight containers at 4 °C with room humidity maintained at 64−70%.

Two catalysts, sodium hydroxide (NaOH) and cholinium lysinate ([Ch][Lys]), were used for pretreatment in 10 L Parr vessels (Parr Instrument Company, model 4555-58, Moline, IL). The details of the conditions are provided in Supporting Information Table S1. The system was heated at a speed of 1.5 °C/min and cooled through a cooling coil inside the reactor to room temperature after the reaction with a cooling rate of 3 °C/min. The slurry was then transferred out and centrifuged using a dead-end centrifuge (Thermo Scientific, Sorvall RC 12BP+) for 10 min at 4800 rpm to obtain the lignin-rich supernatant. The supernatant was then filtered with a 2.7 μm microfiber filter (GE, Grade GF/D) to remove any large suspending particles and prevent fouling of the filtration membranes.

2.2. Tangential Flow Filtration (TFF) Process. A Pellicon 2 Mini TFF system and an Alfa Laval M20 unit were utilized for the lignin fraction work in this study. Tables S2 and S3 show the detailed information of the membranes and process configurations.

For the Pellicon 2 Mini TFF system, the lignin stream was successively filtered using a 0.1 m^2 TFF system (Millipore, Burlington, MA) employing modified polyethersulfone V-screen filter membranes and membrane cutoffs of 0.65 μm, 0.22 μm, 500 kDa, 30 kDa, and 5 kDa. For each filtration, the feed material (2 L) was circulated through the TFF system until ca. 100 mL of the retentate remained. The resulting permeate from each filtration was then filtered through the next smaller membrane cutoff. The transmembrane pressures (TMPs) are about 2 bars for micro- and ultrafiltration. The weight variation of the feed and permeate and the transmembrane pressure were measured. Samples were taken at the end of each filtration from the resulting permeate and retentate.

As for the Alfa Laval M20 test unit (LabStak M20-0.72, Alfa Laval, Lund, Sweden) run, the hydrolysate was first diluted by a factor of 5× and then passed through six different membrane cutoffs (0.5 μm, 25 kDa, 5 kDa, 2 kDa, 1 kDa, to nanosize). For each filtration, four identical membranes (dry membranes, Alfa Laval, Lund, Sweden) were framed by two permeate outflow plates and three spacer plates in the filter stack with a total membrane size of 0.072 m^2. Before each filtration, the membranes were cleaned and prepared according to the manufacturer's instructions. The transmembrane pressures (TMP) are started at 2, 8, and 15 bars for microfiltration, ultrafiltration, and nanofiltration, respectively. During each filtration, the volume of the retentate was monitored, allowing for permeate and retentate samples to be taken at the same concentration intervals regardless of the membrane pore size or starting feed. The permeate and retentate flow rates, as well as the inlet and retentate outlet pressure, were recorded throughout the filtration process. The filtration processes are shown in Scheme 1.

2.3. Sugar Analysis. The laboratory analytical procedure (LAP) method was employed for polysaccharides and monosaccharide analysis.[14] A high-performance liquid chromatograph (HPLC) (Thermo Fisher Scientific, Ultimate 3000, Waltham, MA) equipped with an Aminex HPX-87H column (Bio-Rad, 300 × 7.8 mm^2, Hercules, CA) and a refractive index (RI) detector was used for monosaccharide analysis. The mobile phase was 5 mM sulfuric acid with a flow rate of 0.6 mL/min, and the column oven temperature was set at 65 °C. The samples were treated with sulfuric acid and then autoclaved on a liquid cycle for 1 h at 121 °C to depolymerize the remaining polysaccharides. The high-performance liquid chromatography analysis was then conducted using the same process as that used for the monosaccharides. Although the Aminex HPX-87H column cannot separate all of the sugars such as mannose and galactose, these sugars are minor compared to glucose and xylose and are negligible in the sugar analysis.

2.4. Lignin Characterization. Gel permeation chromatography (GPC), Tosoh Ecosec HLC 8320, was employed for the lignin-molecular-weight-distribution study. A UV detector with

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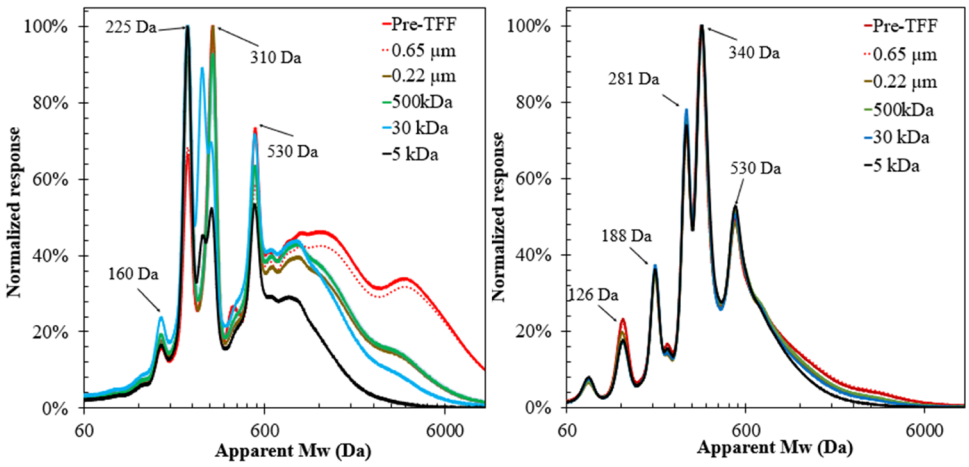

(a) NaOH extracted lignin (b) [Ch][Lys] extracted lignin

Figure 1. Gel permeation chromatography (GPC) of the permeate streams after cascading TFF using the Pellicon 2 Mini (PM) unit: (a) NaOH-extracted lignin and (b) [Ch][Lys]-extracted lignin.

a wavelength setup at 280 nm was used for the analysis. The GPC system was equipped with an Agilent PLgel 3 μm 100 Å (300 × 7.5 mm^2) column with tetrahydrofuran as eluent and a flow rate of 1.0 mL/min at 35 °C. A calibration curve was built using polystyrene standards (Agilent Technologies, Inc.) with a MW range from 162 to 29,150 g/mol. The lignin samples were prepared using a previously reported method.[15] Briefly, 40 mg of oven-dried lignin was mixed with 1 mL of pyridine and 1 mL of acetic anhydride. The mixture was placed in an oven at 40 °C for 24 h with stirring. Then, 0.4 mL of methanol was added to terminate the reaction. Next, 200 μL of samples were aliquoted in another GC sample tube and dried by a nitrogen flow for about 2.5 h. The air-dried samples were then placed in a vacuum oven overnight at room temperature along with sodium hydroxide pellets to absorb acetic vapor. Further, 1.5 mL of the mobile phase in sample tubes was added into an ultrasound mixture for 1 h. The mixture was passed through a 0.2 μm filter until a bubble-free final volume of about 1 mL was achieved. The samples were then analyzed using GPC.

Two-dimensional ^{1}H-^{13}C heteronuclear single-quantum coherence (HSQC) was used for the lignin structure characterization as described by a previous study.[16,17] Lignin sample (0.2 g) was milled by a planetary ball mill using a Retsch PM100 mill fitted with a 50 mL ZrO_2 grinding jar and 10 × 10 mm^2 ball bearings set at 600 rpm under the same conditions as those of ref 16. The ball-milled and dried lignin sample (50 mg) was suspended with 500 μL of DMSO-d_6/pyridine-d_5 (4:1, v/v). The mixture was mixed in an ultrasonic water bath at room temperature for 5 h. Then, the lignin solution was transferred to a 5 mm NMR tube. The HSQC spectra were acquired at 298 K using a Bruker Avance-800 400 MHz NMR spectrometer equipped with a 5 mm inverse gradient ^{1}H-^{13}C cryoprobe, and the hsqcetgpsisp2.2 pulse program was set as ns = 200, ds = 16, number of increments = 256, and d1 = 1.0 s. DMSO peak (δ_C/δ_H = 39.5/2.5 ppm) was employed as a reference peak. The obtained spectra were processed by Bruker's Topspin 3.6.

Each sample's viscosity was measured using a rheometer (Malvern Kinexus Pro, Malvern, Westborough, MA). Each measurement was taken at room temperature (23 °C) using a 40 mm parallel plate geometry (Malvern, PU40 SR0302 SS) with a plate gap of 0.5 mm. Then, 0.8 mL of the sample was loaded between the parallel plates for each measurement. The viscosity was measured with a ramped shear rate ranging from 25 to 200 s^{-1}, where 50 readings were taken linearly between the starting and end shear rates. To ensure that the sample had reached a steady state, a tolerance of 5% for the viscosity reading was used over a 5 s window. This required each measurement taken in the 5 s window to be within 5% of the other readings, indicating the sample had reached a steady state.

Before GPC or NMR analysis, the samples were lyophilized first and then dried in a vacuum oven overnight at 50 °C to remove all of the moisture. Each sample was frozen at −80 °C until fully solidified. The samples were then lyophilized using a FreeZone 6 lyophilizer (Labconco Corporation, Catalog No. 7806021, Kansas City, MO).

2.5. Techno-Economic Analysis. A preliminary techno-economic analysis (TEA) was performed to assess the technical and economic viability of lignin valorization via cascading tangential flow filtration. The layout of the cascade TFF is shown in Scheme 1. A comparative TEA was performed for four cases, namely, the combination of two different biomass pretreated liquor streams obtained using two pretreatment catalysts (NaOH and ChLys) and the recovery of low-MW chemicals (aromatic monomers and hydroxy acids) in the respective lignin streams with either a PM or M20 tangential flow filtration system. The low-MW product recovery costs for the four scenarios include the membrane cost and the electricity cost associated with pumping. The recovery of low-MW lignin and rejection of high-MW lignin were based on the mass balance shown in Figure S1. The total membrane area for each stage was determined based on the flux from the experimental measurement.

Power consumption was based on the assumption that each separation stage required a feed pump and was estimated using eq 1, which was derived from (Arkell et al. 2014)

$$W_{tot} = \sum_{n}^{i=1} \frac{TMP_i}{\eta \cdot VR_i} \tag{1}$$

where i is the TFF stage, W_{tot} is the total power consumption, TMP is the transmembrane pressure, η is the pump efficiency, and VR is the volume reduction (see Table S7, Supporting Information). The incoming lignin feed (black liquor) to the

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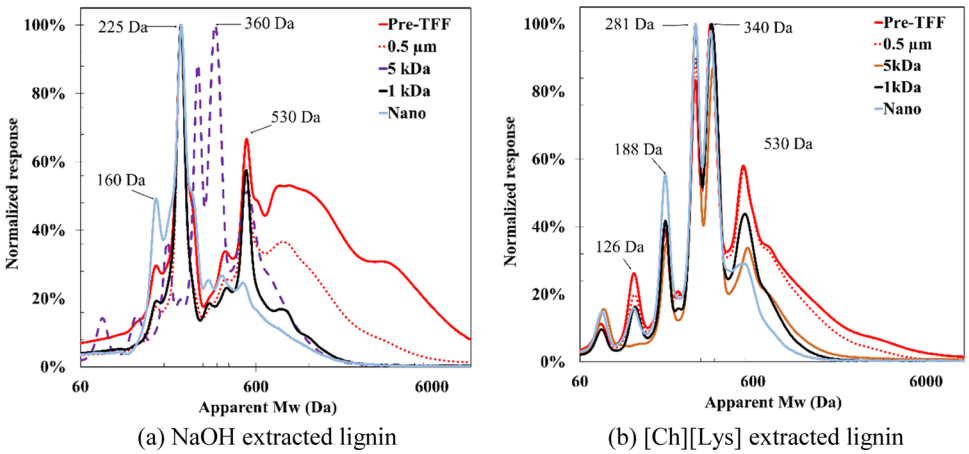

(a) NaOH extracted lignin (b) [Ch][Lys] extracted lignin

Figure 2. GPC of the permeate streams after cascading TFF using the Alfa Laval (AL) unit: (a) NaOH-extracted lignin and (b) [Ch][Lys]-extracted lignin.

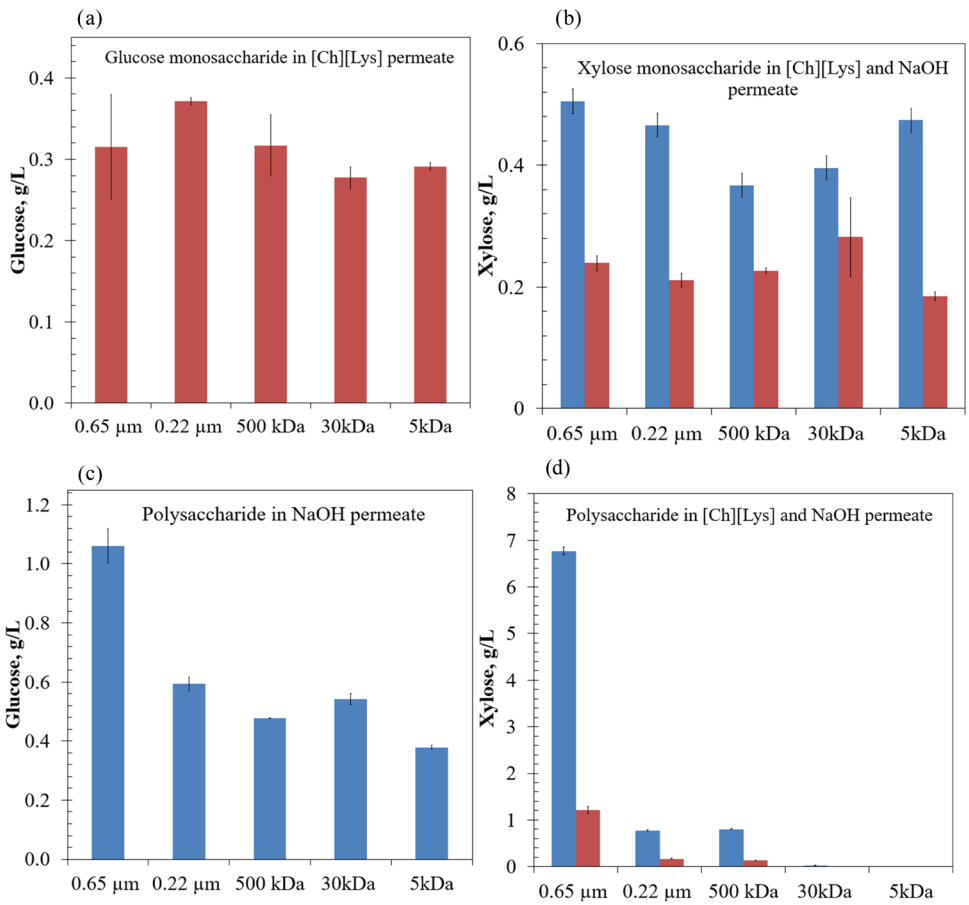

Figure 3. Sugar monomer and oligomer distribution of the permeate streams after the PM TFF: (a) glucose in [Ch][Lys]-extracted stream, (b) xylose in NaOH (blue bar)- and [Ch][Lys] (red bar)-extracted stream, (c) glucose oligomers in NaOH-extracted stream, and (d) xylose oligomers in NaOH (blue bar)- and [Ch][Lys] (red bar)-extracted stream. There were no detectable glucose monomers in NaOH-extracted stream and glucose polysaccharides in [Ch][Lys]-extracted stream.

cascade TFF for the preliminary TEA on the membrane separation step was scaled up from the bench-scale of 5.7 L/min to 10,000 L/h with the on-stream time of 7884 h per year (or 90%). The scope of the current TEA does not include the additional processing steps to upgrade the low-molecular-weight lignin products to chemicals. However, in conjunction with the ongoing R&D efforts in converting these compounds, the future TEA study will include these upgrading steps. Moreover, the recovered low-MW monomers can also be sold directly as natural products and thus do not require further downstream processing.

3. RESULTS AND DISCUSSION

3.1. Effects of TFF on Lignin Molecular Weight Distribution. During the pretreatment process, the catalyst attacks the biomass microstructure and internal chemical

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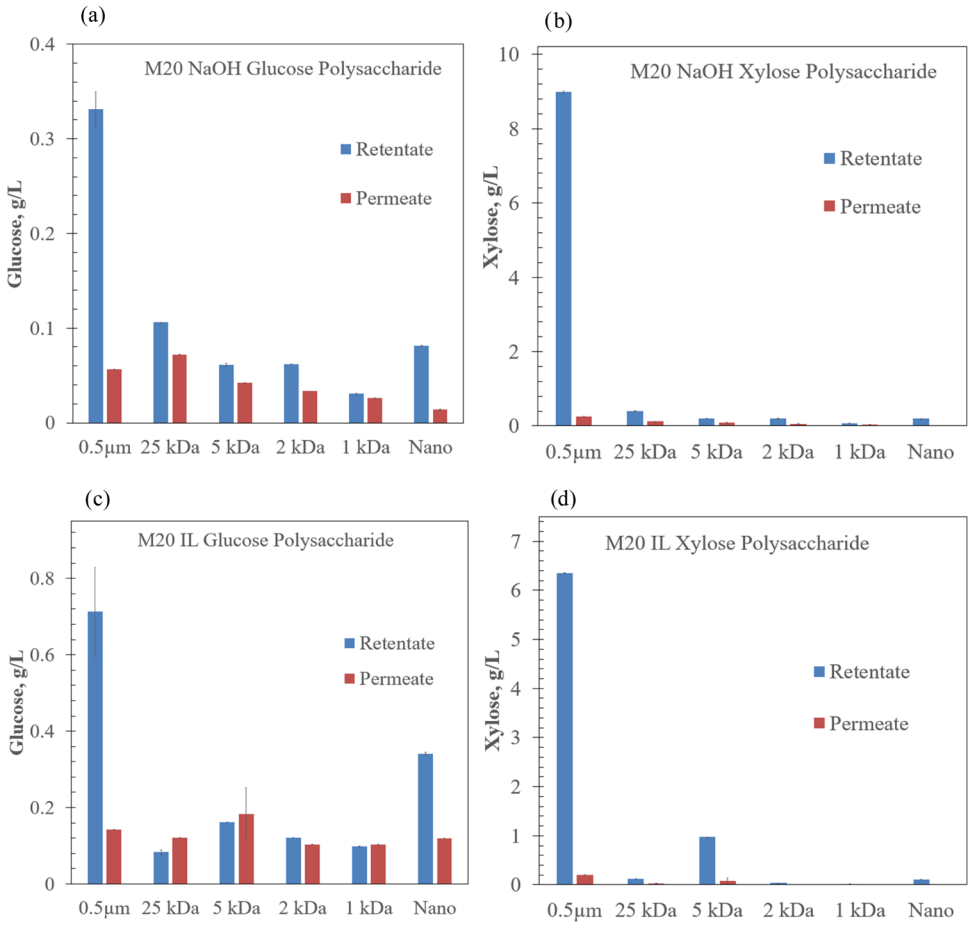

Figure 4. Sugar oligomer distribution of the different streams in the AL TFF process: (a) glucose oligomers in NaOH-extracted stream, (b) xylose oligomers in NaOH-extracted stream, (c) glucose oligomers in [Ch][Lys]-extracted stream, and (d) xylose oligomers in [Ch][Lys]-extracted stream. There were no detectable glucose monomers in NaOH black liquor and glucose polysaccharides in [Ch][Lys] permeate stream.

linkages. Lignin and part of carbohydrates are removed from biomass and dissolved in the liquid stream (black liquor). Lignin removal and degradation are determined by the natural structure of biomass, catalyst, and pretreatment conditions. In this study, two basic catalysts, sodium hydroxide (NaOH) and cholinium lysinate (ChLys), were employed in the pretreatment. The experimental conditions were selected according to previous studies.[18−20] To minimize the membrane fouling and narrow the molecular distribution, two cascading tangential flow filtration (TFF) units, Pellicon 2 Mini (PM) and Alfa Laval M20 (AL) test unit, were set up and tested for lignin fractionation. Tables S2 and S3 show the configurations of the membranes and process parameters. Due to the membrane and pump limitation, PM was operated at a much lower transmembrane pressure (TMP) and cross membrane circulation rate than AL. Table S4 and Figure 1 show the lignin molecular weight (MW) distribution with the PM TFF. One can observe that the starting lignin stream from NaOH extraction has a much higher average molecular weight than that from ChLys extraction. A significant amount of high-MW lignin fraction (MW > 1000 Da) exists in the NaOH-extracted lignin stream. The gradual decrease of high-molecular-weight lignin in Figure 1a indicates that TFF can effectively fractionate NaOH-extracted lignin. The main portion of the lignin fraction passing through the 5 kDa membrane has a MW ranging from 225 to 530 Da. On the other hand (Figure 1b), TFF had a limited effect on the fraction of ChLys-extracted lignin. Low-MW lignin (126−530 Da) was the major portion of the lignin stream after the extraction. It is also observed that the average MW of lignin in the permeate stream is much smaller than the membrane cutoff. One possible reason for this is that the retained lignin formed a prefiltration layer built by fine particles on the top of the membrane,[11] which helped to reject higher-MW lignin during the microfiltration steps. The molecules with MW of 310 Da in Figure 1a were largely removed by the 5 kDa membrane. One possible reason for this is that the lignin components at 310 Da condensed during the filtration. The polydispersity index (PDI) decreased in the permeate stream along with membrane cutoff, which indicates that the filtration process actually improves the homogeneity of the permeate streams and benefits further lignin valorization processes. PDI of the NaOH pretreatment stream was higher than that from ChLys, showing that ChLys pretreatment leads to more uniform lignin reducing the downstream separation effort.

To further narrow down the lignin MW in the permeate stream, an Alfa Laval (AL) unit was tested, which can provide a much higher TMP (8 vs 2 bar) and circulation rate (5.7 vs 0.8 L/min). A higher TMP provides a larger permeation driving force, and a higher circulation rate can minimize the membrane fouling while maintaining the permeate flux. Compared to the PM setup, two smaller pore size membranes, 1 kDa and nanosize, were employed. The GPC results are shown in Figure 2 and Table S5. For both streams, the AL unit can effectively remove the high-MW lignin (higher than 1 kDa). In the nanomembrane permeate, lignin MW ranges from 160 to 530 Da. Compared to

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the PM TFF, the group of lignin with MW at 530 Da was removed in the AL TFF. Based on the GPC data, nanofiltration was recommended to obtain lignin monomers or dimers.

3.2. Effects of TFF on Sugar and Polysaccharide Distribution. In addition to lignin, carbohydrates were also released from corn stover. The sugars together with lignin can be utilized for useful material production.[21,22] The variation of both monosaccharides and polysaccharides along with the TFF process is shown in Figure 3. There is a limited amount of glucose and xylose (less than 1 g/L) present in the lignin streams; however, significant water-soluble sugar oligomers were detected after hydrolyzing the liquid stream using the LAP method.[14] Glucose was only detected in the [Ch][Lys]-extracted lignin stream, while glucose oligomers were present only in NaOH-extracted lignin (Figure 3a,c). More xylose oligomers were extracted compared to glucose oligomers under the basic conditions (6.8 vs 1.1 g/L in 0.65 μm permeate), which is consistent with previous studies.[18,19,23,24] In general, NaOH pretreatment extracts much more carbohydrates than that from [Ch][Lys]. Due to the mild pretreatment conditions in this study, most of the sugars exist in the form of oligomers with the dominant MW larger than 500 kDa and are separated during the TFF process. Figure 3a,b also shows that the monosaccharides (glucose and xylose) can move freely through the membranes and are not affected by the TFF process due to their small MW and high water solubility. Similar behavior was observed in the AL unit process (Figure 4). Most of the polysaccharides were removed in the microfiltration stage (0.65, 0.5, and 0.22 μm). One interesting finding is that the polysaccharide concentration in the retentate stream after nanofiltration is higher than that from the permeate stream. This indicates that nanofiltration can concentrate the polysaccharides, which have an MW range from 25 to 1 kDa.

3.3. Effects of TFF on the Viscosity of the Fractionated Lignin Stream. Viscosity plays an important role in the filtration process. High viscosity decreases the permeate flux and causes issues for the membrane system.[25] The presence of carbohydrates and lignin released from the pretreatment process affects the liquid lignin streams' viscosity. As shown in Figures 5 and 6, the viscosities were changed during the TFF process while polysaccharides and high-MW lignin were separated from the liquid stream. The liquid stream's initial viscosity from NaOH pretreatment is slightly lower than that from [Ch][Lys]. The 2.7 μm microfiber filtration did not change the viscosity substantially for both liquid streams. However, the microfiber filter fouled quickly due to the fine particles. Removal of the fine particles helps to reduce TFF membrane fouling. In the microfiltration stage, the viscosity increased significantly in the retentate stream, which reached a maximum value of 442 cp in NaOH black liquor and 113 cp in [Ch][Lys] with the 0.22 μm membrane filtration. The viscosity in the retentate stream increased faster in [Ch][Lys] than in NaOH. One possible reason for this is that the fine particles in [Ch][Lys]-extracted stream formed a filter layer blocking the flow and became more solid in the retentate stream with the 0.65 μm membrane. When the stream passed through 0.22 μm membranes, the large molecules, including high-WM lignin, polysaccharides, and fine particles from biomass, accumulated in the retentate stream, contributing to the high viscosities. In the stage of ultrafiltration, no significant viscosity variations were observed, which indicated that the monosaccharides and low-MW lignin had very limited effects on the viscosity. The viscosities of permeate and retentate streams passing through 500 kDa remained the same (Figure 5), indicating that the microfiltration not only removes fine particles larger than 0.22 μm but also molecules with MW above 500 kDa (less than 0.22 μm). Considering the GPC shown in Figure 1, the process can be optimized by skipping the 500 kDa membrane separation step.

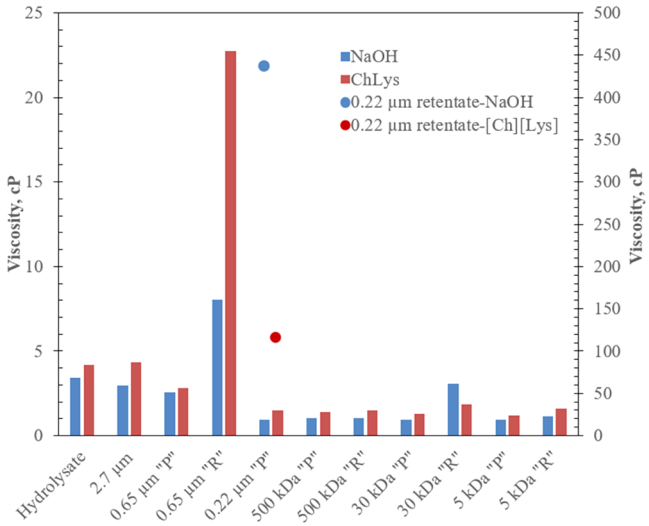

Figure 5. Viscosity distribution of the different streams in the PM TFF process. Data from 0.22 μm retentate is shown in a circle using a secondary y-axis (right axis). The left and right y-axes are presented using the same units (cP). "P" represents permeate stream. "R" is retentate stream.

Due to the minimum volume requirement (2 L) of the AL TFF system, the initial black liquor was diluted five times and then filtered by 0.5 μm membranes. Figure 6 shows the variations of viscosities as a function of membrane cutoffs. Similar to the microfiltration process in the PM unit, the viscosity increased in the retentate stream for both lignin streams after 0.5 μm membrane filtration. However, the maximum viscosities in the AL unit (~4 cp) were much lower than those in PM TFF (~450 cp). One reason for this is the dilution of the feed stream in the AL unit. Therefore, high solid accumulation was avoided in the retentate stream. In the ultrafiltration and nanofiltration stages, no significant viscosity variations (~1 cp) were observed among membranes with different cutoffs, which was similar to the PM TFF.

3.4. Effects of TFF on Lignin Functional Groups: NMR Characterization. To understand the effects of TFF on lignin functional groups, NMR spectroscopy was employed to detect the structure of the lignin before and after treatment. Lignin's chemical structural studies provide important information for further valorization.[26] The HSQC NMR spectra of the lignin streams after the PM TFF process are shown in Figure 7.

NaOH 5 kDa (Figure 7b) contains p-hydroxyphenyl (H), guaiacyl (G), syringyl (S), oxidized syringyl (S′), and β-O-4 units. NaOH 5 kDa has slightly lower quantities of lignin and carbohydrates compared to the lignin passing through the 2.7 μm filter (Figure 7a), indicating that the larger-MW portion of lignin was removed during the 5 kDa filtration process (Figure 3a,b). The [Ch][Lys] 5 kDa (Figure 7d) has much less lignin and carbohydrates than [Ch][Lys] 2.7 μm (Figure 7c). These changes suggest that a lignin moiety with a MW larger than 5 kDa was effectively separated after the 5 kDa membrane filtration. Interestingly, [Ch][Lys] 5 kDa lignin consists of mostly guaiacyl unit while [Ch][Lys] 2.7 μm lignin has both guaiacyl and syringyl units, suggesting that the larger-MW

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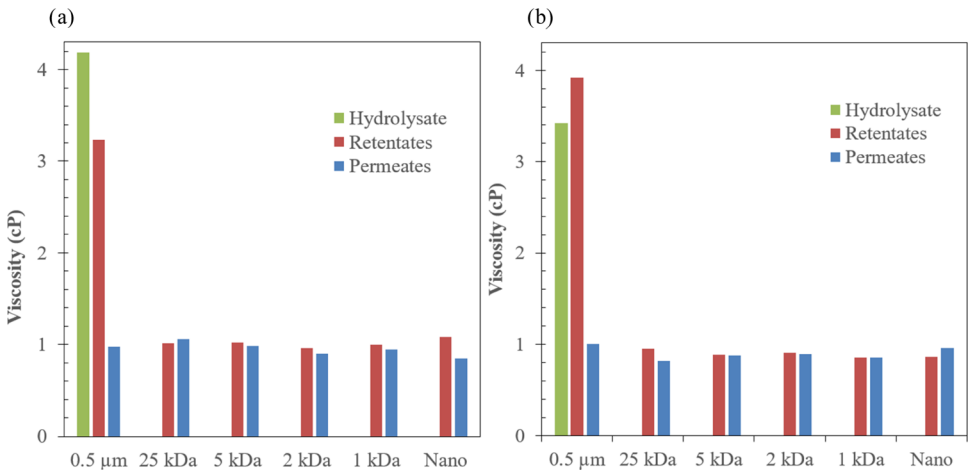

Figure 6. Viscosities of lignin streams (retentates in the red bar, permeate in the blue bar, and hydrolysate represents the extracted streams passing through the 2.7 μm filter) with the microfiltration in the AL TFF process: (a) [Ch][Lys]-extracted stream and (b) NaOH-extracted stream.

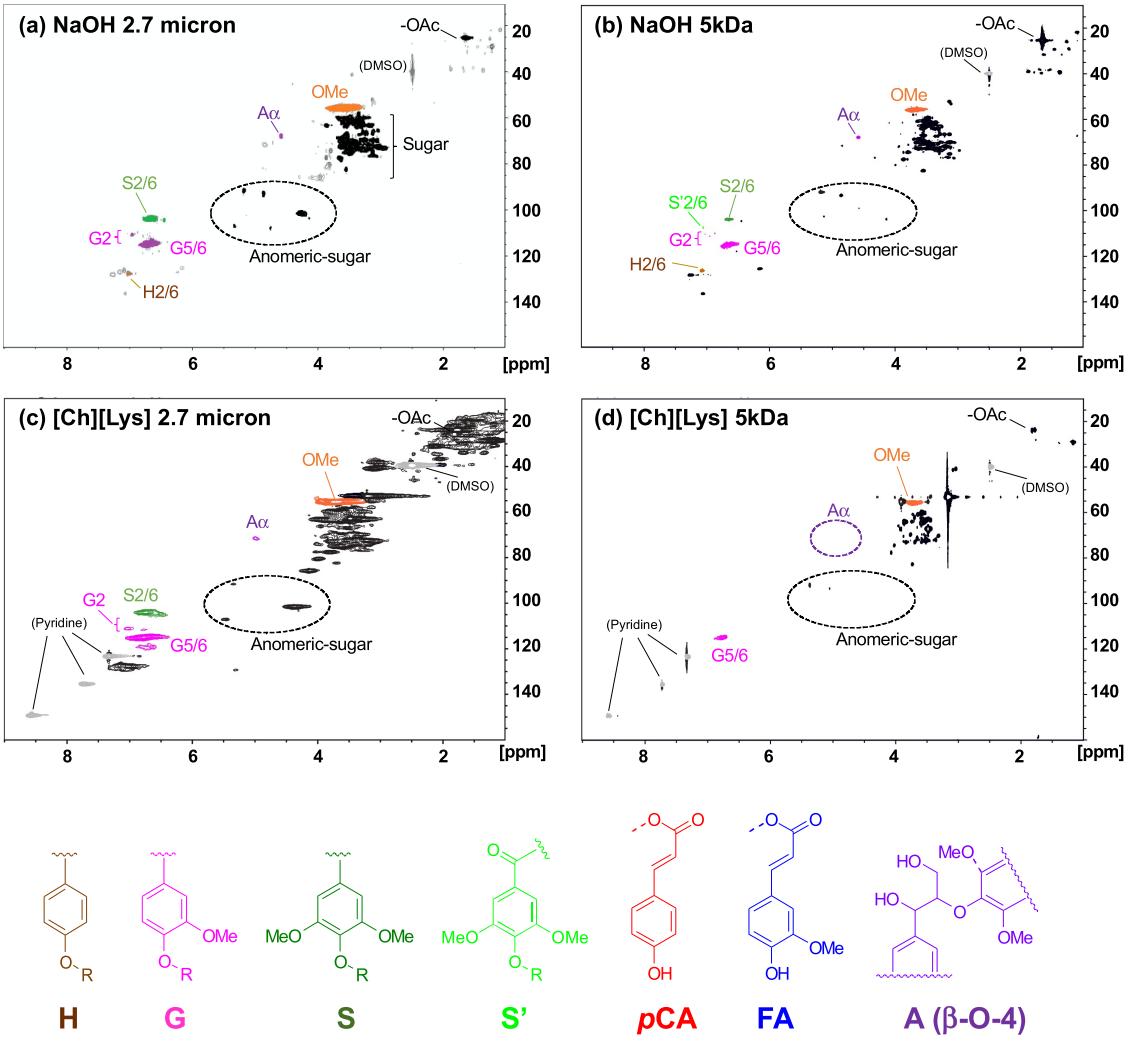

Figure 7. HSQC spectra of the lignin streams after the PM TFF process: (a) NaOH 2.7 μm, NaOH-extracted lignin passing through the 2.7 μm filter; (b) NaOH 5 kDa, NaOH-extracted lignin permeate after passing through the 5 kDa membrane; (c) [Ch][Lys] 2.7 μm, [Ch][Lys]-extracted lignin passing through the 2.7 μm filter; and (d) [Ch][Lys] 5 kDa, [Ch][Lys]-extracted lignin permeate after passing through the 5 kDa membrane. H, *p*-hydroxyphenyl; G, guaiacyl; S, syringyl; S′, oxidized syringyl; *p*CA, *p*-coumarate; FA, ferulate; and A, β-O-4 units.

portion in [Ch][Lys] 2.7 μm lignin, which was fractionated in other permeates, consists of higher syringyl units relatively. The β-O-4 units were not detected in the [Ch][Lys] 5 kDa lignin while the [Ch][Lys] 2.7 μm lignin had a small content of β-O-4 units. This indicates that all of the β-O-4 units were removed during the filtration process. The [Ch][Lys] 2.7 μm lignin has

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more lignin and carbohydrates than the NaOH 2.7 μm lignin, suggesting that [Ch][Lys] pretreatment at a higher temperature (140 °C) has high depolymerization capability for both lignin and carbohydrates than NaOH pretreatment. This result agrees with the GPC data (Table S4) that [Ch][Lys] 2.7 μm has a lower MW than NaOH 2.7 μm (579 vs 1704). The methylene and methine peaks at δ_H/δ_C 1.0−2.5/15−35 ppm in the [Ch][Lys] 2.7 μm lignin are derived from the ionic liquid. Compared to the [Ch][Lys] 5 kDa, the NaOH 5 kDa fraction contains more lignin with syringyl, oxidized syringyl, and β-O-4 units, as well as slightly higher carbohydrates.

3.5. Mass Balance of the Lignin Stream. Mass balance of lignin offers an overview of the filtration process. It is an important factor to study membrane fouling and TFF filtration performance. In this TFF study, the starting lignin steam was obtained from 2.7 μm dead-end filter filtration. The membranes were placed in descending order. Permeate streams were collected after the volume of the retentate reached a minimal value (ca. 100 mL, PM unit) or concentrated 5× (AL unit) and fed to the next step of filtration. The mass of the retentate and permeate streams was recorded after drying in a freeze-dryer. The lignin content was calculated by subtracting the weight of carbohydrates and catalysts (NaOH or ChLys) from the total oven-dried mass. The lignin mass distribution for the two TFF units is shown in Table 1 and Figure S1.

Table 1. Percentage of Lignin Mass in the Permeate Streams

	lignin percentage, % in permeate			
MWCO	NaOH PM unit	ChLys PM unit	NaOH AL unit	ChLys AL unit
0.65 μm	80.9	74.7		
0.5 μm			60.8	71.5
0.22 μm	43.1	62.3		
500 kDa	35.6	50.9		
30 kDa	22.3	36.3		
25 kDa			37.7	52.4
5 kDa	10.7	22.1	22.5	36.8
2 kDa			13.1	28.9
1 kDa			8.9	22.7
nanosize			1.9	2.1

Table 1 and Figure S1 show that lignin distributions were affected by membrane cutoffs and the TFF unit setup. PM TFF recovered 10.7 and 22.1% of lignin in the permeate stream after filtration of NaOH- and [Ch][Lys]-extracted lignin using 5 kDa membrane, respectively. AL TFF recovered 22.5 and 36.8% of lignin in the permeate stream after filtration of NaOH- and [Ch][Lys]-extracted lignin using the same MW cutoff membrane, respectively. The highest lignin rejection rates were observed in the process of microfiltration and nanofiltration. The mass distribution matched the viscosity data of the lignin stream shown in Figures 5 and 6. High lignin mass percentages in the retentate streams correlate with high viscosities in the process of microfiltration (0.65 and 0.22 μm), in which large-size lignin was retained and concentrated. More lignin was collected as the retentate stream from NaOH-extracted lignin than from [Ch][Lys] after passing through the series of membranes. The 500 kDa membrane (PM unit) has a minimum lignin retention rate compared to the other membranes. This indicates that most of the lignin passing through the 0.22 μm membrane has a molecular weight of less than 500 kDa.

In the process of nanofiltration, most of the lignin remained in the retentate stream. The AL unit recovered ca. 2% of monomeric lignin in the permeate stream from NaOH- and [Ch][Lys]-extracted lignin through nanofiltration. By comparing the two TFF unit performances, one can observe that more lignin passed through the 5 kDa membrane using the AL unit. This indicated that the AL unit had a higher filtration efficiency than the PM TFF unit in terms of low-molecular-weight lignin recovery. One main reason for this is that the AL unit has a much higher cross membrane flow velocity (Tables S2 and S3) than PM TFF (5.7 vs 0.8 L/min) due to the higher TMP. The high flow can continuously remove the cake layer formed on the membrane and prevent membrane fouling. Another reason is that the high TMP in the AL M20 TFF provides a more powerful drive for the smaller-size lignin to pass through the membranes.

Overall, the characterization and mass balance data provided a comprehensive baseline dataset on lignin fractionation using TFF including micro-, ultra-, and nanofiltration. Previous publications contain only one or several of the filtration membranes, mainly in the ultra- and nanofiltration range.[5,7−12] Based on the dataset in this study, one could choose appropriate MWCO membranes by balancing lignin recovery rate and MW distributions of the target lignin streams.

3.6. Techno-Economic Analysis (TEA). The preliminary TEA results for the continuous multistage cascade TFF are summarized in Table 2. The experimental data for flux and

Table 2. Summary of Comparative TEA Results

TFF system	Alfa Laval M20 (AL)			
pretreatment catalysts	sodium hydroxide		cholinium lysinate	
lignin (low MW + high MW) in black liquor (g/kg)	44.74		123.4	
MW cutoff	5 kDa	<400 Da	5 kDa	<400 Da
permeate recovery (%)	22.5	1.9	36.8	2.1
annual running cost ($/year)	133,635	216,136	133,635	216,136
annual low-MW lignin production (tonne/year)	794	67	3580	204
low-MW lignin recovery cost ($/tonne)	168	3225	37.3	1058

TFF system	Pellicon 2 Mini (PM)	
pretreatment catalysts	sodium hydroxide	cholinium lysinate
lignin (low MW + high MW) in black liquor (g/kg)	44.74	123.4
molecular weight cutoff	5 kDa	5 kDa
permeate recovery (%)	10.7	22.1
annual running cost ($/year)	175,330	170,376
annual low-MW lignin production (tonne/year)	377	2150
low-MW lignin recovery cost ($/tonne)	465	79.2

membrane areas are summarized in Supporting Information Table S6. It is evident that the lignin product recovery cost is dictated by the interplay of initial black liquor lignin concentration, TFF membrane performance, and operating or running cost. Two pretreatment catalysts give rise to two different initial lignin concentrations in the black liquor. In the PM filtration system, the permeate flux at the 500 kDa membrane cutoff was much higher than the others. One can conclude that the large particles were removed in the stage of microfiltration. Most of the lignin passing through the

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microfiltration had a molecular weight less than 500 kDa. In the ultrafiltration process, the flux decreased with the membrane cutoff, which agreed with the data in Table 1. A smaller pore size of the membranes provided a higher mass transfer resistance. In the M20 filtration system, the flux at 2 kDa was much lower than that at both 1 kDa and nanofiltration. This shows that the lignin stream is a complex system and the permeate flux is affected not only by the membrane cutoff but also by the components of the feed stream. The lignin concentration in the [Ch][Lys] black liquor is almost three times higher than that in the NaOH case, 123.4 vs 44.74 g/kg, respectively. In comparison, the black liquor from the pulping mill was reported to be 60 g/L.[27] The higher concentration for the ionic liquid case also leads to a higher low-MW lignin annual production, which in turn has a positive impact on the recovery cost. At 5 kDa cutoff and with AL TFF (the top part of the table), the corresponding annual low-MW lignin production for the NaOH liquor is 794 metric tons (MT) per year compared to 3580 MT/year for the [Ch][Lys] liquor. Likewise, at 5 kDa cutoff and with PM TFF (the bottom part of the table), the corresponding annual low-MW lignin production for the NaOH liquor is 377 MT/year compared to 2150 MT/year for the [Ch][Lys] liquor.

Additionally, the AL TFF exhibits higher low-MW lignin product recovery than the PM TFF. At 5 kDa cutoff, the alkaline liquor's permeate recovery is 22.5% for AL TFF compared to 10.7% for PM. Similarly, the [Ch][Lys] liquor's permeate recovery is 36.8% for AL TFF compared to 22.1% for PM. Furthermore, with a larger permeation driving force and being less prone to fouling, AL TFF can recover lignin monomers down to the <400 Da cutoff.

The operating costs include the energy cost and the membrane cost. The AL TFF system operates at a higher TMP and cross membrane velocity, and therefore it incurs higher energy consumption. However, as the total operating cost is predominantly attributed to membrane cost, it turns out that the overall annual running cost is lower for the AL system ($133,635/year) than the PM system ($175,330/year) at 5 kDa cutoff.

The recovery cost at 5 kDa cutoff for the NaOH liquor with the PM TFF gives the highest low-MW lignin recovery cost, at about $465 per metric ton (MT), attributed to the combination of the lower lignin concentration in the black liquor and also the relatively lower recovery filtration performance. Conversely, the [Ch][Lys] case using the AL TFF gives the lowest recovery cost, at $37.3/MT. At cutoff <400 Da, for the AL TTF system only, the cumulative annual running cost is $216,136. The annual low-MW lignin production with nanofiltration is 67 and 204 MT/year for NaOH and [Ch][Lys] liquor, respectively, corresponding to the lignin recovery costs of $3225/MT for the former and $1058/MT for the latter. In comparison, the recovery of low-MW lignin compounds via solvent extraction exhibited the recovery cost exceeding $5000/MT, in which about 60% of the cost is associated with the solvent recovery alone.[28] The separation cost could be largely reduced through skipping serval stages of the current process, e.g., one stage for each micro-, ultra-, and nanofiltration.

4. CONCLUSIONS

In this study, TFF was evaluated on ligin fractionation. The lignin streams were obtained from two pretreatment processes: NaOH and [Ch][Lys]. Cascade TFF with molecular cutoff ranging from 0.65 μm to nanofiltration (<400 Da) was employed to minimize membrane fouling and increase the permeate flow rate. The process data show that the lignin stream's MW distribution depends on the extraction process, which impacts the whole filtration process. The extracted lignin from NaOH process has a higher average MW than that from [Ch][Lys]. TFF can fractionate NaOH-extracted lignin while it has no significant effects on the [Ch][Lys] lignin based on GPC data. To separate lignin monomers, a nanofiltration membrane was required, and ca. 2% of lignin monomers were recovered from the nanofiltration permeate in NaOH- and [Ch][Lys]-extracted lignin. Besides lignin, the TFF process can also separate polysaccharides, which contribute to high viscosity in the retentate streams along with the high-MW lignin. The retentate stream viscosity increased significantly during microfiltration. In the ultrafiltration and nanofiltration stages, the liquid stream's viscosity remains at a low and stable level. NMR results showed that different lignin structures were obtained after extraction using the two catalysts.

The preliminary TEA results show that high low-MW lignin extraction can be achieved via a cascade TFF membrane operating at high TMP and cross membrane velocity, as exhibited by AL TFF. Additionally, a high initial concentration of lignin in the black liquor plays a critical role in the lignin product yield and recovery cost. The TEA results in this study can serve as the baseline for future comparison and a basis for optimizing the current processes, as well as for comparing this cascade TFF system with other lignin fractionation and recovery technologies.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.1c02052.

Feedstocks and pretreatment conditions (Table S1); membrane information (Tables S2 and S3); molecular distribution of the lignin permeate stream (Tables S4 and S5); membrane performance and cost assumptions (Table S6); feed pump power consumption and cost estimates (Table S7); and mass distribution percentage of the lignin stream (Figure S1) (PDF)

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Notes

The authors declare no competing financial interest.

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