Evaluation of Membrane Filtration for Treatment of Black Liquor in Small-Scale Pulp and Paper Mills in India

By

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Abstract

Black liquor, a strongly polluting byproduct from the kraft pulping process in pulp and paper mills, is traditionally treated by being passed through multiple effect evaporators and burned in a recovery boiler to produce energy and recover chemicals. However, the traditional treatment of black liquor is not economically viable for the small-scale kraft paper mills in India that uses waste agricultural products as raw material to produce brown paper. Membrane ultrafiltration treatment has been advocated by many scholars as a possible alternative treatment method for black liquor, and this study attempts to address industrial concerns on the cost-effectiveness of membranes for black liquor concentration and treatment. Utilizing a cross-flow hollow fiber membrane module in a recirculation system operating under constant pressure, black liquor is recirculated through the system over an extended period of time to observe the quantity and quality of the lignin in the concentrate and the permeate, and how they vary over time. Additionally, the permeate flux rate change over time is also observed to determine the required frequency of cleaning membranes from reversible fouling of membranes, as well as the frequency to replace membranes due to irreversible fouling. Cost of cleaning and changing membranes, as well as the profit gained from lignin retained can be estimated and compared with literature to determine the cost-effectiveness of ultrafiltration membranes in treating black liquor.

Experimental results suggest that operating at a pressure of 207 kPa and a cross-flow velocity of 1.06 m/s, the average permeate flux of black liquor is 7-21 LMH when concentrating lignin in black liquor from a concentration of 38 g/L to 185 g/L, which compares favorably to literature results. However, a membrane cleaning frequency of every 4 to 6 hours and an estimated membrane lifetime of several weeks, predicted by experimental results, significantly raises the cost of cleaning and changing membranes in comparison to the commonly estimated membrane cleaning frequency of once per day and lifetime of 1.5 year in literature. The permeate lignin concentration, which increased up to 40 g/L at the end of a concentration cycle, would also decrease the profit gained from reusing the permeate stream in the cooking process. The increased cost factors associated with both intense membrane fouling and the need for permeate stream re-treatment require to be addressed in future research, in order to more comprehensively evaluate membrane filtration process as a cost-effective alternative for treating black liquor.

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Table of Contents

1 Introduction

An overview of the background for this research is introduced in this chapter. The generation of black liquor waste in the papermaking process along with the challenges of black liquor treatment are introduced in Section 1.1. The traditional treatment method and the associated difficulty for small-scale paper mills in using this method is described in Section 1.2. Alternative treatment methods are then introduced, and the motivating factors for focusing the current study on membrane methods are explained. An outline of this thesis is then listed out at the end in Section 1.3.

1.1 Black Liquor Generation

Black liquor, the wastewater of concern in this research, is a byproduct in the kraft papermaking process. During papermaking, sodium hydroxide and sodium sulfide (or sodium sulfite) are used to pulp raw materials, which is a process that removes lignin from the raw material in order to facilitate the separation of cellulose and hemicellulose fibers and improve the papermaking properties of fibers, as shown in Figure 1-1 (Tran and Vakkilainnen 2008; Hung and Sumathi 2005) The fibers extracted from the pulping process go on to be further refined to create paper. Lignin, mixed in the cooking chemicals, will form a dark-brown form of wastewater, commonly known as "black liquor." After the cooking process, black liquor is usually separated from the bulk of the pulp by several round of washing, and eventually goes on to wastewater treatment processes.

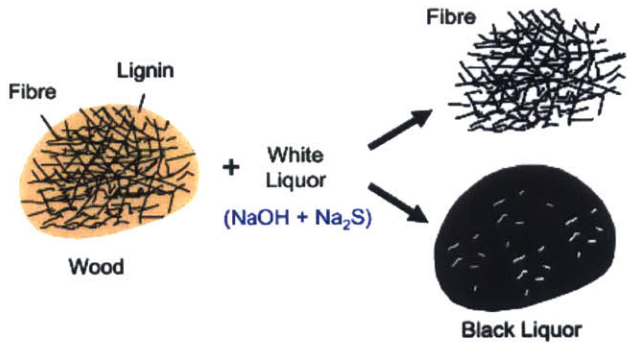

Figure 1-1: Cooking chemicals (sometimes known as "white liquor", usually consisting of NaOH and Na2S, but occasionally Na2SO3 as well), are combined with wood or agro-based raw materials in the digestor and cooked at around 170°C for an extended period of time to ensure that the white liquor extracts the lignin from the raw material, which then separates out the fiber to go on for papermaking (reproduced from Tran and Vakkilainnen 2008).

Black liquor, usually with a total solids level of more than 10%, mainly consists of 30-45% alkali lignin, 25-35% hydroxy acids (mainly degradation products from hemicellulose in the original woody raw materials) and 17-20% sodium (in frequently in forms of NaOH, Na_2S, Na_2SO_3 or Na_2SO_4) in the solids content, and generally have high COD (Chemical Oxygen Demand) and BOD (Biological Oxygen Demand) that are over 10000 mg/L, with some COD as high as 150,000 mg/L and BOD as high as 35,000mg/L (Tiku et al. 2007; Hung and Sumathi 2005; Jain et al. 2001; Sundholm 1999). The lignin content is highly resistant to microbial digestion due to its high molecular weight and the various biologically stable carbon-to-carbon and ether linkages. Lignin molecules also have a tendency to self-consolidate in solution, resisting degradation to simpler molecule species and thus causing a very high COD to BOD ratio (Kumar, Kumar, and Bhardwaj 2011; Garg, Mishra, and Chand 2010). Thus, the microbial treatment in a regular effluent treatment

plant (ETP) cannot successfully degrade lignin and extra measures is needed for black liquor treatment.

In this study, the black liquor in question is produced by small-scale paper mills in India. The pulp and paper industry has a long history in India, with around 406 registered pulp and paper mills as of 2007 (Tiku et al. 2007). Only around 34 mills have a capacity of more than 100 tons per day of production. A large majority of the paper mills are considered small-scale mills with less than 30 tons per day of production. While the traditional raw materials used in production is still wood and bamboo, other alternative raw materials have become more and more popular, including bagasse, straw and so on (Tiku et al. 2007). While non-wood raw materials only account for around 10% of the total pulp and paper production worldwide, non-wood derived paper is still relatively common in developing countries (Sridach 2010). For example, in India, apart from the recycled-waste based paper (47%), the paper, paper board and newsprint production consist of 32% wood-based raw material and 21% agro-based (Dixit, Jain, and Mathur 2012).

For the smaller paper mills, especially small paper mills with non-wood raw materials, the infrastructure for treating black liquor is frequently lacking due to economic non-viability (the details will be further explained in Chapter 3). Thus, these paper mills are facing serious challenges and causing high levels of wastewater pollution: in some cases, the untreated black liquor is being directly discharged into surface waterways.

1.2 Treatment Methods

The traditional treatment of chemical recovery is briefly introduced in this section, followed by some innovative alternative treatment proposals including acid precipitation, microbial treatment and membrane treatment. A general comparison between the methods is also be carried out.

The standard treatment for large wood-based white paper mills is a multiple effect evaporator followed by a Thomlison recovery boiler (as shown below in Figure 1-2), which burns the black liquor down for energy production from the organics and recovers the left over alkali inorganics as cooking materials (Vakkilainen and Oy 2003; Dixit, Jain, and Mathur 2012). The initial concentration of the fresh (or "weak") black liquor is usually around 7-15% dry solids, and will be concentrated up to 65% - 85% dry solids content in the evaporation plant, which will be then passed on to the boiler to be burned in large units (Adams 1997). Any black liquor wetter than the required level of concentration may potentially cause a blackout of the furnace and may even become an explosion hazard as the pyrolysis of the black liquor may produce a large amount of combustible gas (Adams 1997). The design of recovery boilers is frequently very complex in order to optimize both the recovery of cooking chemicals and energy (Adams 1997). In large factories that implement chemical recovery boilers, the electrical energy generation capability has continue to grow as technology advances. For example, some modern Scandinavian mills can produce surplus electricity of up to 7 GJ per ton of pulp simply through the combustion of organic matter

in black liquor, creating net revenue and making the treatment of black liquor an actual profitable practice (Vakkilainen and Oy 2003; Arkell, Olsson, and Wallberg 2014).

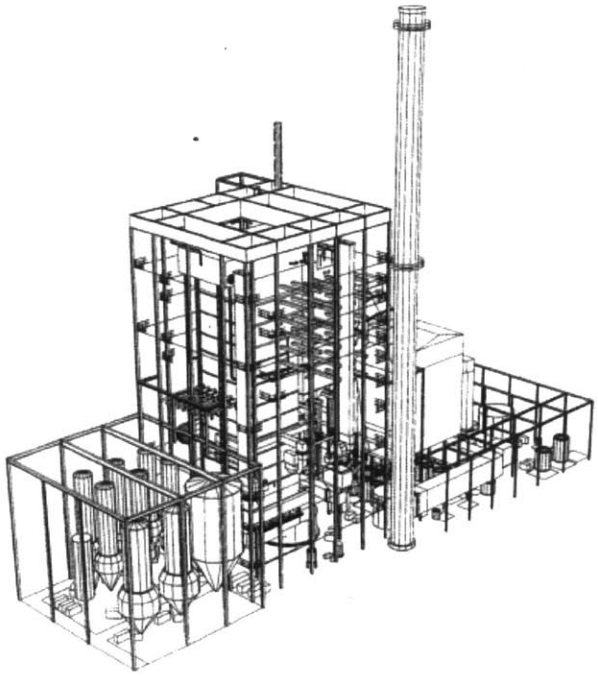

Figure 1-2: General arrangement of a kraft recovery boiler system. Toward the front in the figure is a set of evaporators, and the boiler is suspended in the middle structure which also holds fans, tanks and other additional equipment (reproduced from Adams 1997).

However, the situation is very different for small scale paper mills that use non-wood agro products for paper production. The chemical compositions of non-wood materials have large variations, leading to variation in chemical and physical properties different from the relative consistency of wood-based fibers (Sridach 2010). The species of the non-wood stock as well as local soil and climate conditions could all come into effect in determining the quality (Sridach 2010). In general, black liquor from non-wood raw materials demonstrates poor chemical and thermal efficiencies in the recovery boiler system due to lower total solids concentration, higher viscosity, higher contents of non-process elements in the boiler such as silica, potassium and chlorides and poorly dispersed organic macro-molecules (Dixit, Jain, and Mathur 2012; Jain et al. 2001; Liu et al. 2004). The high-levels of non-process elements will have strong bearings on the boiler, causing issues including plugging and scaling and low heat recovery that largely reduces the efficiency of resource recovery. Black liquor viscosity is also an issue, which leads to the firing of black liquor at an unfavorable concentration and lowering energy generation (Dixit, Jain, and Mathur 2012). Much current research is focused on removal of these elements (e.g., desilication of black liquor by the lowering of pH through CO_2 enriched flue gas; removal of chlorides scaling from the furnace with sulfuric acid and so on) as well as heat treatment of semi-concentrated black liquor

for better viscosities, so that black liquor treatment by chemical recovery boilers can still be economically preferential (Jain et al. 2001; Mandavgane, Paradkar, and Subramanian 2006; Mandavgane and Subramanian 2006; Dixit, Jain, and Mathur 2012; Vadivel, Umarani, and Rajesh 2012). Nevertheless, these pre-treatment methods are still challenging – for example, the co-precipitation of lignin makes filtration of precipitated silica in carbonated black liquor very difficult (Mandavgane and Subramanian 2006).

Even as techniques for pretreating non-wood black liquor for better chemical recovery are developed, the chemical recovery boiler solution is still economically difficult for small-scale paper mills, especially brown paper mills, due to the low concentration and low alkali level in their black liquor, potentially due to the use of fewer chemicals in the pulping process and the less efficient washing cycles (Tiku et al. 2007). Overall, the non-wood black liquor still presents a much lower heat value compared with wood black liquor (Liu et al. 2004). There is also a high initial investment and long payback period for this technique, which is highly challenging for smaller mills (Central Pollution Control Board 2008).

Apart from the traditional chemical recovery boiler treatment methods, other alternative treatments have been briefly explored. Some general physical and chemical treatment methods for black liquor include chemical precipitation, filtration processes and adsorption processes. While effective to a certain degree, the challenge with these methods is frequently the high cost of treating hundreds of tons of wastewater each day. Biological treatment beyond the regular activated sludge treatment has also been explored, but there is still yet to be a specific microbial flora that's proven to be cost-effective in degrading highly concentrated lignin.

Due to such difficulties, many mills simply send their black liquor directly to effluent treatment plant without any recovery, causing heavy pollution discharge into nearby streams. Currently, new treatment technologies for black liquor are still under exploration specifically for small-scale pulp and paper mills, and the methods will be described in more details below.

1.2.1 Low Temperature Incineration

The Low Temperature Incineration (LTI) techniques employ very similar concepts to the chemical recovery boiler system of evaporation to recover the alkali products, but operate at a lower temperature using a fluidized bed reactor system instead of a boiler (Rangan and Rangamannar 1997). This is a cheaper alternative for small-scale mills that cannot afford the high capital cost of a large-scale chemical recovery boiler. While high non-process chlorides are also challenging for this process, the tolerance of high viscosity and other non-process elements is generally higher for LTI, making it possible to operate on agro-based black liquor without too much pretreatment (Olazar et al. 2002).

It is important to note that LTI treatment does not employ waste heat recovery system from the combustion of lignin (Rangan and Rangamannar 1997). Hence, while it reduces initial investment, the profit that it extracts from black liquor is less than chemical recovery boilers, making LTI not

as economically preferable in the long run. From our interviews in India, we have come to learn that LTI is likely to serve as an intermediate step before the paper mill secures sufficient funds for an upgrade to a full chemical recovery plant.

1.2.2 Acid Precipitation

During acid precipitation treatment, black liquor is acidified to a pH of 2-3 and lignin is expected to precipitate in colloidal form (Central Pollution Control Board 2008; Jain et al. 2001). Lignin is then filtered through solid and liquid separation, where the lignin dries off to become a value-added product and the filtrate is recycled or neutralized for further treatment processes. Acid precipitation has been tested at pilot plants where lignin is generally acidified by adding sulfuric acid or hydrochloric acid, and then filtered through a filter press system to eventually become sun dried for chemical usage or biofuel (Central Pollution Control Board 2008). To further promote the precipitation of lignin, the use of coagulating and flocculating agent has also been suggested along with acid precipitation (Jain et al. 2001; Garg, Mishra, and Chand 2010; Ahmad et al. 2008).

The challenge in both cases are the purity of the lignin produced. Lignin and silica precipitate at very similar pH levels, resulting in a lignin product of lower-grade quality especially when coagulants are added, which does not justify the cost of the chemical and energy input (Jin et al. 2013; Toledano et al. 2010). Additionally, the highly acidic filtrate creates operational problems (Jin et al. 2013). Due to these issues, acid precipitation has not been widely applied in small-scale mills.

1.2.3 Microbial Treatment

While lignin is highly biorefractive and cannot be processed by most microbes, some studies have also investigated specific strains of bacteria that may successfully digest lignin (Gupta, Minocha, and Jain 2001; Kumar, Kumar, and Bhardwaj 2011; Lara et al. 2003). Species including *Aeromonas formicans* and *Trametes elegans* have been shown to degrade lignin by over 70%, which largely reduces of the COD and color of the effluent, making it possible for a regular effluent treatment plant to treat afterwards (Gupta, Minocha, and Jain 2001; Lara et al. 2003).

White-rot fungus, *S. commune,* have also been reported to degrade lignin, the major component of black liquor. However, white-rot fungus may only work with continuous addition of extra carbon sources and relatively low levels of lignin (Belsare and Prasad 1988).

Overall, the experiments have only been carried out on a lab scale, and the black liquor is generally diluted before treatment (Gupta, Minocha, and Jain 2001; Kumar, Kumar, and Bhardwaj 2011; Lara et al. 2003) The bacteria were also in pure and isolated form. These conditions are very different from the case for the pulp and paper mill industry, and the ability for such a solution to be scaled up may seem questionable due to these limits and carefully controlled conditions at the bench scale.

1.2.4 Membrane Treatment

There has also been a considerable amount of research of using membrane treatment as an alternative treatment method. Due to the relatively large molecular weight of lignin, lignin in black liquor can be concentrated through ultrafiltration, and the permeate containing low molecular weight lignin and inorganics can be reused in digestors as cooking liquor (Ross et al. 1986; Wallberg, Jönsson, and Wimmerstedt 2003b; Wallberg and Jönsson 2003; Bhattacharjee and Bhattacharya 1992; Dafinov, Font, and Garcia-Valls 2005). For small-scale pulp and paper mills, the study of membrane treatment is to search for a cheaper and less energy intensive solution for black liquor that allows for the separation of lignin to create value-added products, or as an alternative way to concentrate black liquor instead of using the energy-intensive multi-effect evaporators (Bhattacharjee and Bhattacharya 1992; Bhattacharjee and Bhattacharya 2006). On the other hand, the aim in development of membrane treatment method for large-scale factories is to make effective use of the large energy surplus that can go up to 7GJ per ton of pulp produced (Wallberg, Jönsson, and Wimmerstedt 2003b; Wallberg, Jönsson, and Wimmerstedt 2003a). By extracting lignin through membrane methods from the black liquor and finding alterative usages for it, the surplus energy production from lignin can be recovered.

Many studies have looked at how variables such as transmembrane pressure (TMP), feed temperature, flow rate, and membrane molecular weight cutoff (MWCO) affect the performance of the membrane. While the conclusions varied, most studies indicated that lignin can be successfully extracted and the retention rate can be as high as 80% (Liu et al. 2004). Flux decline is also a major concern when considering scaling up the membrane treatment method. This is generally attributed to gel formation, osmotic pressure retardation or membrane fouling caused by reversible or irreversible pore plugging (Bhattacharjee and Bhattacharya 2006). Consequently, many studies have been focusing on how flux varies with TMP and MWCO, as well as how flux declines over time (Bhattacharjee and Bhattacharya 1992; Wallberg, Jönsson, and Wimmerstedt 2003b; Mosqueda-Jimenez, Narbaitz, and Matsuura 2004). While a continuous drop in flux is observed in most experiments, it has been shown that a back flush system can usually help maintain a stable flux (Cortifias et al. 2002). Membrane rotation modules has also been proposed as an effective means to minimize flux decline (Bhattacharjee and Bhattacharya 2006).

Apart from flux decline, the high capital and maintenance costs of the membranes also account for why membranes have not yet been widely adopted in the field. Due to the slightly higher pH value and high total solids value of the black liquor, membranes may tend to have a much shorter lifetime and needs to be cleaned frequently, all of which add to the maintenance cost (Liu et al. 2004). A study in Sweden calculated a net cost of around 33 euros to recover one ton of lignin assuming a lifetime of 18 months for polymeric membranes and 6 years for ceramic membranes, and indicated that the cost would be lower if lignin was sold in specialty chemicals rather than biofuels (Jönsson and Wallberg 2009).

One ceramic membrane treatment pilot plant had been set up in Sweden and ran relatively

continuously for eight months using black liquor coming directly from the digestor. While serious fouling was experienced with softwood black liquor, there were no serious issues with hardwood black liquor if the membrane was cleaned once a week (Wallberg and Jönsson 2006). No records of membrane treatment plants have been found for agro-based paper mills yet, but a few companies (e.g. Aastropure; http://www.aastropure.com/) in India are currently working to setup pilot plants for the concentration of black liquor for further biofuel utilities (Satish Agrawal of Aastropure, personal communication, India, Jan 2015). These pilot-scale studies are great reference points and indicate a high possibility for the eventual adoption of some form of membrane technology in the field of black liquor treatment.

A summary of the alternative methods and their advantages and disadvantages are listed in Table 1-1.

Considering the current status of all existing treatment methods, more potential can be observed for membrane treatment relative to other technologies along metrics of effectiveness in assisting the treatment of black liquor. This method may be especially interesting to explore for black liquor from agro-based brown paper mills, where the black liquor has relatively low total solids levels. For lower concentration, less fouling may be expected, giving agro-based black liquor an advantage over wood-based black liquor in applying membrane-based methods. Local paper mill industries have indicated that their attempts at low temperature incineration have not been successful, both due to mechanical issues of the facilities and due to the fact that they would lose a large margin of profit when operating the incineration system (Pankaj Agrawal of Bindlas Duplex, personal communication, Muzaffarnagar, India, Jan 2014). Attempts have also been made at acid precipitation methods, but the neutralization of the acid solution has caused some leftover lignin to re-dissolve, and the Central Pollution Control Board has already decided to restrict the application of this method due to concerns that wastewater will be discharged at highly acidic pH (Bindlas Duplex staff, oral communications, Muzaffarnagar, India, Jan 2014). Membrane treatment as an alternative for concentrating black liquor, in contrast, still remains a valid possibility according to literature evidence and the interest of the location paper industries. The general scheme of membrane method is described in Figure 1-3. As we can see, the output retentate or concentrate stream of concentrated lignin solution can be further processed to either directly extract lignin or recover chemicals similar to the chemical recovery process. The output permeate stream of the solution of sodium compounds and other caustics could potentially be reused in the cooking process. These two output streams are very similar to the outputs of the boiler chemical recovery process, suggesting that membrane treatment could potentially be an effective alternative for the evaporators and boilers, if the cost can be justified.

Table 1-1: Summary of alternative treatment methods for black liquor.

Methods	Advantages	Challenges	Current Status

Acid Precipitation (potentially with coagulants)	Relatively simple and convenient operational procedure with little capital cost; lignin can be precipitated out for further usage.	The usage of coagulants may increase costs; precipitated lignin contains coagulations and may affect its purity and value; waste stream becomes highly acidic and would require further pH adjusting before discharge or reuse.	Has been implemented for a short period of time but then stopped by the Pollution Control Board due to concerns with the acidic discharge.
Microbial Digestion	Bacteria may have ability to use lignin and cellulose as carbon source; lignin can be digested with no further disposal concerns; Natural and eco-friendly	Research has only dealt with highly diluted black liquor; the bacteria may require additional nutrients needed to survive in the wastewater; lignin is digested can not be further utilized for profit.	Research was only conducted at lab-scale with pure and isolated streams of bacteria; this method has not been implemented in the field.
Ultrafiltration	Precise control of the retention of lignin can be achieved by using different membranes; lignin can be obtained in concentrated form for further utility; pilot studies have been carried out successfully	Potential high maintenance cost and quick decline of flux during operation due to fouling (may not be as serious with less concentrated black liquor from small-scale mills); limited temperature and pH stability	Pilot plants were in operation for a few months in Sweden. companies in India are also in the process of scaling up membrane setups for black liquor treatment.

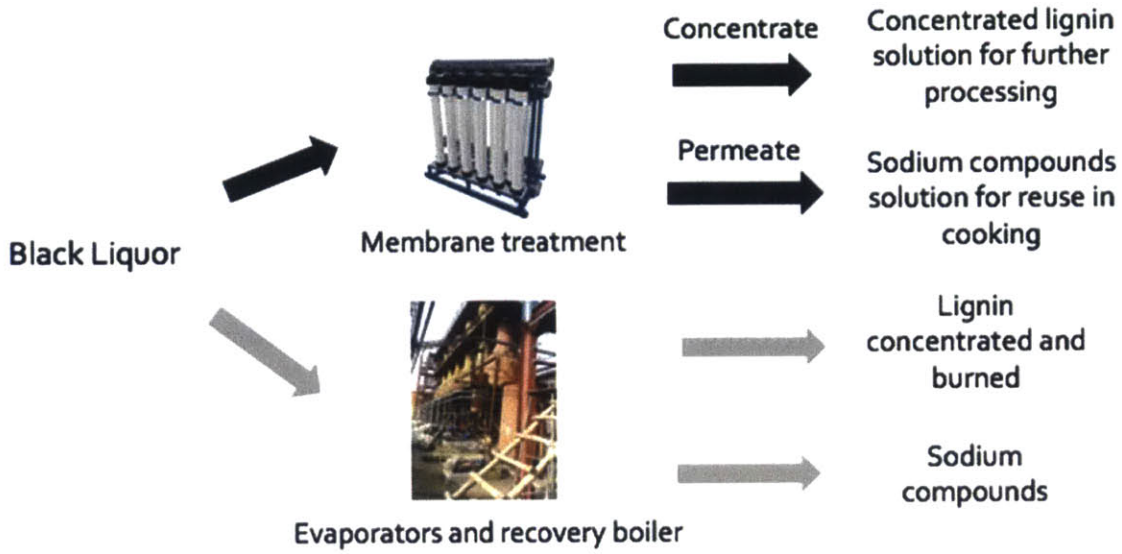

Figure 1-3: Comparison of the output streams between membrane treatment methods and chemical recovery processes.

In order to verify whether membrane method is an appropriate cost-effective alternative for the treatment of small-scale paper mills with agro-based raw materials, membrane experiments that mimic field-scale treatment would be carried out at the lab scale to evaluate the effect of treatment. Due to the large variability of different forms of black liquor and the non-uniform structure of lignin, experimental methods would be a more direct reflection of the complex treatment reality. In comparison, more abstract methods such as modeling would require more precise and uniform data that are not available for black liquor. To illustrate the rationale for the experimental design, this thesis will first present in Chapter 2 a literature review on the current development of membrane methods in the field of black liquor treatment and determine major gaps in literature that should be filled by further experimental evaluations in order to comprehensively predicts the potential of membrane treatment's applicability in this field.

1.3 Thesis Outline

Overall, this thesis aims at evaluating the cost-effectiveness of utilizing membrane as an alternative treatment method in concentrating black liquor wastewater streams for further utilization, mostly through lab-scale analysis.

In Chapter 2, we will take a look at the current literature on membrane treatment for black liquor, mainly focusing on the specific types of black liquor that have been worked with, the experimental variables that were studied and useful experiment results and conclusions about the applicability of membranes that were obtained from literature. The limits in the current experimental methods,

limits in the applicability of the conclusions to the type of paper mill and black liquor in question, and the current barriers to implementation will also be addressed. In Chapter 3, we will move on to further characterize the specific type of black liquor to be considered, how it is produced, its chemical and physical properties and the crucial parameters for experimental purposes. Chapter 4 will detail the membrane experimental design utilized to generate the results in Chapters 5 and 6. Chapter 5 and 6 will introduce respectively results from fresh field fresh black liquor produced in India paper mills and results from synthesized black liquor in U.S. labs. The final chapters will discuss and conclude on the implication of lab results, and the estimated cost-effectiveness of membrane treatment based on current results. Future work will also be proposed in the conclusion.

Stakeholder analysis and implementation plans for the work are included in the appendix.

2 Literature Review

In this chapter, a general overview of literature on membrane treatment of black liquor is first given in Section 2.1, with a focus on experimental studies. The experimental methods and results of these studies are then detailed in Section 2.2 and 2.3, with Section 2.4 concluding on the key gaps in literature. The overall research objectives are then defined in Section 2.5 based on the gap analysis.

2.1 Overview

Membrane methods have been receiving attention for the treatment of black liquor and general pulp and paper mill effluents in order to retrieve valuable organics and maintaining environmental pollution standards (Bhattacharjee and Bhattacharya 1992; Bhattacharjee and Bhattacharya 2006).

Membrane treatment has been most extensively studied by lab groups in Europe (mostly Sweden, Norway and Finland), India and China. Generally, for studies performed in Europe, the raw material for papermaking is wood, while for studies in developing countries such as China and India, the raw material is agricultural waste such as rice straw, bagasse and so on (agro-based paper production). The quality of the black liquor also differs accordingly.

The studies of membrane treatment of black liquor in Europe began back in the 1970s and have traditionally been related to spent sulfite liquor, the equivalent of black liquor in sulfite pulping mills, due to the prevalence of sulfite pulping methods during that time (Olsen 1980; Jönsson and Wimmerstedt 1985; Tanistra and Bodzek 1998). Some studies have expanded to industrial scales with membranes areas as large as 1120 m^2 with multiple-stage modules (Olsen 1980; Jönsson and Trägårdh 1990). More recent studies are focused on optimizing lignin concentration and fractionation in kraft paper mills through ultrafiltration and nanofiltration membranes (Wallberg, Jönsson, and Wimmerstedt 2003b). The membranes in these studies are capable of directly treating fresh black liquor with composition and temperatures mimicking industrial conditions, while still showing positive results. Moreover, while most experimental studies were only conducted from a few hours to a few days, pilot plant studies have also been set up with membrane areas up to 1.715 m^2 and total run time up to 8 months. (Wallberg and Jönsson 2006).

On the other hand, studies in India and China have been more limited. Studies of black liquor have started in the 1990s when reducing environmental pollution began receiving significant attention (Bhattacharjee and Bhattacharya 1992). However, most of the studies only focused on lab-scale experiments and modeling of experimental results, and many of them still used dead-end configurations, a lab-scale configuration that is generally more prone to fouling in comparison to the more widely adopted cross-flow configuration at an industrial scale (Bhattacharjee and Bhattacharya 1992; Bhattacharjee and Bhattacharya 2006). Almost none of the experiments directly dealt with fresh black liquor with no pre-treatment. Dilution, mesh filtration or microfiltration are generally applied to the feed before it comes into contact with the membrane (Bhattacharjee and Bhattacharya 1992; Bhattacharjee and Bhattacharya 2006; Liu et al. 2004). While some experiments did run continuously over a long period of time, concentrating feed studies were not reported. The knowledge of membrane effectiveness and limits in concentrating non-wood black liquor is therefore limited. Consequently, despite the positive results from the present lab-scale research, there are still no reported industrial-scale membrane treatment plants or even pilot-scale studies for black liquor. The gap between lab research and industrial scale

application is still large in developing countries. The limited resources and experiences of small-scale paper industries raises even more challenge for these mills to adopt new membrane technology, and the risk may be too high with a treatment method with a high initial capital investment cost (Jönsson and Wallberg 2009). Thus, this research attempts to help bridge this research-industry gap and help take one step closer to the eventual acceptance (or rejection) of membrane treatment methods.

2.2 Experimental Conditions

To better understand the conclusions as well as gaps from previous literature, we then turn to explore the different experimental setups and experimental results from the key literatures in detail.

Common types of membrane (with different pore sizes) and the corresponding operating conditions are shown in Table 1.

Table 2-1 Common membrane filtration types: MF (microfiltration), UF (ultrafiltration), NF (nanofiltration) and RO (reverse osmosis), with their corresponding operating conditions (reproduced from Toledano et al. 2010).

Process	Membrane type and pore size	Membrane material	Driving force (bar)	Applications
MF	Symmetric microporous (0.1–10 μm)	Ceramics, metal oxides (aluminium-, titanium-, zirconium-), graphite, polymers (cellulose nitrate or acetate, PVDF, polyamides, polysulfone, ptFE)	1–5	Sterile filtration, clarification
UF	Asymmetric microporous (1–10 nm)	Ceramics, polysulfone, polypropylene, nylon 6, PTFE, PVC, acrylic copolymer	1–10	Separation of macromolecular solutions
NF	Thin-film membranes	Cellulosic acetate and aromatic polyamide	10–30	Removal of hardness and desalting
RO	Asymmetric skin-type (0.5–1.5 nm)	Polymers, cellulosic acetate, aromatic polyamide	Up to 200	Separation of salts and microsolutes from solutions

For black liquor specifically, both organic and inorganic membranes have been used. Polyethere sulfone (PES), which is known for low fouling rates and broad pH compatibility, has been used directly to filter untreated black liquor (Bhattacharjee and Bhattacharya 2006). Cellulose triacetate membranes have also been used (Bhattacharjee and Bhattacharya 2006). Multi-channel tubular ceramic membranes with a skin layer of TiO_2 and ZrO_2 have also been applied to concentrate black liquor effluent, and the chemical and temperature resistance of the ceramic membranes have been shown to be favorable in treating hot black liquor (up to 90°C) fresh from the digestor (Dafinov, Font, and Garcia-Valls 2005). The tubular membranes at the lab-scale are usually around 25cm long with channel diameters of 3.6 mm (Dafinov, Font, and Garcia-Valls 2005). Larger-scale modules have also been set up for experimentation, using 15 kDa ceramic membranes that are 1.2 m in length (Jönsson and Wallberg 2009). Ceramic membranes have been shown to generally have better chemical stability, high mechanical strength and better fouling resistance than polymeric membranes (Liu et al. 2004). Despite the advantages, studies have also shown that ceramic membranes may exhibit a larger cost compared to polymeric membranes (Arkell, Olsson, and Wallberg 2014).

As for the pore size of membranes studied for black liquor treatment, microfiltration has been studied to remove suspended colloidal matter from kraft black liquor, which would then be partially recycled to the digestor in traditional pulping processes (Cortifias et al. 2002). In this process, the colloidal removal would greatly enhanced the paper quality (Cortifias et al. 2002). Microfiltration and centrifugation as a pretreatment of black liquor before further filtration has also been shown to be highly efficient in decreasing the level of membrane fouling (Bhattacharjee and Bhattacharya 1992). Filtration has been coupled with crystallization to extract carboxylic acid from black liquor (Niemi et al. 2011). However, the majority of the studies focus on the retention and concentration of lignin with ultrafiltration and nanofiltration membranes. Both ultrafiltration and nanofiltration of black liquor have been studied. Both are able to significant remove hemicelluloses and lignin from the permeate stream and concentrate them in the retentate stream, but usually unable to separate the two families of organics that comprises the majority of organics in black liquor (Arkell, Olsson, and Wallberg 2014). Membranes of smaller pore sizes may incur higher costs due to a lower flux, but may also incur a higher benefit due to a stronger retention of organics – in fact, Wallberg et al. have shown that 5 kDa membranes may be more cost-effective than 15 kDa membranes for extracting lignin (Wallberg, Holmqvist, and Jönsson 2005; Wallberg, Jönsson, and Wimmerstedt 2003b). Ultrafiltration were also explored as a pretreatment method for nanofiltration, and the consecutive configuration of the two types of membranes have also been said to help with separating between hemicellulose and lignin and producing purer lignin (Arkell, Olsson, and Wallberg 2014). The additional cost of such levels of pretreatment would be relatively high.

Experiments have been carried out in stirred cell configurations (a type of membrane filtration configuration of a dead-end flow cell with a stirring rod stirring at the surface of the membrane to alleviate the fouling layer on the membrane). For example, Bhattacharjee and Bhattacharya have tested dilute black liquor with around 20 g/L of total solids in a stirred cell configuration with polymeric membrane of a 5 kDa molecular weight cut-off (MWCO) (Bhattacharjee and Bhattacharya 1992). Flux as high as 45 LMH were observed under 830 kPa (Bhattacharjee and Bhattacharya 1992). Bhattacharjee and Bhattacharya have augmented the system with a rotating disk membrane module to alleviate the flux decline problem by increasing the shear rate to approximately 2×10^{-5} s^{-1} through rotation and preventing the cake layer formation (Bhattacharjee and Bhattacharya 2006). The rotation of the membrane has been shown to be much more effective in reducing concentration polarization and thus reducing flux decline (Bhattacharjee and Bhattacharya 2006). The system was operated at 200 – 800 kPa with stirrer and membrane rotating speed going up to 1000 rpm (Bhattacharjee and Bhattacharya 2006). At around 500 kPa pressure, the flux can go up to almost 30 LMH with a high speed membrane rotation (Bhattacharjee and Bhattacharya 2006). These systems, while capable of yielding highly concentrated retentate streams in single pass, are high in cost and can only hold limited membrane area up to 2-3 m^2 (Bhattacharjee and Bhattacharya 2006). Consequently, stirred cells are generally not widely applied at an industrial scale and these results may be limited in their ability to predict larger scale operations in the paper mills.

Experiments have also been carried out in cross-flow settings. Dafinov et al. (2005) have treated wood pulping black liquor with 1, 5 and 15 kDa membranes in tubular modules (as shown in Figure 1) with a flow velocity of around 2 m/s at transmembrane pressures (TMP) of 300, 500 and 700 kPa. The runs were generally conducted for only around an hour to observe a relatively steady flow (where no significant flux decline can be observed). Flux generally increased as pressure increased. Retention of organic matter such as lignin depended mostly on pore size, but also exhibited a slight increase with increasing transmembrane potentially due to more increasing gel layer compaction on the membrane. Fractionation of lignin by diafiltraion (diluting and re-filtering the retentate) or different MWCO ultrafiltration membranes in series has also gained more attention as a method to obtain higher-purity lignin of a specific molecular weight range, potentially increasing its value (Liu et al. 2004; Toledano et al. 2010; Helander et al. 2013; Wallberg and Jönsson 2003; Wallberg, Jönsson, and Wimmerstedt 2003b). To obtain a purer permeate stream, low MWCO membranes were preferred, while to obtain purer lignin, high MWCO were used (Wallberg, Jönsson, and Wimmerstedt 2003b).

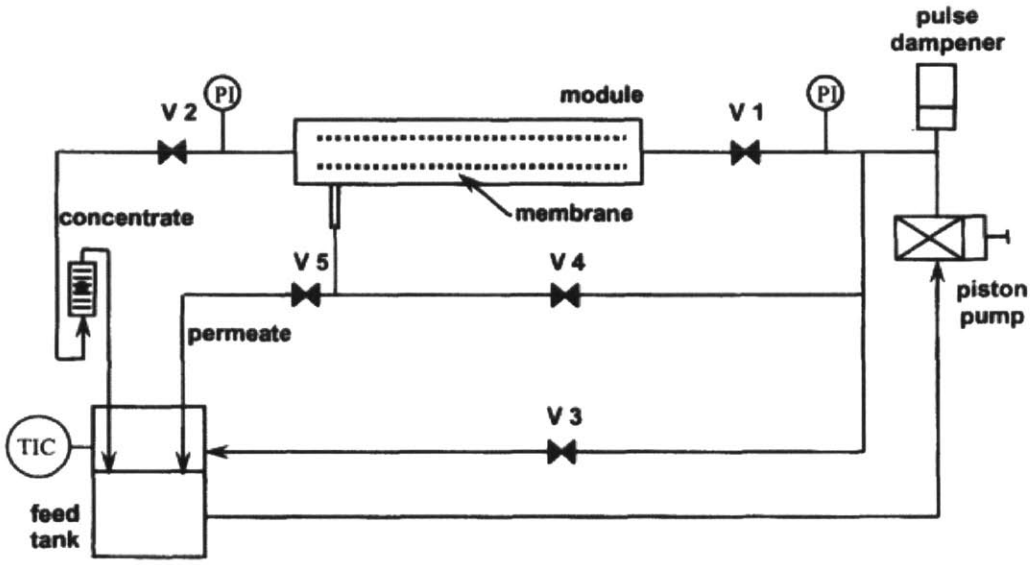

Figure 2-1: Standard membrane testing equipment for cross-flow filtration (reproduced from Dafinov, Font, and Garcia-Valls 2005)

Concentrating feed mode has also been tested, and permeate flux have been shown alongside the volume concentration factor of black liquor – while in some cases flux continuously declined due to more intense pore blockage as volume decreases and black liquor concentrates, in other cases the flux would stabilize after a certain concentration (Wallberg, Jönsson, and Wimmerstedt 2003a; Dafinov, Font, and Garcia-Valls 2005). The concentration tests are closer to what would be expected in industry where black liquor needs to pass through membrane multiple times to achieve the ideal concentration.

Pilot-scale studies for kraft black liquor have been reported by Wallberg and Jonsson (Wallberg and Jönsson 2006). The pilot plant was run relatively continuously for 8 months, and typical flow rates of 100 LMH were observed at 4 bar TMP for 15 kDa membranes. Pilot scale studies revealed many additional layers of issues that cannot be observed in lab studies. For black liquor from hardwood pulping, the membranes exhibit little fouling if cleaned once a week. However, for softwood black liquor, the membrane fouled badly and some flow channels became blocked within 10 days of operation (Wallberg and Jönsson 2006). A flow channel larger than 3.5 mm was recommended for future plants in treated fresh black liquor. Valve and pipeline blockage has also occurred. Although many issues that have not been observed in experimental settings emerged during large-scale studies, the pilot plant still proved the membrane treatment plants feasible in the long run despite the need for further improvements.

2.3 Experimental Results

Lignin retention, while largely related to membrane pore sizes, still differed among experiments due to other experimental parameters. For instance, while Wallberg et al. studied polymeric membranes of pore sizes 4, 8, 20 kDa and found the retention of lignin to be around 80%, 67% and 45% respectively (Figure 2-2), Wallberg and Jonsson also showed that 5 kDa ceramic membranes had a 66% recovery, even lower than 67% of 8kDa (Figure 2-3) (Wallberg, Jönsson, and Wimmerstedt 2003b; Wallberg, Jönsson, and Wimmerstedt 2003a). The retention of inorganic contents such as sodium and sulfur were usually 0% (Wallberg, Jönsson, and Wimmerstedt 2003b). Liu et al., on the other hand, found over 80% lignin retention for polymeric membranes up to 60 kDa, in a stirred-cell module (Liu et al. 2004). This variance may be due to the difference in lignin measurement methods, but may also be caused by other factors. For example, literature has shown that decreasing the cross-flow velocity increased the retention of lignin and non-process elements, potentially due to stronger collection of colloidal matter at the membrane surface (Wallberg and Jönsson 2003). Lignin retention also increased with increase in pressure due to more liquid permeating through the membrane and leaving more solutes to be retained, which may potentially block the pores of membranes and increase rejection further (Holmqvist, Wallberg, and Jönsson 2005; Ross et al. 1986).

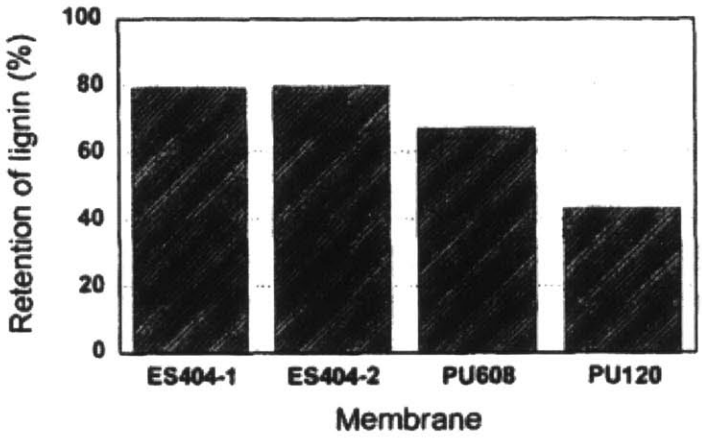

Figure 2-2: Retention of lignin for ultrafiltration of black liquor, where ES404, PU608 and PU120 are organic tubular membranes with 4, 8 and 20 kDa MWCO correspondingly. The retention of 8kDa membrane is 67%. (reproduced from Wallberg, Jönsson, and Wimmerstedt 2003b)

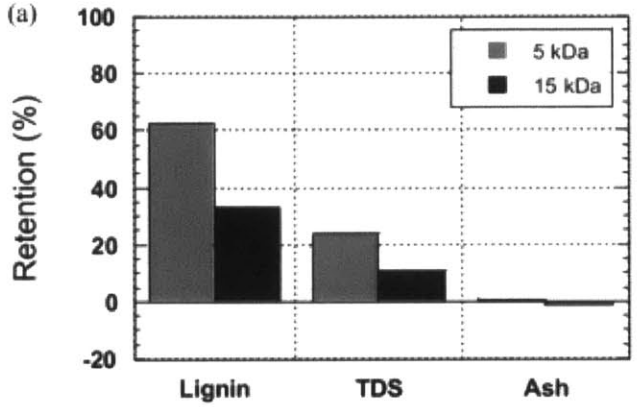

Figure 2-3: Retention of lignin for ultrafiltration of black liquor with 5 and 15 kDa ceramic membranes (reproduced from Wallberg, Jönsson, and Wimmerstedt 2003a). The retention ratio of 5 kDa membrane was 66%.

Flux also varied greatly depending on transmembrane pressure, cross-flow velocity, feed temperature, concentration and type of black liquor and so on. For example, fluxes around 90 LMH were observed at 60°C for 15 kDa ceramic membranes operating at approximately 1 bar TMP and 4.5 m/s cross flow velocity, as shown in Figure 2-4, while higher flux can be obtained with similar 15 kDa membranes under a slightly higher temperature and pressure, as shown in Figure 2-5 (Wallberg, Jönsson, and Wimmerstedt 2003a; Wallberg and Jönsson 2003; Wallberg, Holmqvist, and Jönsson 2005). As Figure 2-4 and Figure 2-5 also show, flux generally increased linearly with increasing TMP, but tend to level-off at higher TMP, potentially due to cake layer formation on the membrane (Wallberg, Jönsson, and Wimmerstedt 2003a; Ross et al. 1986). Flux also increased with increasing cross-flow velocity, as shown in Figure 2-6, and the correlation has been shown to be linear in non-black-liquor organic fouling studies as shown in Figure 2-7 (Choi et al. 2005;

Arkell, Olsson, and Wallberg 2014). Ceramic membranes also potentially gave a larger flux likely because it is more fouling-resistant and slightly less dense than polymeric membranes (Arkell, Olsson, and Wallberg 2014). While flux generally decreased with membranes of smaller pore-size as shown in Figure 2-6, Liu et al. have also found no relationship between flux and MWCO, as shown in Figure 2-8 (Liu et al. 2004).

The parameters mentioned above are the most studied factors in determining performance of a membrane system. However, even by holding these parameters constant – operating at similar TMP of around 2-3 bar and cross flow velocity of around 2-3 m/s, flux for similar 10 kDa polymeric membrane in cross-flow modules can still range from less than 20 LMH to over 50 LMH (Liu et al. 2004; Arkell, Olsson, and Wallberg 2014). There are still other parameters and conditions that may differ, such as the quality of the black liquor. For example, pretreating black liquor also almost always enhanced the flux (Arkell, Olsson, and Wallberg 2014).

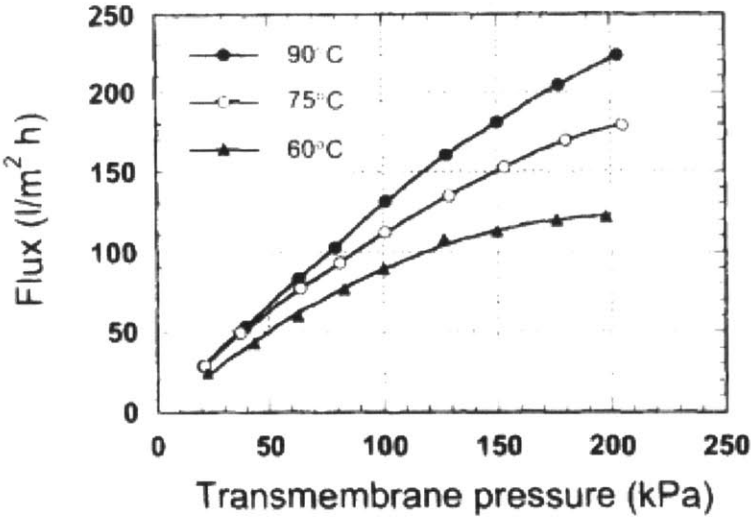

Figure 2-4: Influence of TMP on flux for kraft black liquor ultrafiltration for 15 kDa ceramic membrane (reproduced from Wallberg, Jönsson, and Wimmerstedt 2003a). 90 LMH was observed at 60°C and 100 kPa.

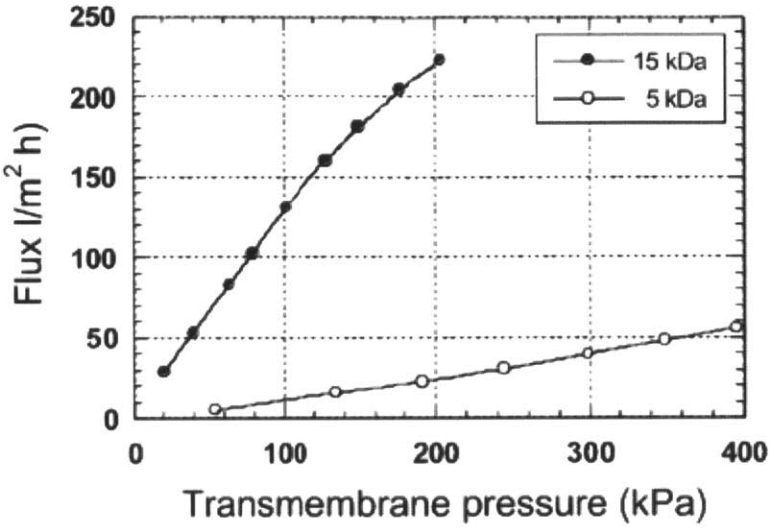

Figure 2-5: Influence of TMP on flux for kraft black liquor ultrafiltration for 5 and 15 kDa ceramic membranes. Flux higher than 90 LMH can be observed for the 15 kDa membrane (reproduced from Wallberg and Jönsson 2006).

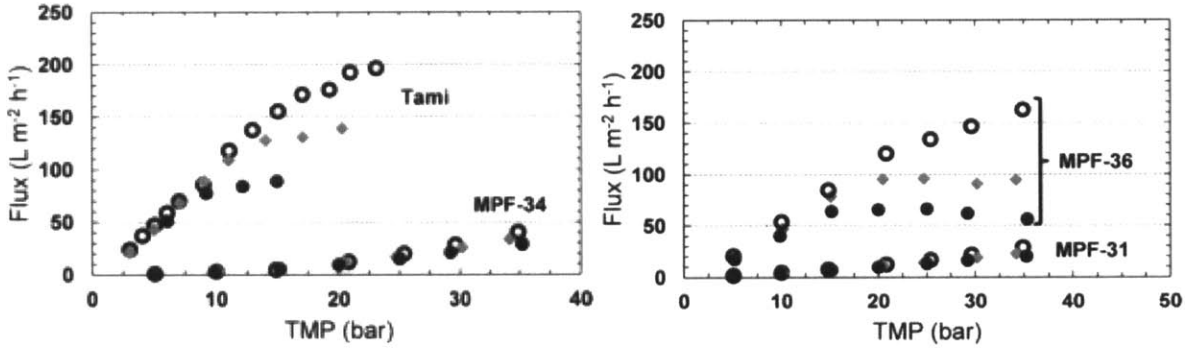

Figure 2-6: Flux variation as a function of TMP for Tami (1 kDa ceramic), MPF-36 (1 kDa polymeric), MPF-31 (600 Da polymeric) and MPF-34 (200 Da polymeric) membranes at different cross-flow velocity: 2 m s^{-1} (black circle), 3 m s^{-1} (grey rhombus) and 4 m s^{-1} (white circles). A roughly increasing flux with increasing pore size can also be observed (reproduced from Arkell, Olsson, and Wallberg 2014).

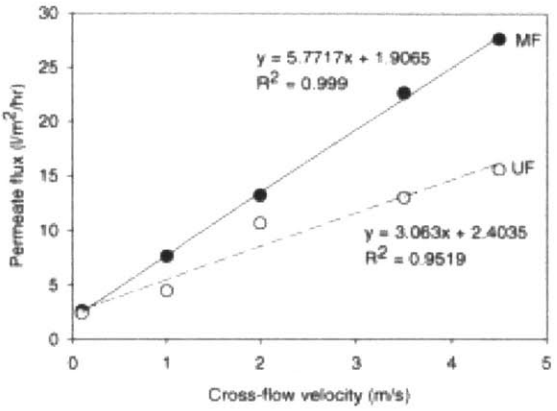

Figure 2-7: Permeate flux varies roughly linearly with cross-flow velocity in biological suspension ultrafiltration (UF) and microfiltration (MF) experiments reproduced from Choi et al. 2005).

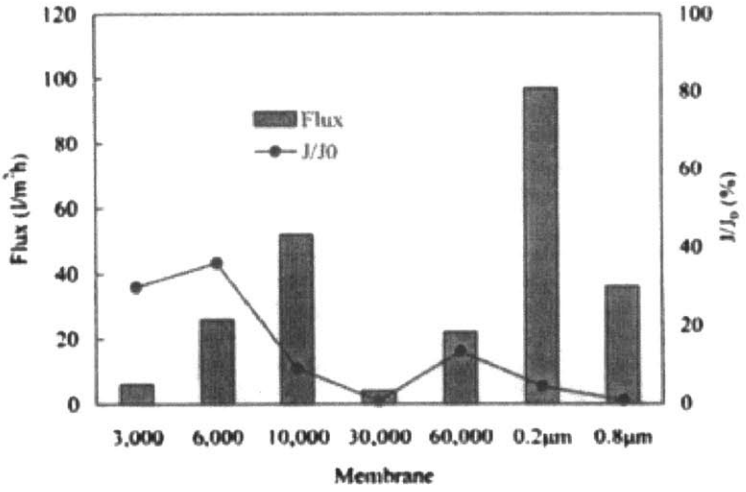

Figure 2-8: Stable flux for membrane of different pore sizes. According to Liu et al., there is no clear correlation between flux and pore size (reproduced from Liu et al. 2004).

In continuous feed tests, flux generally declined over time. Liu et al. have shown a decline of 25% with microfiltration of black liquor over 374 hours of operation, as shown in Figure 2-9 (Liu et al. 2004). Flux decline has been primarily attributed to lignin (Ross et al. 1986). In concentrating feed tests, flux generally declines as the feed becomes more concentrated. Wallberg et al. showed that the flux dropped to less than 17% of the initial flux as the lignin concentration in the feed increased 3-fold, as shown in Figure 10 (Wallberg, Jönsson, and Wimmerstedt 2003a; Wallberg and Jönsson 2003; Wallberg, Holmqvist, and Jönsson 2005). Wallberg et al. also showed that flux was directly correlated to lignin concentration until a limiting concentration is reached when further concentration is difficult and flux becomes independent of TMP (Wallberg, Holmqvist, and Jönsson 2005). For 5 kDa ceramic membrane, this concentration was around 240 g/L and the flux

dropped below 5 LMH.

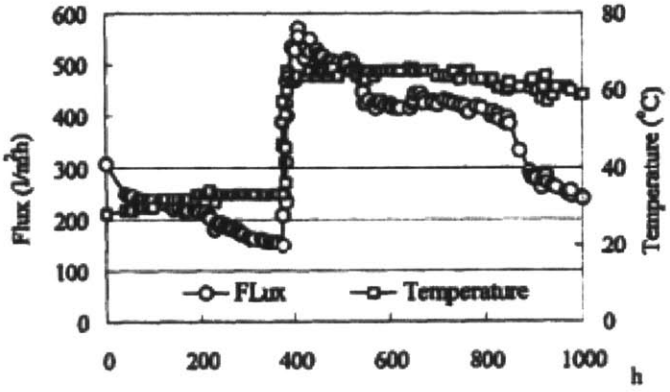

Figure 2-9: Long-term performance of 0.2 μm inorganic membrane at 200 kPa and 2.3 m/s cross-flow velocity. 25% flux decline can be observed over the first 374 hours of operation, before the temperature increase in the operation which largely increased the flux (reproduced from Liu et al. 2004).

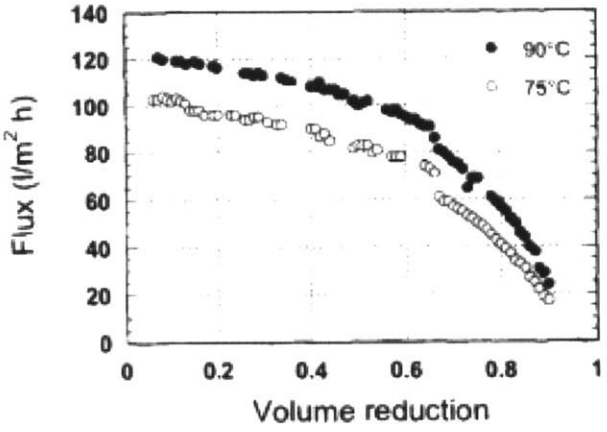

Figure 2-10: Flux during concentration operation of kraft black liquor at 75 and 90°C at 100kPa TMP (reproduced from Wallberg, Jönsson, and Wimmerstedt 2003a).

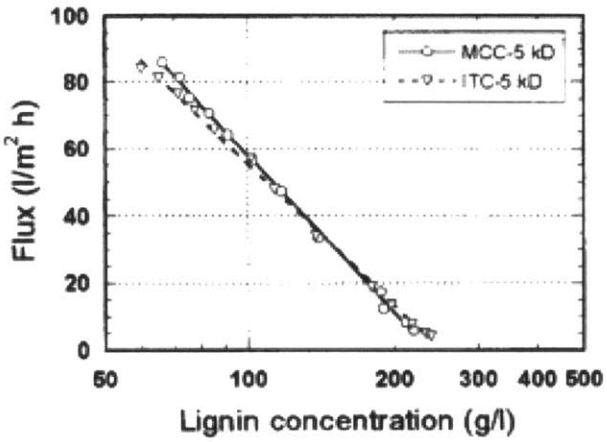

Figure 2-11: Influence of concentration on flux during filtration of MCC (modified continuous cooking) and ITC (isothermal cooking) black liquor. Limiting concentration can be observed at around 240 g/L – 250 g/L for 5 kDa membrane where further concentration cannot take place and flux becomes independent of TMP (reproduced from Holmqvist, Wallberg, and Jönsson 2005).

Flux and lignin retention results in general have shed light on the membrane performance difference between black liquor from batch and continuous digestion, and the difference between different treatment results for black liquor extracted at different pulping stages (Wallberg, Holmqvist, and Jönsson 2005; Holmqvist, Wallberg, and Jönsson 2005). More importantly, the results are crucial in assisting the selection of optimal operating parameter including membrane pore size, TMP, cross-flow velocity, and temperature and so on.

The ability of cleaning to regenerate membrane permeability also varied. While some research shows that 70-80% can be restored by backwash and almost full permeability can be recovered after chemical wash, others have shown that only 50% - 80% can be restored even with chemical washing – this may be mostly due to the difference in membrane materials, washing methods and operational conditions (Liu et al. 2004; Wallberg, Jönsson, and Wimmerstedt 2003b; Wallberg, Holmqvist, and Jönsson 2005; Holmqvist, Wallberg, and Jönsson 2005; Bhattacharjee and Bhattacharya 2006).

A summary of experimental conditions and experimental results from a sample of the representative literatures reviewed in this section is attached in Table 2-2.

Table 2-2: Summary of experimental conditions and results from key literatures

:k or v :ri	Black liquor pH	Black Liquor lignin (g/L)	Membrane material	Membrane modul e	Membrane area (m2)	Membrane channel diameter (mm)	Pore size (kda)	TMP (kpa)	Cross flow velocity (m/s)	Flux around 200 kpa (LMH)	Lignin rejection at around 5kDa MWCO	Note
e d e w	8.8	5	cellulose triacetate	stirred cell with rotating disc	0.002	-	5, 15	300 - 800	stirring up to 1000 rpm	16 (300 kPa)	60-75% (5 kDa)	Black liquor is pretreated by centrifutation followed by microfiltration
)d	12	-	ceramic (ZrO2, TiO2)	tubular	0.0094	3.6	1, 5, 15	300, 500, 700	2.1	30 (300 kPa)	total organic rejection: 30%	Both continuous and concentrating feed runs carried out
w	11	26	polyethersulfone	stirred cell	0.0038	-	3, 6, 10, 30, 60	200	stirring at 250 rpm (2.3 m/s)	30	98% (6 kDa)	Long-term monitoring over 1000 h also carried out for MF tubular membranes
wo l	13-14	56	ceramic (Al2O3, TiO2)	tubular		6	15	50-200	4.5	110 (60°C)	30 - 40% (15 kDa)	Both continuous and concentrating feed runs carried out
ce d e	13-14	45-65	polysulfone or polyethersulfone	tubular	0.047	12.5	4, 8, 20	100-700	4	10 (60°C)	80%	Both continuous and concentrating feed runs carried out
wo l	-	61	ceramic (Al2O3, TiO2)	tubular	0.245	3.5	5	200	4.2	85 (90°C), 20 (5x concentration)	65%	Only concentrating feed runs, at high temperatures > 90°C

two d	13-14	62	ceramic (Al2O3, TiO2)	tubular	0.15 5	6	15	200	4.5	150 (90°C), 50 (5x concent ration)	40% (15 kDa)	Only concentrating feed runs, at high temperatures > 90°C
two and dw od	13-14	58-69	ceramic (Al2O3, TiO2)	tubular	1.71 5	3.5	5	200	4.2	40-60 (>120° C)	30%	Pilot plant scale and continuous feed-and-bleed mode for almost 8 months
dw od	13-14	85-112	ceramic (Al2O3, TiO2)	tubular	0.15 5	6	15	100, 400	5, 3.7	50 (100 kPa, 400 g/L TDS, 90°C)	30-50%	Most extensive cost estimate carried out
two d	13.4	64	ceramic (TiO2) and polymeri c	tubular	0.06 - 0.2	6 or 12.7	0.2 - 1	200-3500 kPa	2-4	<25	80-90% (1 kDa)	For some experiments, ultrafiltraion is used as a pretreatment for nanofiltration

2.4 Gap Analysis

2.4.1 Modeling

Predicting flux as a function of time using classical models is still difficult for liquids such as black liquor and remains one of the limitations in designing black liquor membrane treatment processes. A combination of models (e.g. film theory, gel theory and filtration theory) have been used to predict the flux for stirred cell once a cake foulant layer has been formed and the resistance is known (Bhattacharjee and Bhattacharya 1992). However, this model behaved more favorably with standard macromolecular solutes such as polyethylene glycol (95% predicted values fall within 25% of experimental values), but behaved with more variability for a complex mixture of solutes that black liquor consists of (86% predicted values fall within 25% of experimental values) (Bhattacharjee and Bhattacharya 1992). The Spiegler-Kedem model has also been applied to simulate permeate flux and rejection for a 5 kDa stirred cell, and the predictions showed relatively good results with deviations within 10% (Sarkar et al. 2006).

As for cross-flow membrane modules, there is yet to be a fully developed model for black liquor to predict the initial black liquor flux and the decline of flux over time. Flow through cross-flow membrane modules and the flux decline over time have been modeled for general colloidal solutes (Chen and Kim 2006; Hong, Faibish, and Elimelech 1997), but they have not yet been closely applied to black liquor filtration. While a model would help predict membrane cleaning cycles and would be useful in analyzing the cost-effectiveness of the membrane method, there would be many challenging factors due to the non-uniform shape and structure of lignin and the varying black liquor characteristics. The morphology of the same alkali lignin even varied greatly in solutions of different concentrations (Liu et al. 2004). Thus, black liquor does not behave as predictably as most standard colloidal solutions, and there is not yet a modeling method that can best capture all the different components of black liquor. Consequently, it may be more realistic to start with using experiment simulations at the lab-scale to predict large-scale operations, rather than relying on models that are still yet to be adapted and perfected.

The focus of this research will be mostly on lab experiments in understanding the potential for membrane treatments.

2.4.2 Industrial Application

While many lab-scale experiments have been carried out, more comprehensive field pilot-scale studies and industrial-scale analysis have been missing. There have been establishments of membrane plants for treating spent sulfite liquor, the equivalent of black liquor in sulfite pulping paper mills, in countries including Norway and Canada. These membrane systems can reportedly concentrate the waste liquor up to around 20% total solids with a flux of around 40 LMH (Jönsson

and Wimmerstedt 1985). The membrane lifetimes can go up to one year with a cleaning frequency of 2-6 times a week (Jönsson and Wimmerstedt 1985). However, it is important to note that the major component of spent sulfite liquor is lignosulfonate rather than lignin, and the pH of the concentration is 2-3, therefore quite acidic (Jönsson and Wimmerstedt 1985; Bhattacharya et al. 2005; Tanistra and Bodzek 1998). For membrane methods in Kraft paper mills, pilot scale experiments carried out in Sweden were highly effective in helping local industries understand the limits and potentials of this method, but their operating conditions (e.g. using wood instead of agro-base raw materials and at a much larger scale) and financial circumstances largely differs from those of industries in developing nations such as India (Wallberg and Jönsson 2006; Jönsson and Wallberg 2009). These experiments and pilot plants shed light on the long-term outlook and generate potential strong interests in the application of membrane methods in pulp and paper industries. However, due to the difference in raw materials and pulping methods, there is still a lack of directly applicable industrial results for developing communities in India, and the barrier between lab-scale studies and pilot-scale studies still exist.

It is also important to note that most existing lab-scale experiments are run under conditions that may be impractical for industrial practices, including diluting the black liquor before treatment or carrying out extensive pretreatment before going through the membrane (Bhattacharjee and Bhattacharya 2006; Ross et al. 1986; Liu et al. 2004).

Most experiments are single-pass experiments with constant-composition feed that do not address the change in feed as black liquor becomes continuously concentrated, while generally to achieve the desired concentration multiple passes are required. Research on wood-sourced black liquor has been carried out to observe the flux as concentration increases, and while some experiments have shown no significant decline in flux even after the black liquor feed has been concentrated two-fold, others have shown relatively remarkable decline in flux over concentrating cycles with membranes of the same MWCO (Dafinov, Font, and Garcia-Valls 2005; Holmqvist, Wallberg, and Jönsson 2005; Jönsson and Wallberg 2009). Lignin rejection has also been observed to decrease as concentration increases (Jönsson and Wallberg 2009). These results clearly indicated the important effect that concentrating conditions have on experimental results. However, many of these experiments were done in discontinuous batches and may not realistically capture the effect of both time and concentration increase on flux decline (Dafinov, Font, and Garcia-Valls 2005). This, in addition with the contradicting flux results and differing raw materials, suggest that the predictive ability of these results for non-wood India black liquor may be limited.

With our research, we intend to approximate field conditions as much as possible to help bridge this gap between literature research and industrial conditions. More specially, with fresh black liquor directly from the Indian paper mills, our experiment will attempt to use limited pretreatment. Some of the experiments will also simulate a continuously concentrating setup that operates over a longer period of time. The results from such lab and field explorations may effectively help with filling in these gaps.

2.4.3 Experimental Variables

In the membrane selection section, the literature mostly focused on how variables such as MWCO, pressure and time affected flux. Optimization for parameters such as cross-flow velocity, which generally have a large impact on flux across membranes, were not closely accounted for (Choi et al. 2005).

Also, the types of membrane used in experiments were generally flat sheet membranes (or spiral wound modules that can be simulated by flat sheets), while industries recently have also been widely applying hollow fiber membranes. The flow mechanism behind the two different membrane types can vary, so it would be helpful to explore hollow fiber membrane configurations for the treatment of black liquor separately.

In addition, most experiments only monitored short-term reversible decline, but have not monitored long-term irreversible flux decline after backwash and membrane chemical cleaning. Usually over repeated operations, some membrane fouling may become permanent and cleaning is unable to return membrane surfaces to a pristine state, and initial permeate flux would be a poor indicator of the evolving surface condition of the membrane (Weis et al. 2005). As the number of filtration cycle increases, the fraction of membrane that has been irreversibly fouled will also increase (Crozes et al. 1997). Chemical cleaning of the membrane is usually avoided due to the higher cost for shutting down the system and for extra chemicals needed, but when backwashing is not as effective, the extra chemical step may be needed (Crozes et al. 1997). A typical flow pattern is shown in Figure 2-12. Literature results for irreversible fouling in surface water treatment have indicated that changes in transmembrane pressure and cross-flow velocity may affect the effectiveness of cleaning schemes and the rate of long-term irreversible fouling (Crozes et al. 1997). Increasing the backwash frequencies, cross-flow velocity and maintaining the transmembrane pressure below a certain threshold pressure could largely reduce the rate of irreversible fouling (Crozes et al. 1997).

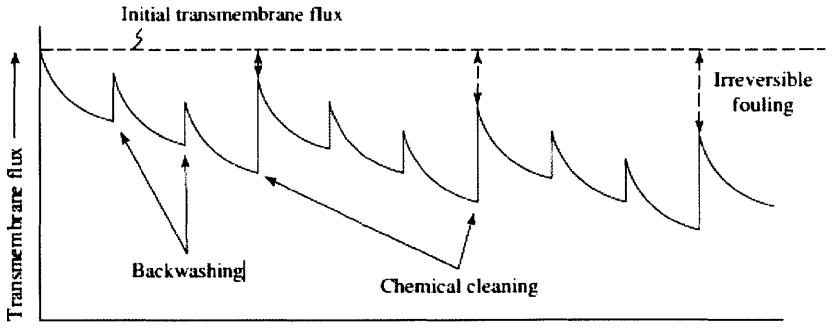

Figure 2-12: Demonstration of partial restoration of transmembrane flux (under constant pressure scheme) by backwashing and chemical washing of membranes. The horizontal axis is compressed and the vertical axis is expanded for clearer illustration of membrane deterioration (reproduced from Davis 2010, 12-7).

Even with surface water, irreversible fouling can be significant within 2-3 days of operation (Crozes et al. 1997). Polysaccharide-like organic content has been shown to be one of the major causes of irreversible fouling, and with the large concentration of similarly structured organics (e.g. hemicellulose), irreversible fouling should be an important concern for black liquor (Susanto et al. 2008; Kimura et al. 2004). Consequently, a more long-term monitoring results for irreversible fouling are essential to estimating the lifetime of membranes used for black liquor filtration. This has not yet been explored thoroughly for black liquor membrane treatment.

Most experiments in the literature did not run continuously through enough washing cycles to observe the long-term performance of membranes. When estimating long-term cost-effectiveness of membranes, most people simply assumed a membrane cleaning frequency and expected lifetime that is given by the manufactures (Holmqvist, Wallberg, and Jönsson 2005; Arkell, Olsson, and Wallberg 2014). General predictions of one-year life span with two to six times per week of cleaning have also been reported, but only for sulfite mills with acidic waste liquor. Considering the concentrated and relatively viscous nature of black liquor, simply assuming the standard factory estimates may not be realistic, especially considering the high cost of membrane replacement (Holmqvist, Wallberg, and Jönsson 2005). It may be important to examine membrane performance over multiple operational periods to determine the ability of cleaning agents to return membrane surfaces to a pristine state and to understand whether there is irreversible damages to the membrane (Weis et al. 2005). If these additional factors are taken into account, a better understanding of the economic and implementation viability can be achieved. Researches on irreversible fouling has been carried out for the filtration of other solution containing organic and inorganic foulants, and the experimental methods can be readily adaptable to the case of black liquor treatment (Crozes et al. 1997; Kimura et al. 2004; Katsoufidou, Yiantsios, and Karabelas 2007).

2.4.4 Method Selection

While general qualitative overviews of the existing treatment and potential new methods for black liquor are present in literature, there is limited detailed analysis on these industrial-scale operational parameters. Current literature focuses on the advantages and disadvantages of each method as suggested in the previous sections, but a quantitative description and comparison of the cost and effectiveness of membrane treatment methods, especially in comparison with current existing treatments is missing.

This gap in literature is reasonable considering how costs vary with location and time, and are frequently considered to be confidential from the industries' point of view. So often the costs may not be disclosed publicly or in the literature. Through interviews with industries and local manufactures, our research attempts to obtain more quantitative information to fill this gap and create a rough cost model for membrane treatment method in small-scale paper mills in India, and potentially how it may compare to current existing methods. With this model, it is possible to gain insight into how different variables in the installation and operation process may affect the capital

cost, operational cost and treatment effectiveness of the various method and understand why one method may be preferred over another in certain cases.

While literature on black liquor treatment covers a wide variety of methods, there is little information about the choice among these methods. With the wide selection of methods, it is necessary to carry out a rough comparison between methods so that the information can be better utilized by the paper and pulp industries as they decide on a specific treatment method for black liquor in the future. There is yet to be a study that offers information on selecting the optimal treatment method according to the status of the industry, and this research intends to offer more information on comparative analysis. While many treatment methods have been detailed in this literature review, a comparison would be most useful among the cost-effectiveness of concentrating black liquor up to a certain concentration by membrane treatment and current treatment methods. The former has been most widely studied and has the largest potential as detailed earlier in this section, while the latter is the current industrial practice in most larger-scale paper mills. Consequently, such a comparison may have the largest appeal to local industries and researchers alike, and may provide insight to industries when selecting treatment methods and to researchers when selecting their future focus of black liquor treatment study.

2.5 Research Objectives

According to the gap analysis, this research will evaluate the feasibility of membrane treatment as a solution for black liquor in small-scale paper mills:

- Given modeling limitations, this research will focus on experimental research and using the result from the experiments to predict behavior at a larger scale.
- Considering the impractical conditions in many of the experiments, this research will use fresh Indian black liquor (obtained directly from Indian paper mills and used in experimentation within a few days of production) to the extent possible to best approximate industrial conditions. A continuous concentration cycle will also be performed. When it is not possible to use fresh black liquor, synthesized black liquor of similar composition may be used.
- Many variables have been explored in past literature. In order to best assess the potential of membrane methods considering the limitations of time, variables that are directly related to capital cost, operational electricity cost and membrane replacement cost are prioritized. These costs have been shown to be the dominating cost in membrane plants (Holmqvist, Wallberg, and Jönsson 2005; Jönsson and Wallberg 2009)
- While many cost analyses and pilot-scale trials have been conducted in Europe, there is yet to be a feasible analysis of membrane treatment methods for small-scale paper mills in India to estimate the potential of this method in comparison to more traditional treatment such as evaporative methods. More research is needed to determine whether this method's outlook at

an industrial scale is promising (Bhattacharjee and Bhattacharya 2006; Liu et al. 2004).

With these research focuses in mind, the ultimate objective of this research thesis will be two-fold:

- Understanding long-term reversible and irreversible changes to membrane filtration capability while treating and concentrating black liquor from India small-scale brown paper mills;
- Through experimenting on the most essential variables of membrane treatment at a condition as similar as industrial reality as possible, estimate the overall feasibility of the membrane method as an alternative for evaporative methods in concentrating black liquor.

3 Black Liquor Characterization

The characteristics of black liquor used in the present study are detailed in this chapter. After an overview in Section 3.1, a comparison between the chemical composition of fresh black liquor used in this study and other black liquor in literature is carried out in Section 3.2. Synthesized black liquor used in the experiments is also characterized and compared with fresh black liquor in Section 3.3. The method to determine lignin concentration in black liquor is then described in Section 3.4.

3.1 General Black Liquor Review

Black liquor is usually generated from the process described in the Chapter 1, where cooking chemicals such as sodium hydroxide and sodium sulfide/sulfite are combined with woody raw materials to break down the lignin the binds the fiber together in order to extract the fiber and go on to further papermaking.

The process of black liquor production is described in detail in the flow chart in Figure 3-1, which is a rough snapshot of the mass flow of the pulping process using 100 tons of wheat straw in Bindlas Duplux, a paper mill in Muzaffarnagar, India that produces brown craft paper. As shown in the flow chart, wheat straw is digested with caustic soda, sodium sulfite, and steam in the digestor, before being washed several times. The excess wash water is forced out of the pulp through the two screw presses, generating the black liquor, as we know. The black liquor used in the experiments of the present work was directly from the two screw presses in Bindlas Duplux. The amount of water added to the mix for washing is based on the concentration that the conveyor system can transport. For transporting within the screw pressure, a concentration of less than 15% is required and for the further refining process at the end, a concentration of less than 5% is required, as indicated by the field engineers of Bindlas Duplux. Water is added to the wash accordingly to create the appropriate concentration for the pulp mix.

3.2 Varying Black Liquor Characteristics

In the previous chapters, we explored the differences between black liquor generated in wood and non-wood agro-waste pulping processes. Generally speaking, the non-wood black liquor has been shown to have lower total solids concentration, higher viscosities and higher contents of non-process elements. However, there is quite a bit of variety even among non-wood black liquor from different paper mills. In this section, a general overview will be made for black liquor characteristics from different sources of literature, and from testing results of the fresh black liquor collected for experimentation in Bindlas Duplux. Data from Bindlas Duplux, the brown paper mill that we worked with, Bindles, a mill nearby Bindlas that produces white paper, and from Hung and Sumathi (2005), CPCB (Central Pollution Control Board) (2008), Dixit et al. (2012), Jain et al. (2001) and Bhattacharjee and Bhattacharya (2006) were included in the overview, and listed in Table 3-1.

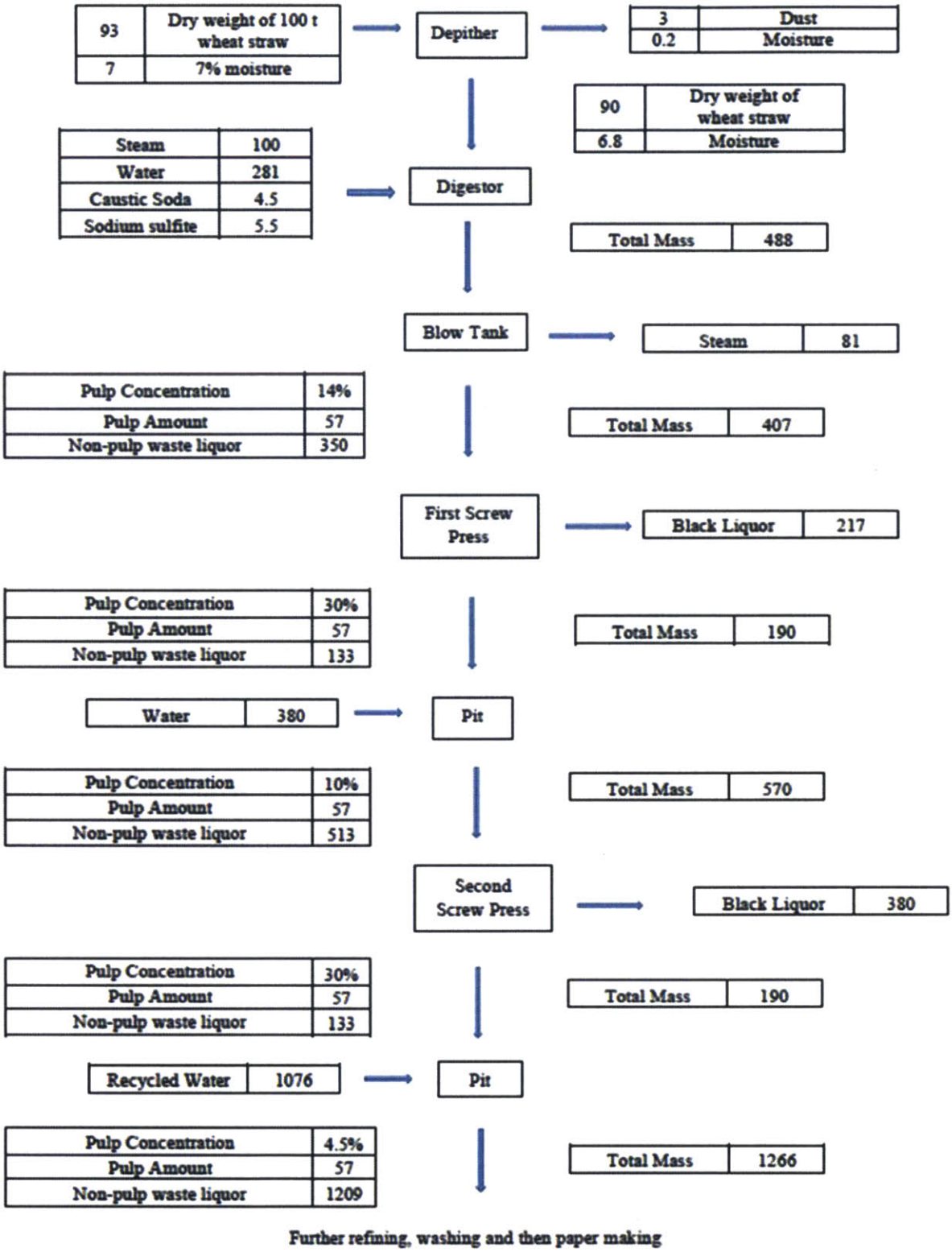

Figure 3-1: Sample black liquor generation process documented by Bindlas Duplux when using 100 ton of wheat straw as raw material. All units in tons.

ics of black liquor from a variety of sources as well as field testing. The first five samples are field samples from a brown ux) and a white paper mill (Bindles) in Muzaffaranagar, U.P., India. The tests were done through CPPRI (Central Pulp and) in Saharanpur, SGS in Gurgaon and the laboratory on-site in Bindlas, as specified in the data source. All other entries are extracted or calculated from literature data as specified in the data source.

nple me	TDS (mg/L)	TSS (mg/L)	TS (mg/L)	pH	Si, weight ratio	Na, weight ratio	Lignin, weight ratio	COD (mg/L)	BOD (mg/L)	Adjusted COD (mg/L)	Adjusted BOD (mg/L)	BOD: COD	Data Source
uz own SGS)	93085	5575	98660	8.7	1.0 %			93546	38333	78910	32336	0.41	Muz Brown 14 (SGS)
uz own 4 PRI)	53468	6900	60368	7.9	2.3 %	11%	27%	56400	15410	77754	21245	0.27	Muz Brown 14 (CPPRI)
uz own 5	82364	860	83224	9.3	0.4 %	13%	46%	80000		80000			Muz Brown 15 (CPPRI & lab)
uz te 13	96640	4340	100980	12.7	0.9 %	20%		99680	37500	82153	30906	0.38	Muz White 13 (SGS)
uz te 14	108866	116	108982	11.5	2.0 %	19%	32%	106000	30520	80947	23307	0.29	Muz White 14 (CPPRI)
CB - 1	75472	1760	77232	8.5		17%	31%	65247	18025	70309	19423	0.28	CPCB 2008
CB - 2	24798	4360	29158	10.2		21%	33%	33685	10236	96145	29216	0.30	CPCB 2008
CB- 3	8995	1150	10145	8.6			23%	8748	3429	71764	28130	0.39	CPCB 2008
CB - 4	95600	3070	99765	11.6	7.1 %	14%	29%	104616	31954	87271	26656	0.31	CPCB 2008

it et - 1			113400	12.0	1.3 %	19%							Dixit et al. 2012
it et - 2			113400	12.4	3.2 %	20%							Dixit et al. 2012
it et - 3			18360 0	12.5	7.5 %	19%							Dixit et al. 2012
et al. 1			44000	9.7	2.4 %		36%	48700	15550	92114	29412	0.32	Jain et al. 2001
et al. 2			42000	10.2	3.2 %		31%	45600	13800	90357	27345	0.30	Jain et al. 2001
et al. 3			38000	8.8	12.0 %		38%	40000	16500	87604	36137	0.41	Jain et al. 2001
ttach e et l.			12340	8.8				16800	6600	113303	44512	0.39	Bhattacharje e et al. 2006
	71032	3126	75953	10.2	3.6 %	17.3 %	32.5%	61463	19821	85279	29052	0.34	
	32694	2191	44491	1.6	3.3 %	3.2%	6.1%	31792	11330	10904	6453	0.05	
	8995	116	10145	7.9	0.4 %	11.2 %	22.5%	8748	3429	70309	19423	0.27	
	10886 6	6900	18360 0	12.7	12.0 %	20.6 %	46.1%	10600 0	38333	113303	44512	0.41	

First of all, the level of silica, one of the main non-process elements that has the potential to scale the boilers, has been compared across different raw materials based on the raw materials used in the different samples, as shown in Figure 3-2. As expected from Chapter 2, rice straw-based black liquor has a relatively higher level of silica content in comparison with wheat straw and bagasse based black liquor and wood-based black liquor, making it challenging to treat in chemical recovery plants. On the other hand, the silica levels are actually significantly lower in black liquor with wheat straw and bagasse as the raw material.

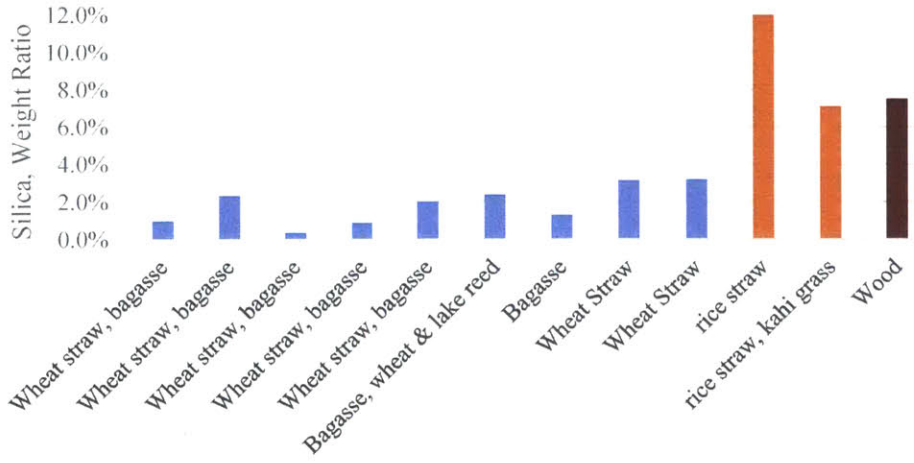

Figure 3-2: Range of silica weight ratios of black liquor from raw materials – black liquor from wheat straw/bagasse are colored in blue, rice straw colored in orange while wood colored in brown.

The total solids level (consisting of total dissolved solids and total suspended solids) can be observed in Figure 3-3. Even though the suspended materials are only a small portion of the total solids, they still constitute a relatively significant amount ranging from 116 mg/L to 6900 mg/L. This level of suspended substance would be of concern during membrane filtration, suggesting that some level of pre-filtration or sedimentation may be required. The total solids level varies widely from 10,145 mg/L and 183,600 mg/L, and the total solids level of black liquor from Bindlas is at an average level of around 70,000 mg/L. The one with the highest total solids level from Dixit et al. (2012), was the only one that came from a wood-based pulping process (as a comparison for all other samples from agro-based pulping), as expected. This again confirms the theory that non-wood black liquor would present a challenge in the recovery boiler process.

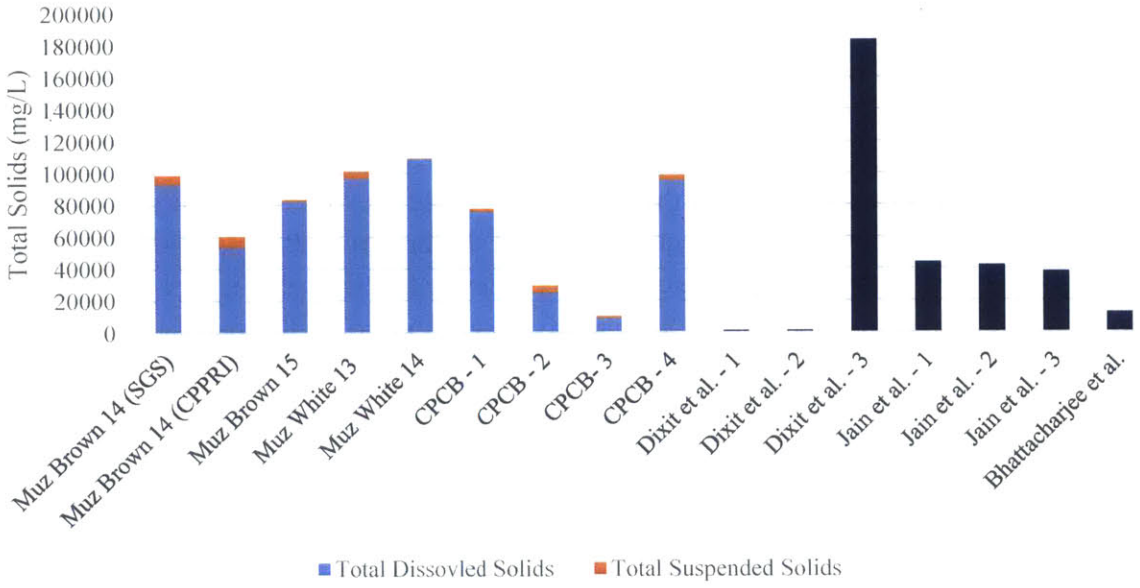

Figure 3-3: The range of total solids values from field testing and literature. Total dissolved solids (TDS) and total suspended solids (TSS) were colored with blue and orange respectively. The ones with no separate data for TSS and TDS were colored with dark blue. The columns named with "Muz" after samples from Muzaffaranagar, India, taken in two different factories (Bindlas Duplux, the brown paper mill and Bindles, the white paper mill). The 13 – 15 numbers are the year that the sample was taken.

The pH ranges from 7.9 to 12.7 with an average of 10.3, shown in Figure 3-4. Although generally in the basic range, the values still vary quite a bit from sample to sample. The columns in orange are from Bindlas Duplux, the mill that we will be taking our black liquor samples from. The pH of the samples from Bindlas ranges from 7.9 to 9.3, which is on the lower end of the pH spectrum.

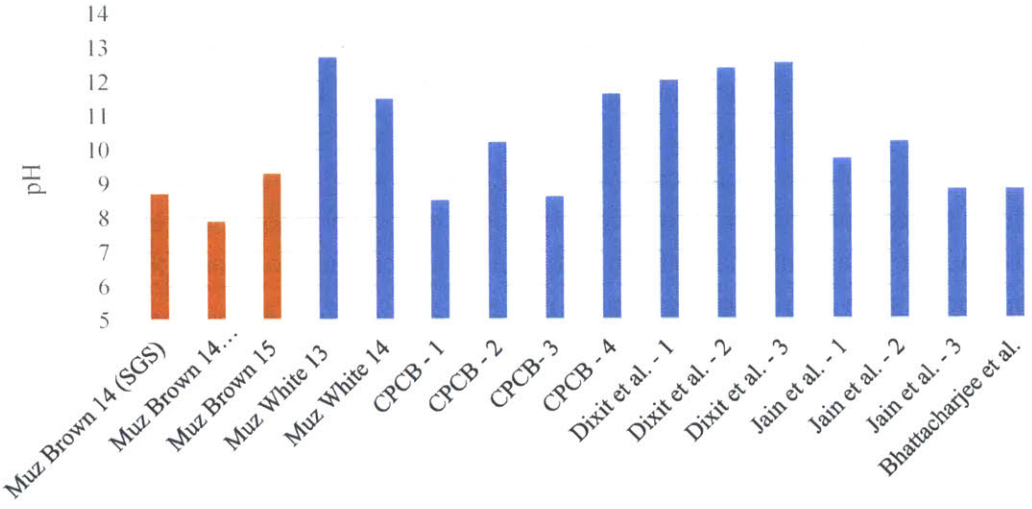

Figure 3-4: The range of pH values of black liquor from field testing and literature.

Similarly, plotting the weight ratio of sodium over total solids would also give a rough range from

11% to 21%, similar to the 17% – 20% average from wood-based black liquor as shown in Figure 3-5 (Sundholm 1999). However, the black liquor from Bindlas, with 10% – 15% sodium content would be on the lower end of the spectrum. This suggests that the black liquor of interest contains a relatively low level of alkali in comparison to other black liquor. The local engineers, through field interviews, suggested that this may be due to the fact that brown paper mills do not need to add such large amounts of chemicals in the digestor, because they do not require as strong of a separation of lignin from fiber. The expected quality of the brown craft papers is not as high, so even if the lignin is not completely extracted due to the lower levels of alkali, it is acceptable. The leftover lignin may give a darker color and more rough texture to the paper, which is more acceptable for brown paper productions in comparison to white paper.

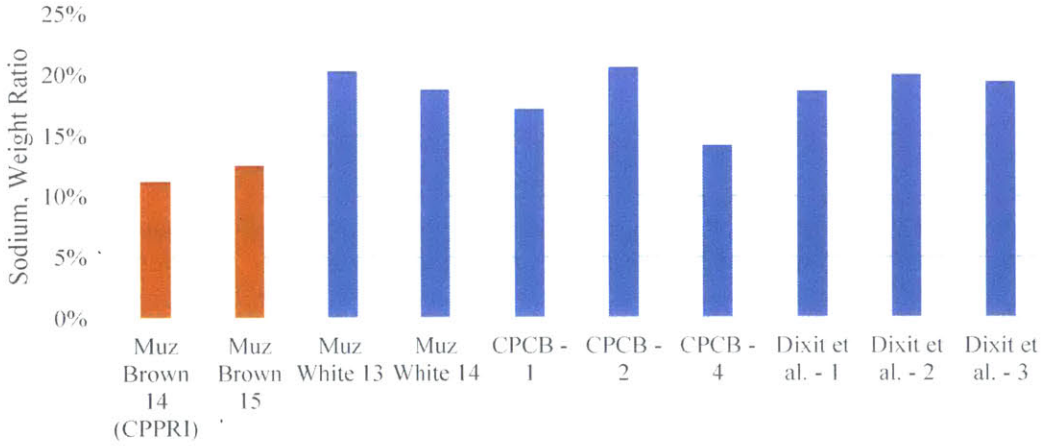

Figure 3-5: The range of sodium weight ratios of black liquor from field testing and literature.

This can also be demonstrated by comparing the pH of samples that are from white paper mills with the samples from brown paper mills, shown in Figure 3-6. The pH of black liquor from brown mills average 8.6 while that from white mills average 11.2. The lower alkali level in black liquor again would add to the expense of the chemical recovery system, because the amount of useful chemical recovered would be significantly smaller. Evaporating a much larger amount of water (due to the low solids content) only to recovery a much smaller amount of reusable alkali again shows the barriers to implementing the traditional treatment methods and the need to explore alternative methods such as membrane treatment.

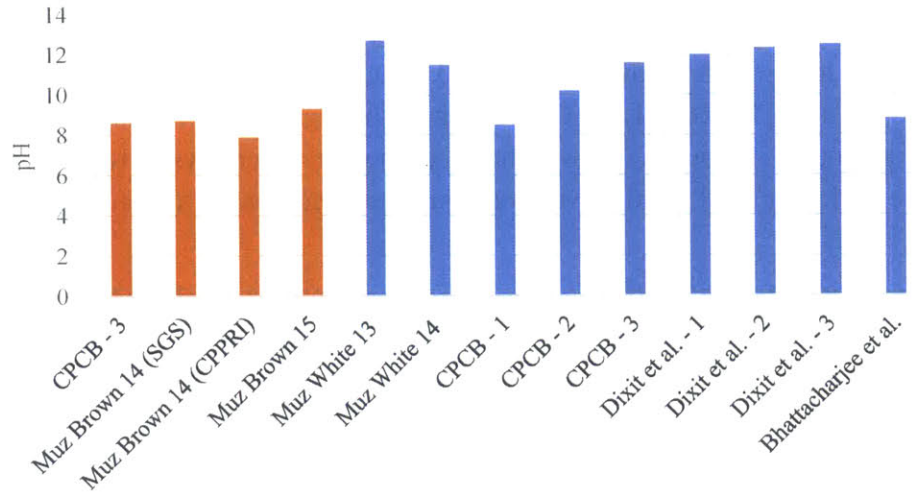

Figure 3-6: pH comparison of black liquor that are from brown paper mills (bars in orange) and white paper mills (bars in blue).

As shown in Figure 3-7, the lignin weight ratio (the dry weight of the lignin component as a ratio of the dry weight of black liquor) is around 23% - 46%, which is similar to the expected values from literature reviews. The lignin level is generally measured through measuring the absorbance of the 280nm peak through UV spectrophotometers, which will be detailed later in this chapter. This is still a relatively wide range, most likely due to the uncertainties in the digesting process and the exact amount of lignin dissolved and separated from the fiber may vary from time to time. This is especially true for smaller paper mills such as Bindlas, where product process is not streamlined and the amount of chemicals added daily into the digestor is more often roughly estimated.

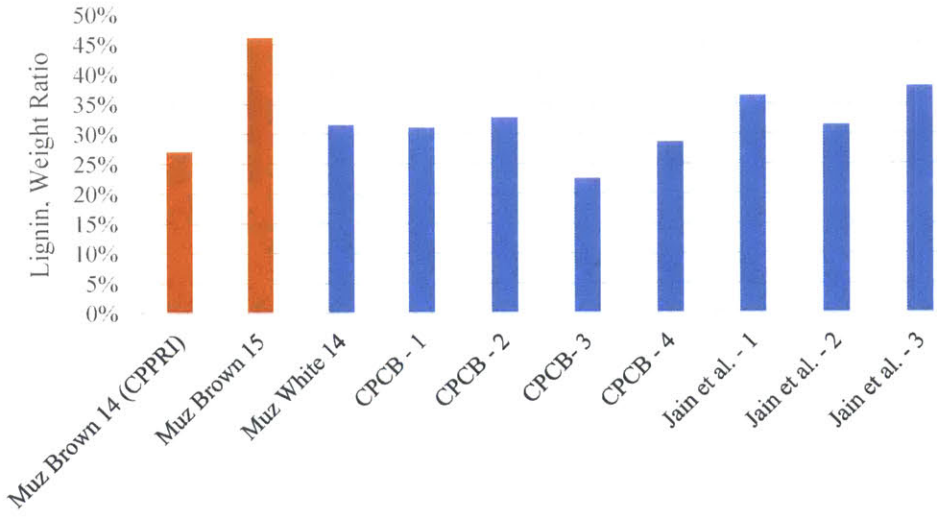

Figure 3-7: The range of lignin weight ratios of black liquor from field testing and literature.

Biological Oxygen Demand and Chemical Oxygen Demand, both water pollution indicators have

also been measured for black liquor from different sources. According to Figure 3-8, the COD ranges from 8748 mg/L to 106000 mg/L with an average of 58332 mg/L, and BOD ranges from 3429 mg/L to 38333 mg/L with an average of 18910 mg/L. Black liquor from Bindlas averages 76649 mg/L for COD and 25872 mg/L for COD, both on the higher end of the spectrum, suggesting the high level of pollution it would induce if dumped into the waterways only partially treated or untreated, despite its lower total solids level and alkali level compared to black liquor from other sources.

While the BOD and COD levels seem to vary widely, if we normalize them against the total solids level of the black liquor from Bindlas Duplux in 2015 (which is the black liquor that utilized in the experiments in this study) as shown by the adjusted BOD and COD levels in Figure 3-9, the variation is much less significant. The adjusted BOD and COD values are calculated by:

The specific black liquor's original BOD and COD value * (Muz Brown 15's black liquor total solids level / the specific black liquor's total solids level).

The standard deviation decreases by half for both COD and BOD. This suggest that the variation in pollution is mostly still due to the concentration of black liquor, but the overall polluting capabilities of the dry solids content in black liquor are still similar to each other. The COD: BOD ratio is on average 0.33 with only 0.05 standard deviation, confirming that a large portion of the organic polluting materials are not biodegradable and hence not treatable with traditional wastewater treatment schemes.

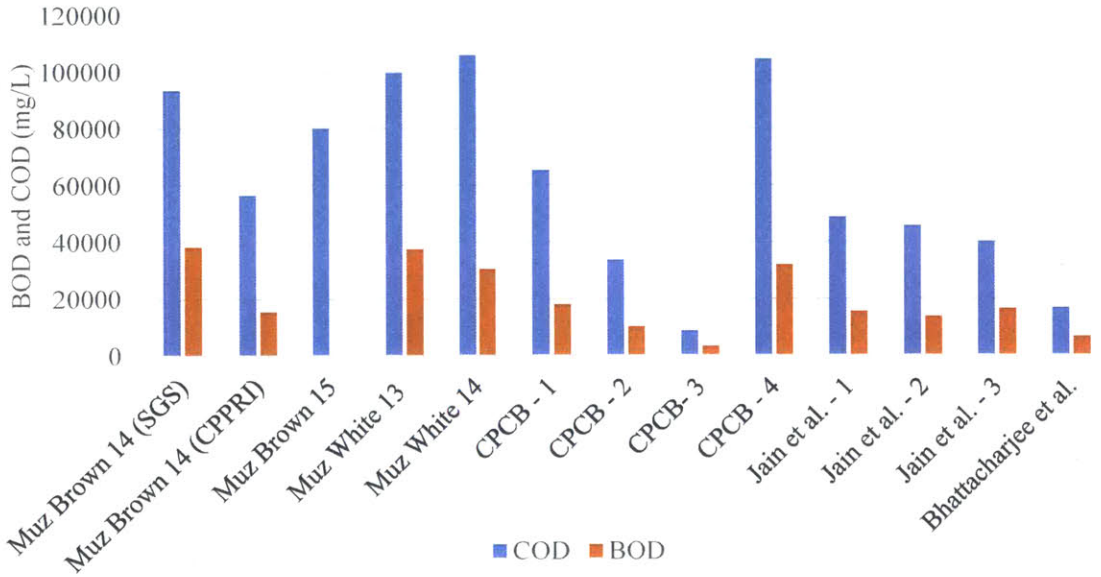

Figure 3-8: The COD and BOD levels of black liquor from field testing and literature.

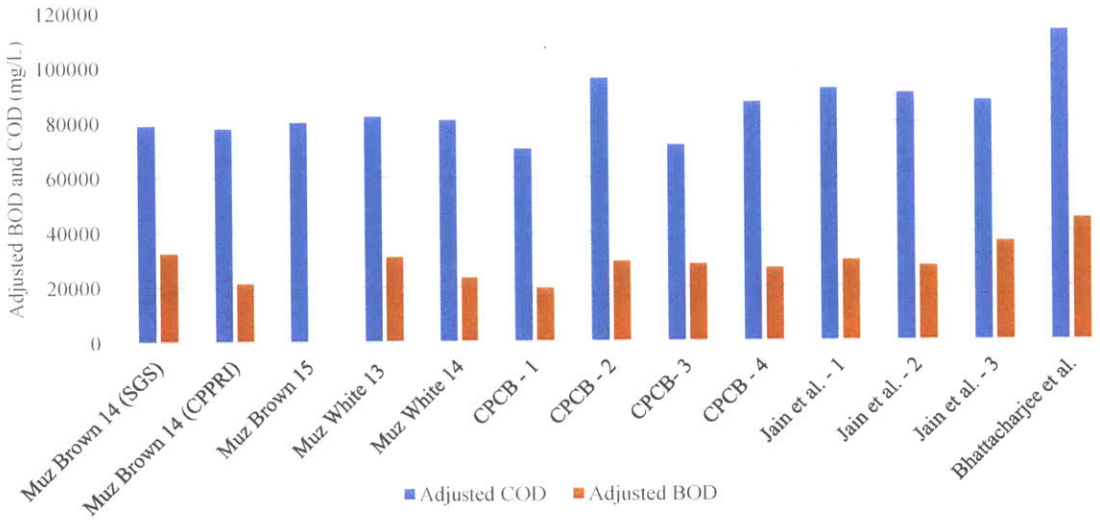

Figure 3-9: The adjusted COD and BOD levels of black liquor.

In conclusion, the black liquor from the wheat-straw and bagasse based brown paper mill Bindlas Duplux in Muzaffaranagar, India has the traditional qualities of agro-based paper mills where the total solids levels are on the lower end. In addition, it also has a low alkali value and lower pH due to the lower pulping requirements for brown paper mills. These levels, which are not beneficial for recovery boiler processes, help broaden the selection of chemically compatible membranes. Adjusting for the total solids content, the lignin level and the COD and BOD pollution parameters are not significantly different from other sources of black liquor.

The final black liquor utilized in our research are from the same batch as "Muz Brown 15." But the parameters documented in Table 3-1 is only a snapshot of the quality of the black liquor during one of the days of the experimental run. The black liquor quality change from day to day as the cooking batches vary.

Even with the same batch of black liquor, its quality changes as time goes by. The trend of the total dissolved solids and suspended solids can be shown in Figure 3-10 and Figure 3-11.

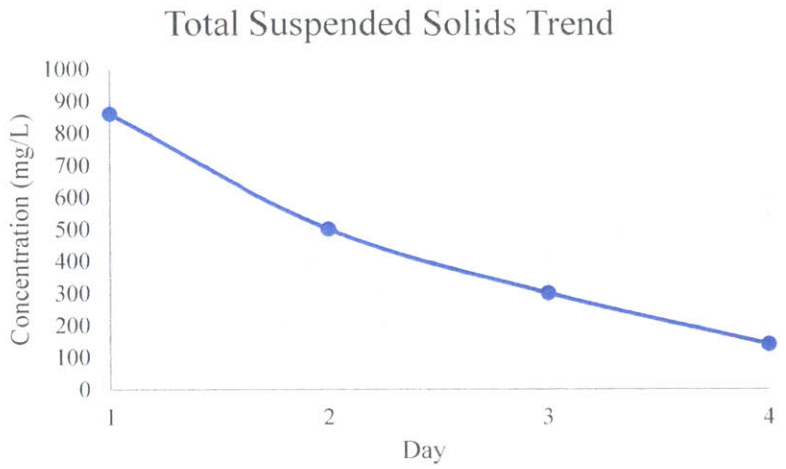

Figure 3-10: The trend of total suspended solids, measured by the vacuum filtering the black liquor through a #41 Whatman filter and measuring the leftover solids content on the filter paper.

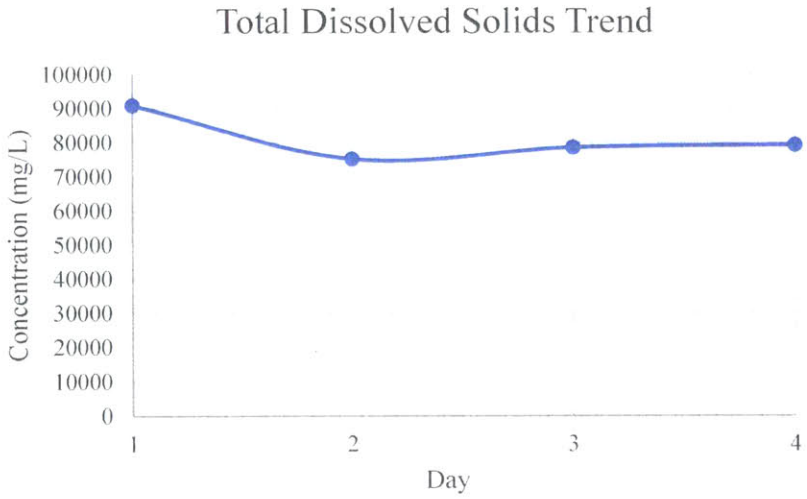

Figure 3-11: The trend of total dissolved solids for black liquor, measured by drying the black liquor at 100C until the weight is steady to obtain the total dry solids content, and then subtracting by the suspended solids content.

As we can observe, the suspended solids level decrease significantly as time goes on, which is expected due to sedimentation. The suspended solids level decreased by around 800 mg/L, from around 900 mg/L to around 100 mg/L. Interestingly, the total dissolved solids also decreased dramatically during the first day and decreasing much more significantly than the decrease in suspended solids level. The dissolved solids level decreased by around 10000 mg/L, from around 90000 mg/L to around 80000 mg/L. This is likely due to the precipitation of lignin and other solid content in the liquor. The fresh black liquor had a much higher temperature, and may have been

able to dissolve more lignin, but as the temperature significantly lowers within day 1, some of the lignin may have dropped out of the solution and deposited, as shown in Figure 3-12.

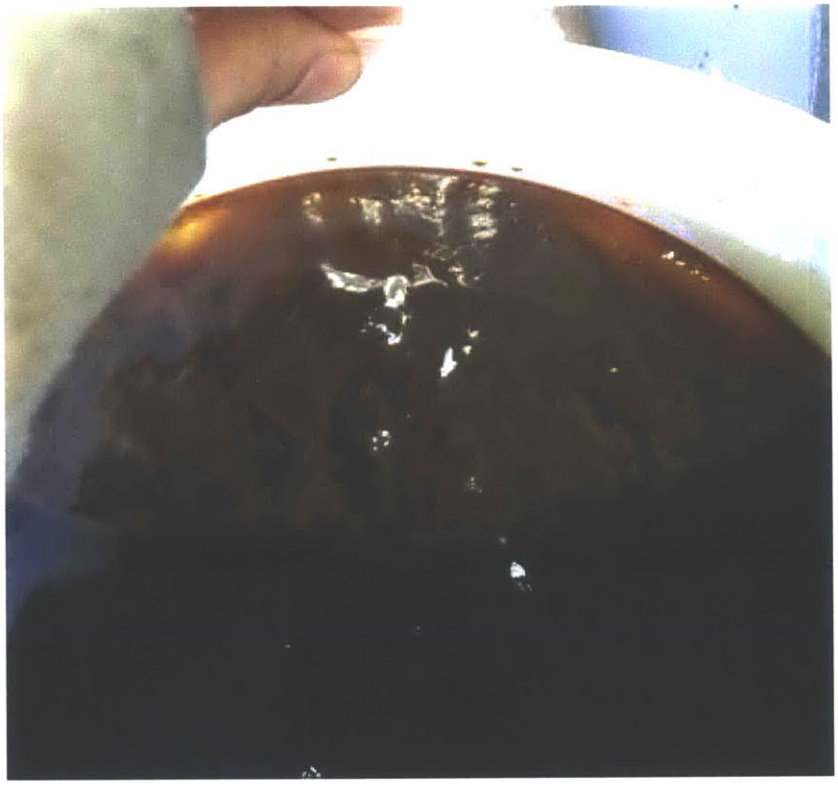

Figure 3-12: Traces of deposited lignin and other solids at the bottom of the fresh black liquor container

In practice, to make sure there is sufficient decrease in suspended solids and some substantial level of precipitation to minimize the chance of lignin precipitating onto the membrane, the membrane treatment of black liquor was often carried out after 1 day of sedimentation. However, even after sedimentation, there may be mixing and turbulence causing some re-suspension in the process of transferring black liquor to the feed containers, and there was still significant clogging of the membranes when processing untreated black liquor. The spikes of the inlet pressure, as shown in

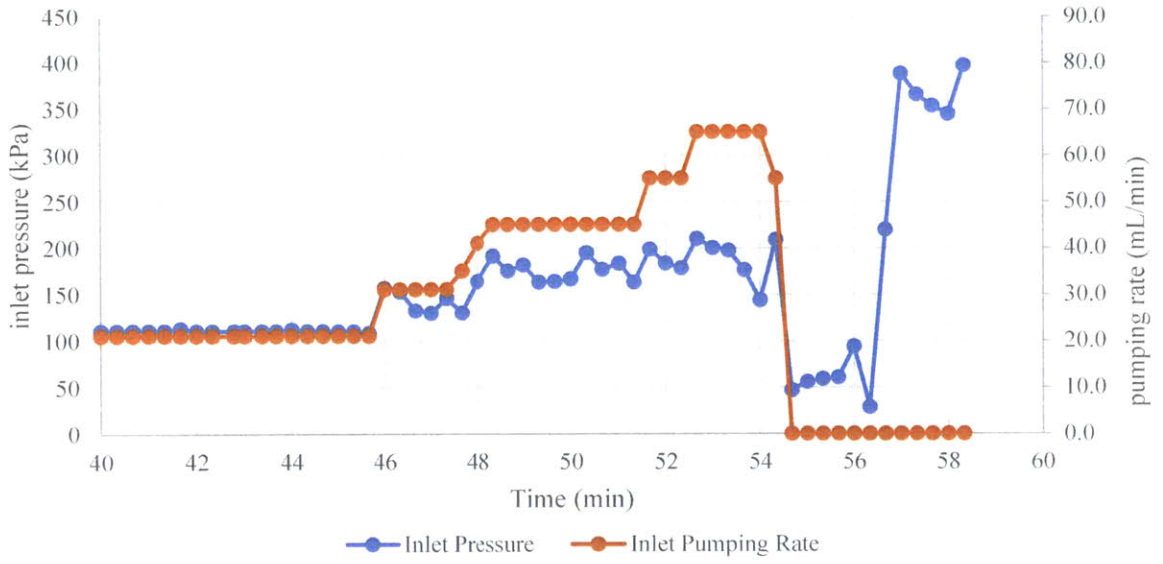

Figure 3-13, indicate severe membrane clogging that prevents black liquor from traveling through the membrane channels smoothly. The membrane has to be continuously flushed afterwards to resume a consistent flow again. Several repeated attempts have been made after a longer sedimentation of the black liquor, but the clogging issue remained. Based on these issues, it was decided that black liquor would be pre-treated by Whatman #41 vacuum filtration before membrane filtration.

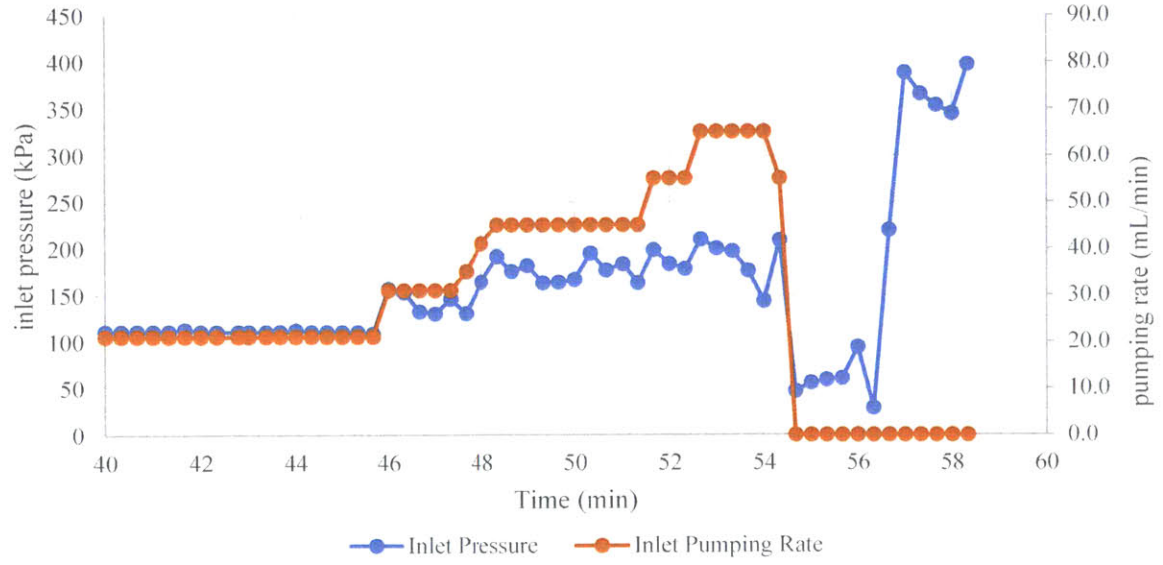

Figure 3-13: Membrane clogging when processing the original fresh black liquor. As pumping rate slowly increased, the inlet pressure rose above the 207 kPa limit around 54 min and the system stopped automatically (as shown by the drop in pumping rate). The expected inlet pressure created with a 60 mL/min pumping rate is much lower than 207 kPa. The pump was restarted around 56 min but

immediately automatically shut off due to the huge spike in inlet pressure above 345 kPa. Due to the immediately shutoff, the pumping rate was not recorded and not displayed in the figure, but the spike of pressure can be observed. As we can see, the clogging was so severe that the inlet pressure remained high even after the pump has been shut off, and only dropped until the inlet tube was unplugged.

Overall, the fresh black liquor utilized in the membrane experiment had the following characteristics in Table 3-2 during a snapshot measurement on Jan 21, 2015. The exact black liquor qualities vary from sample to sample, and the key parameters will be re-measured before each experiment.

Table 3-2: General characteristics of black liquor utilized in the membrane experiment (same as the 2015 Muzaffarnagar black liquor as described in Table 3-1 apart from the filtered out TSS)

Black Liquor Source	Bindlas Duplux
Date of Sample	1/21/2015
TDS (mg/L)	82364
TSS (mg/L)	0
TS (mg/L)	82364
pH	9.3
Na (mg/L)	10420
Na, weight ratio	13%
Lignin (mg/L)	38345
Lignin, weight ratio	46%
COD (mg/L)	80000

3.3 Synthesized Black Liquor

Fresh Indian black liquor was used in all experiments conducted in India. In light of the difficulty of shipping black liquor from India, experiments in the U.S. needed alternative black liquor source. Black liquor found in the U.S. have a variety of differences due to the use of different pulping schemes and different raw material, and as a result its filtration results may not compare effectively with the results in India. Instead, it may be better to simply single out the components of concern – lignin (along with other smaller components of hemicelluloses and other organics), which is the main organic component that we are trying to concentrate and make use of due to its inability to be decomposed with the traditional wastewater treatment methods. Another important criteria is the pH of the black liquor, because a high pH may affect membrane performance, but lignin may not be stable and may precipitate in low pH environments, as evidenced by the precipitation of lignin during the 4-day black liquor trend monitor. According to Ross et al., synthetic black liquor has been created by dissolving Indulin AT and sodium hydroxide in solution, where the Indulin AT is a kraft lignin in powder form produced by precipitating lignin out of black liquor (Ross et al. 1986). pH adjustment of the solution was made with sodium hydroxide to dissolve the Indulin-AT lignin and to mimic the realistic pH of black liquor. This simplifies the focus of the black liquor filtration to only the lignin component, rather than dealing with various additional complicating

factors of difference between the U.S. black liquor and India black liquor.

While we understand that there are additional organic compounds, they are mostly hemicelluloses that have been broken down into hydroxyl acids. Some of the typical organic compositions can be shown in Table 3-3. The amount is smaller in comparison to lignin, and they are generally much smaller in their molecular sizes. They are expected to pass through the membranes which have 3 – 10 kDa molecular weight cut-offs. The only concern is that they may affect the viscosity of the black liquor and affect its flow performance in membrane processes. However, it is hard to measure the exact organic composition of the various hemicellulose, and the first step would be to look at lignin alone for general conclusions and consider adding the extra organic matters if necessary in the future.

Table 3-3: Typical composition of black liquor with details on the organic compounds (reproduced from Olsson 2013)

Total lignin	**61,4 mg/g**
Acid-insoluble lignin	**53,9 mg/g**
Acid-soluble lignin	**5,03 mg/g**
Total dry substance	**147 mg/g**
Ashes	**97,6 mg/g**
Hemicelluloses	**3,14 mg/g**
Arabinan	**0,80 mg/g**
Galactan	**1,00 mg/g**
Glucan	**0,23 mg/g**
Xylan	**1,07 mg/g**

The Indulin AT is from MeadWestvaco in North Charleston, SC. Another concern is that the Indulin AT is extracted from black liquor in the U.S. that used wood as the raw materials, and the types of lignin and the molecular weight ranges may differ from what is expected in agro-based paper mills. Due to the limited abilities of the paper mills in India to generate pure lignin powder from their black liquor, we were only able to obtain a very small sample of dry lignin sample from black liquor generated in agro-based mills with the help of Central Pulp and Paper Research Institute (CPPRI). With limited methods to compare the difference in the organic structure between the two samples of dry lignin, a rough CHNS elemental analysis was carried out to compare the overall material differences between the two different lignin samples, as shown in Table 3-4. Despite some differences in the carbon ratios, the elemental analysis shows levels that are within the same orders of magnitude of each other. Accounting for the large variabilities in black liquor components, this difference should be acceptable. More tests in the future comparing the filtration results between the two lignin samples can be conducted to help confirm the validity of the Indulin AT results.

Table 3-4: CHNS elemental analysis results for agro-based paper mill lignin from India and wood-based paper mill lignin from the U.S. Test results are from Elementar's CNHS elemental analyzer instrument.

	Agro-based mill lignin	Indulin AT - lignin

Source	Bindlas Duplux, India	MeadWestvaco, US
N [%]	0.68	0.77
C [%]	44.40	62.82
H [%]	6.16	6.85
S [%]	3.74	1.44
C/N Ratio	65.31	81.88
C/H Ratio	7.20	9.17

In order to mimic the lignin composition as demonstrated in Table 3-2, approximately 38 g/L lignin and a pH level between 9 and 10 would be appropriate for the experiment. Approximately 0.24 g/L of NaOH is added to dissolve the 38.3 g/L Indulin AT, resulting in a final pH of around 9.85. The procedure of the lignin measurement and addition only allowed for a level of precision around 0.1 g/L for lignin concentration in black liquor. Although some sedimentation of lignin can still be observed, test with the UV Spectrophotometer still showed a satisfactory amount of lignin in solution. This will be the final composition of the synthesized black liquor to use in tests in the U.S. A comparison of this synthesized black liquor with black liquor from Bindlas Duplux is shown in Table 3-5. The crucial variables of pH and lignin of the synthesized black liquor are very similar to the fresh black liquor. The total dissolved solids are less than half of the original, mainly due to the lack of addition inorganic compounds some small components of organic compounds dissolved in the solution (including Si and other Na-compounds as suggested by the previous section). In theory, most of these dissolved compounds that are not represented in the synthesized black liquor should be small enough to pass directly through the membrane with cut-offs larger than 3000 Da without affecting flow behavior. Based on the current information, it seems reasonable to ignore the additional dissolved solids in the fresh black liquor and not replicate them in the synthesized black liquor. However, it is possible that some of the additional components could alter the surface chemistry of the membrane, which means that they may still affect the filtration process despite the small amount. It would be useful to explore this effect in future studies.

Table 3-5: A comparison of characteristics between fresh black liquor from Bindlas Duplux and synthesized black liquor in the U.S.

Black Liquor Source	Bindlas Duplux	Synthesized in the U.S.
TDS (mg/L)	82364	38240
TSS (mg/L)	0	0
TS (mg/L)	82364	38540
pH	9.3	9.85
Lignin (mg/L)	38345	38000

3.4 Lignin Concentration Measurement

A number of method detailing the lignin concentration measurements have been documented, and the most commonly mentioned methods include the acid precipitation method and the UV Spectrophotometer method (Xiao, Sun, and Sun 2001; Holmqvist, Wallberg, and Jönsson 2005). However, the precipitation method included procedures such as precipitating with ethanol and then with HCl until the pH lowers to 1.5 (Xiao, Sun, and Sun 2001). The process includes generation of more hazardous waste, and requires larger amount of solution samples for measurement, which we would not have if we wanted to capture snapshots of the lignin concentration in the membrane permeate. Consequently, the UV Spectrophotometer method would be utilized in determining the concentration of lignin in black liquor.

Lignin contains phenolic groups that absorb light, and it would be possible to measure the concentration of lignin by measuring the light absorption at 280 nm due to the phenolic groups (Holmqvist, Wallberg, and Jönsson 2005). The absorbance was measured in standard 10mm cuvettes, with T80+ UV/Vis Spectrometer from PG Instruments in India, while measured with Cary 7000 Universal Measurement Spectrophotometer in the US. The lignin samples are usually diluted to below 100 mg/L for the most accurate measurements (Lara et al. 2003). According to literature results, absorption constants that translate absorbance values to concentration values range were shown to be a number of different values between 20 – 25 L/g*cm (Holmqvist, Wallberg, and Jönsson 2005; Jönsson and Wallberg 2009). Using the Indulin AT and the lignin powder from Bindlas Duplux black liquor, calibration curves were created as shown in Figure 3-14 and Figure 3-15.

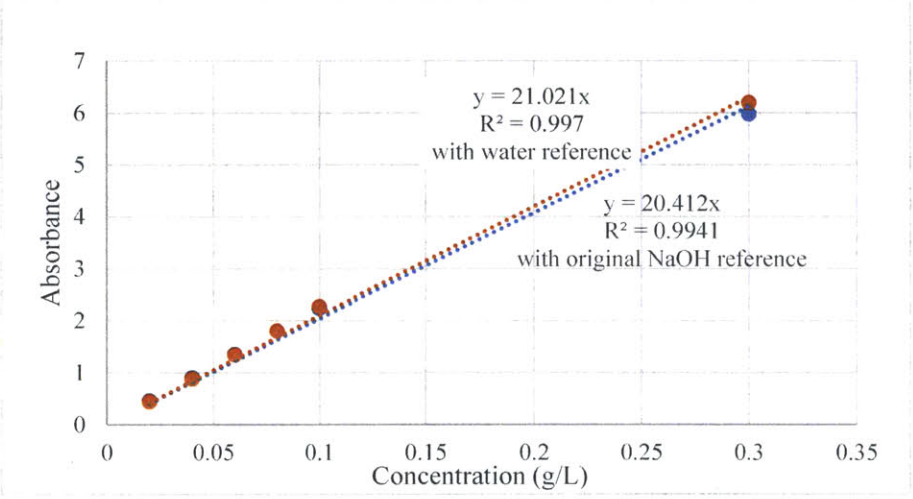

Figure 3-14: UV calibration curve for Indulin AT – lignin (absorbance vs. lignin concentration at 280 nm and the corresponding linear fit). The original samples were both diluted with water and with the background level of 0.24 g/L NaOH to observe if there would be a significant difference in the absorbance

constant.

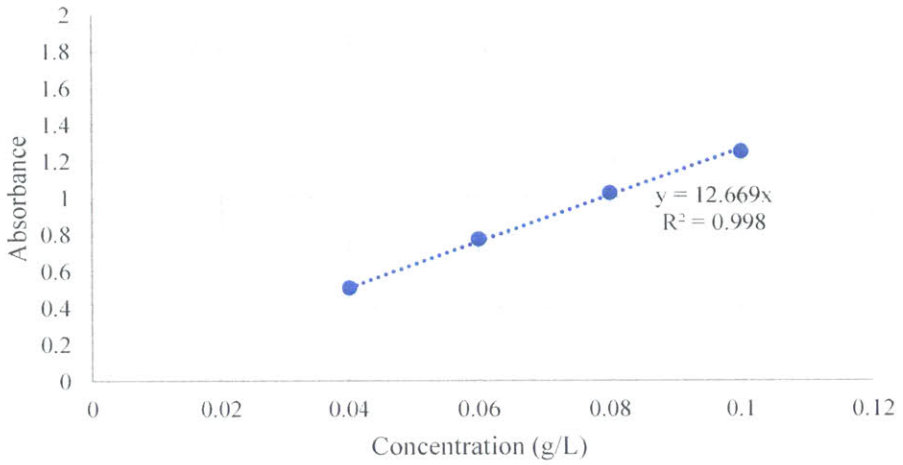

Figure 3-15: UV calibration curve for Bindlas Duplux lignin (absorbance vs. lignin concentration at 280 nm and the corresponding linear fit).

As shown in Figure 3-14, the absorbance constant is 21.021 L/g*cm when diluting the black liquor samples with water and 20.412 when diluting the samples with the background NaOH concentration of 0.24 g/L. The difference of 3% between the two values are negligible, so the easier option of diluting future samples with water would be taken. Also the calibration curve was shown to be linear up to 0.3 g/L of lignin concentration. As shown in Figure 3-15, the absorbance constant is 12.669 L/g*cm for lignin from Bindlas Duplux, which is quite different from the Indulin AT constant and most constants found in literature.

The concentration of both types of lignin can now be determined by first diluting the solution with water, usually by 100 or 200 times, so that the lignin level falls below 0.3 g/L, then measuring the absorbance value at 280 nm and calculating the concentration value based on the absorbance standard of 21.021 L/g*cm for Indulin AT lignin and 12.669 L/g*cm for Bindlas Duplux lignin. However, the purity of the lignin powder from Bindlas Duplux, due to the unknown exact procedure of the experiment[1], may be in question, especially because the value cannot yet be validated from literature results, and experts from the Central Pulp and Paper Institute have suggested a general value of 20 L/g*cm that is applied to all types of lignin, which puts the 12.669 value into further question. For the purpose of this study, the 20 L/g*cm value would be used for India black liquor, as validated by literature and local interviews with research institutes. The value can be further updated once better calibration curves can be created from lignin that are confirmed to be pure and of good quality.

[1] The extraction procedure were performed by Central Pulp and Paper Research Institute, but the exact procedure of extraction, the purity and other detailed information was not disclosed.

3.5 Summary

In summary, based on the analysis of the characteristics of black liquor, we can conclude that:

- Total dissolved solids level of agro-waste-based black liquor varies widely based on the different pulping process, but is generally significantly lower than wood-based black liquor
- The pH and sodium level of the fresh black liquor from Muzaffarnagar are generally low due to less caustic chemicals added in the pulping process.
- The lignin concentration, COD and BOD levels are overall consistent across different types of black liquor when normalized against the total solids level.
- The fresh black liquor from Muzaffarnagar showed strong deposition of lignin and other solids as times goes on and as the black liquor cools down.
- Synthesized black liquor is composed of approximately 38 g/L Indulin AT and 0.24 g/L sodium hydroxide to mimic the lignin and pH condition of fresh black liquor.
- Lignin concentration in black liquor can be measured through UV Spectrophotometer measurements, with 20 L/g*cm as the absorbance standard for fresh Indian black liquor and 21.021 L/g*cm as the absorbance standard for synthesized black liquor.

4 Methods

This section describes experimental methods used for this study. The general objectives of the experiments are outlined in Section 4.1, following by a detailed description of experimental system setup and preparation in Section 4.2 and 4.3. The experimental operations in constant feed mode and concentrating feed mode are detailed in Section Section 4.4 and 4.5, followed by the membrane cleaning methods in Section 4.6.

4.1 Experiment Objectives

In order to realistically estimate the feasibility of membrane treatment as an alternative to the traditional evaporative methods in concentrating black liquor, the experiments are designed with the following objectives in mind:

- Determine the optimal operating variables in the membrane treatment process, including transmembrane pressure, cross-flow velocity and membrane pore-size, and how these parameters affect membrane performance.
- Assess the long-term reversible and irreversible changes of membrane function in treating and concentrating black liquor.

The goals and the key experimental variables and experiment outcomes are determined based on the key variables generally needed to determine the cost and benefits of the treatment system, summarized in Table 4-1 (Jönsson and Wallberg 2009).

Table 4-1: Key variables for determining the cost-effectiveness of the filtration system

Cost/Benefit Categories	Key Experimental Variables
a. Operation	Pumping pressure, cross-flow velocity
b. Maintenance	Membrane cleaning frequency
c. Membrane Replacement	Membrane irreversible change
d. Capital cost	Membrane area, average flux
e. Lignin	Lignin concentration in retentate stream
f. Caustics	Lignin and caustics concentration in the permeate stream

The cost parameters focused on operational cost (electricity cost), membrane maintenance and replacement cost and capital cost factors, which has been suggested in Chapter 2 to the bulk of the cost. The optimized pumping pressure and the feed flow rate is related to the operational cost of the membrane systems. The cleaning and replacement of the membrane is related to the maintenance and membrane replacement costs. The average flux during the course of the filtration can help determine the membrane area required to process the daily generated amount of black liquor, which determines the capital costs for the membrane modules. The lignin concentration in the retentate stream is associated with the profit obtained through the concentrated lignin solution, while the caustics concentration in the permeate steam is associated with the profit obtained through reusing the caustics in the cooking process. The lignin concentration in the permeate stream is also crucial for the calculation of the profit, because it determines if the permeate solution is suitable for reuse in the cooking process.

With these key variables in mind, we have designed the following procedure to achieve the two objectives.

For the first objective, the flux of black liquor will be observed while increasing the transmembrane

pressure to determine if a limiting flux can be observed at a high pressure. This is the pressure where the cake layer starts to significantly build up, and further increase in pressure will only compact the cake layer further and will no longer result in a linear increase in flux (Baker 2012). The optimal pressure of operation is typically the pressure right before the point where limiting flux starts to occur. The observation of optimal pressure and limiting flux will be carried out for membranes of different pore sizes and three different cross-flow velocities to also determine the effect of these parameters on the flux.

For the second objective, the membrane system would be operated at an appropriate constant transmembrane pressure and constant cross-flow velocity, as determined by methods described in the previous paragraph, over a long period of time to observe the long-term change in flux due to reversible and irreversible fouling. The change in flux over time will be observed for a constant-concentration feed case to observe the characteristics of fouling at the same concentration of black liquor over time. This can help determine the estimated lifetime of a membrane. The change in flux will also be observed when the feed is continuously concentrated, which approximates industrial operational. This approach also determines the average flux of the membrane treatment system when it concentrates black liquor up to the ideal concentration for further use.

The results from these experiments can help determine the cost of the membrane treatment system (including capital cost, operational cost and maintenance cost), and will assist in evaluating the feasibility of a membrane system in treating black liquor.

4.2 Hollow Fiber Cross-flow Filtration System

As suggested in the literature review, industrial-scale membranes are generally set up with cross-flow modules to ensure maximum flux with minimum fouling; and experimental results from dead-end cells do not give the a reasonable approximations of a cross-flow module (Wallberg, Holmqvist, and Jönsson 2005). Thus, we selected a cross-flow cell module. Cross-flow sheet membranes and tubular membranes have been studied in previous literature of black liquor membrane treatment (Liu et al. 2004). Hollow fiber membranes, on the other hand, have not been explored. Hollow fiber units generally offer the highest packing density in terms of the membrane area offered per unit volume, ideally giving the highest productivity with the lowest basic equipment cost (Hsieh 2006). Also, as Arkell, Olsson, and Wallberg (2014) suggested, even though ceramic membranes are more chemically resistant and fouling resistant, the benefits do not yet outweigh the costs, and polymeric membranes may still be cheaper for treating black liquor. Thus, despite the fact that hollow fiber membranes may experience issues with fouling and channel clogging from larger particulates, this research will still focus on a method that is likely to be the least costly. Results from this initial exploration would then allow an extension to other potentially more effective setups.

The hollow fiber membrane system in use is the KrosFlo Research IIi Tangential Flow Filtration

System from Spectrum Labs for processing R&D volumes, as shown in Figure 4-1 and Figure 4-2. This system is portable and allows for transportation between U.S. and India, and can also house small membranes that are scalable modules capable of giving predictive results for large-scale systems.

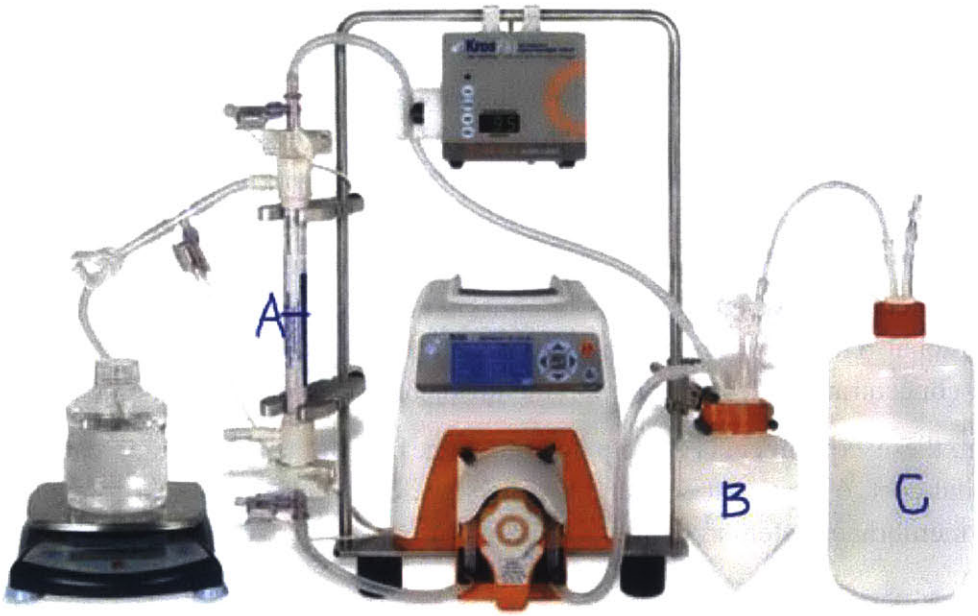

Figure 4-1: The general configuration of Krosflo Research IIi Tangential Flow Filtration System, where A is the membrane module, B is the process reservoir and C is the feed reservoir. A simpler flow diagram of the system is depicted in Figure 4-2.

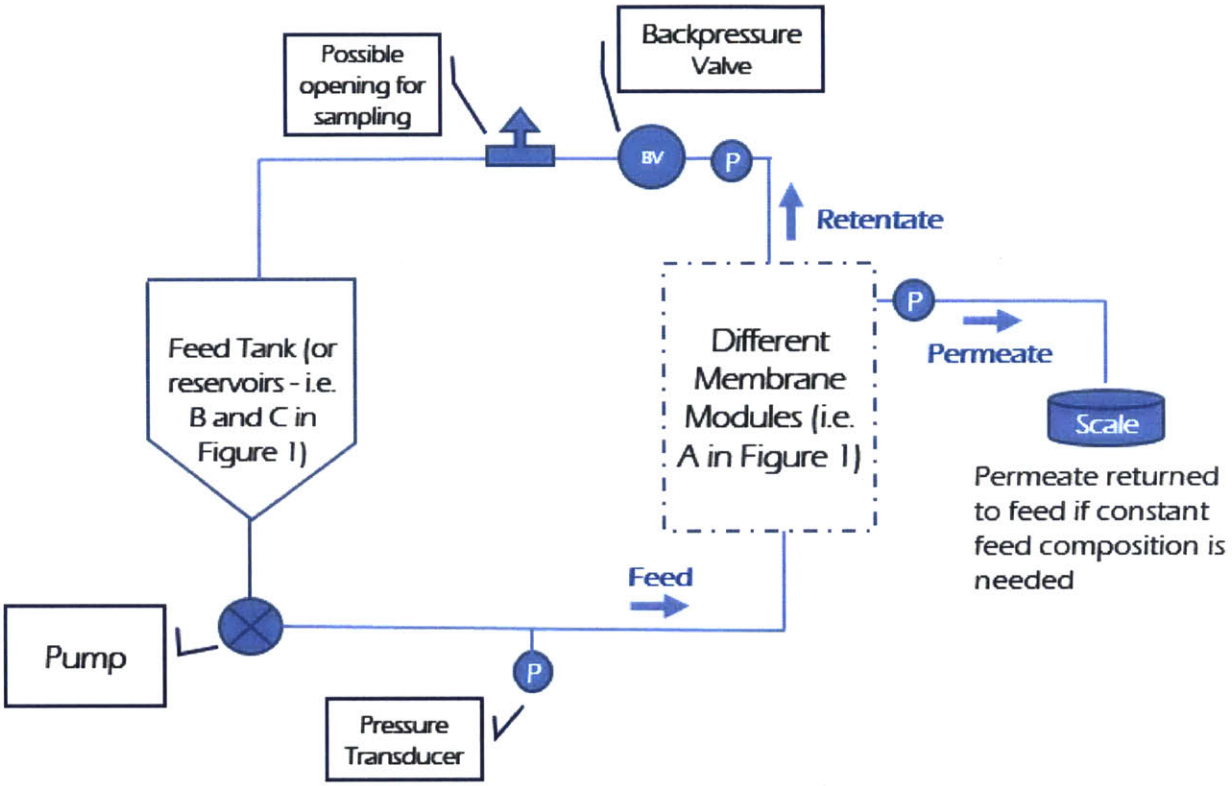

Figure 4-2: A diagram of the membrane system configuration and flow direction corresponding to the system of Figure 4-1.

Modified Polyethersulfone (mPES) membranes are used for the process because of this material's compatibility with black liquor's high pH, its low protein-binding properties and the resulting anti-fouling characteristics. Based on the general MWCO range of membranes studied in literature and their filtration capabilities, membranes around 10 kDa are studied most frequently. Consequently, the following mPES membranes from Spectrum Labs in Table 4-2 are utilized primarily in the experiments.

Table 4-2: Characteristics of membranes utilized in the experiments.

Pore size	Part Number	Fiber Inner diameter	Effective Length	Total Length	Surface Area
3 kDa	D02-E003-05-N	0.5 mm	20 cm	25 cm	115 cm^2
5 kDa	D02-E005-05-N				
10 kDa	D02-E010-05-N				

4.3 System Preparation

4.3.1 Black Liquor Pretreatment

As suggested in the previous section, fresh black liquor directly from the paper mills goes through coarse prefilteration due to the high spikes of inlet pressure increase caused by channel clogging of the membranes. The black liquor is be prefiltered by Whatman #41 filter paper. The materials that are filtered out are generally only large suspended solids. For industrial practices, sedimentation or other processes can replace filtration as cheaper alternatives of pretreatment to remove suspended large particulates (such as small pieces of undigested wheat straw).

4.3.2 Hydraulic Compaction

Prior to the experiment, the membranes are subjected to water wash to rinse the glycerin that membranes are soaked with for storage purposes. Compaction with deionized water at relatively high pressure is also required to prevent any future change of membrane hydraulic resistance (Bhattacharjee and Bhattacharya 2006). More specifically, for each new membrane, water is run through the membrane at the highest recommended transmembrane pressure of 207 kPa for a long period of time until the permeate flux becomes steady and does not decline further or until the change of flux over time is within the acceptable range.

4.3.3 Optimal Parameter Selection

In order the find the optimal pressure for system operation, a flux variation with pressure profile is needed to find the critical pressure and critical flux when treating black liquor, as shown in Figure 4-3. Long-term performance of membranes are optimized when operating below the critical pressure, above which the marginal increase in flux declines significantly when increasing pressure, and the flux-pressure curve flattens out quickly (Baker 2012). Operating at higher pressures no longer increase the transmembrane flux but only increases the amount of macromolecular materials that are condensed at the membrane surface, which over time which form a layer of gel deposits on the surface that creates a low permeability barrier potentially causing permanent fouling and significantly lowering the flux in comparison to the initial flux value. Ideally, the critical pressure and critical flux is when the first gel layer started to form on the membrane surface, so that below these critical operational parameters, permanent fouling would be minimal. In reality, fouling would still happen but the results would still be optimized if the operation is conducted around the critical pressure and flux.

To search for the critical operating parameters that optimized flow and reduces permanent fouling, we would carry out the flux-pressure test as described below. For each different membrane, the transmembrane pressure is slowly increased from around 69 kPa to over 207 kPa to observe the trend of flux as pressure varies (the flux-pressure test). Through the curve, an optimal pressure can

be selected close to the critical pressure. If the optimal pressure may is beyond the maximum operating pressure of the membrane, then the maximum operating pressure of the membrane will be selected as the optimal pressure.

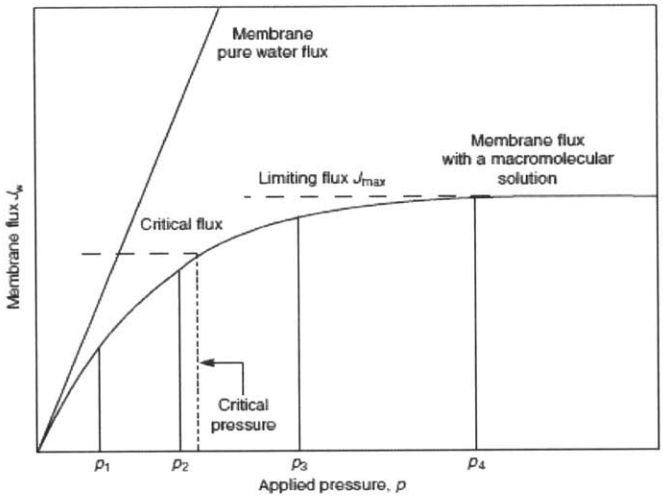

Figure 4-3: Flux vs. applied pressure curve for filtration of macromolecular solution. Membranes are ideally best operated below p2 when the first gel layer has not yet formed. Operation at pressures higher than p3 usually leads to thick gel layer deposits that consolidate over time and lead to permanent fouling. In reality, the critical pressure is usually selected between p2 and p3 to optimize flow while minimizing the chances of permanent fouling (reproduced from Baker 2012).

In addition to selecting the optimal pressure, the optimal feed flow rate also needs to be determined. As suggested by Choi et al. (2005), for the ultrafiltration of flux generally increases linearly with cross-flow velocity, as shown in Figure 4-4, until a threshold where the marginal increase in flux declines. Similar to the flux-pressure test, the optimal cross-flow velocity should also be the critical point before the decline in marginal flux, beyond which the increase in pumping power can only ineffectively generate limiting increase in flux. To determine this point, the flux-pressure test will be run at three different feed flow rates (165 mL/min, 300 mL/min and 450 mL/min) to observe the effect of the cross-flow velocity on permeate flux and determine the optimal cross-flow velocity.

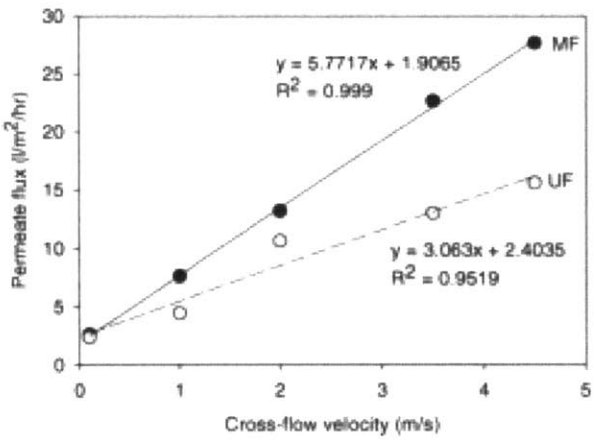

Figure 4-4: Below a certain threshold, permeate flux would vary roughly linearly with cross-flow velocity in biological suspension ultrafiltration (UF) and microfiltration (MF) experiments (reproduced from Choi et al. 2005).

4.4 Constant Feed Mode Runs at Constant Pressure

Constant feed experiments are conducted where the feed black liquor (either fresh black liquor or synthetic black liquor) is maintained roughly at the same composition. The permeate is frequently re-mixed with the retentate and channeled back into the feed to recreate the feed and maintain the original feed composition. As shown in Figure 4-2, this is done by returning the retentate line directly to the feed (knowing that the retentate flow is generally at a much higher level than the permeate). While the permeate is not immediately channeled back into the feed due to the need to measure the permeate flow rate through a scale, the permeate will usually be emptied back into the feed before the concentration change in the feed exceeds 5%, to ensure an approximately constant composition of the feed.

The system will be operating at the optimal pressure and cross-flow velocity over a long period of time to observe the change in flux over time. When the flux declines significantly (e.g. cleaning must be conducted before 40% flux decline according to Methatham and Ratanatamskul (2011)), or when the operation has gone on for a significant period of time and the flux decline is no longer prominent, one cycle will be terminated and mechanical membrane cleaning will be conducted. Changes of the membrane function will be observed through pure water permeability tests as well as the initial black liquor flux through the membrane after each wash. When changes to the membrane become significant, chemical membrane cleaning will be conducted. After chemical cleaning, any remaining changes in the membrane function will be considered irreversible changes and the rough irreversible changes over a certain length of operation can be determined. The process can be repeated to further determine the rate of accumulation of irreversible damages to the membranes. Through the process, lignin level in the permeate concentration will also be observed roughly every 2 hours to determine any significant changes in the filtration capability of

the membrane as foulant accumulates. Lignin level, as mentioned before, will be measured through the UV spectrum generated by Cary 7000 Universal Measurement Spectrophotometer. The concentration of lignin can be roughly predicted by the absorption level at 280 nm.

4.5 Concentrating Feed Mode Runs at Constant Pressure

In concentration feeding mode, the retentate and permeate are no longer re-mixed. Instead, to mimic the feed-and-bleed mode of operation (Figure 4-5), the retentate line will return to the feed line, and the permeate will not be returned to the system anymore. The new system configuration is shown in Figure 4-6. The appropriate pressure and cross-flow velocity is again the same optimum value as in the constant feed mode and will also be constant through the experiment. The change in flux over time and as a function of the feed concentration will be observed. The change of the permeate concentration will also be observed over time. The experiment will continue until the flux declines to a minimum level (increasing TMP cannot alter the limiting flux anymore) and further concentration can no longer achieved.

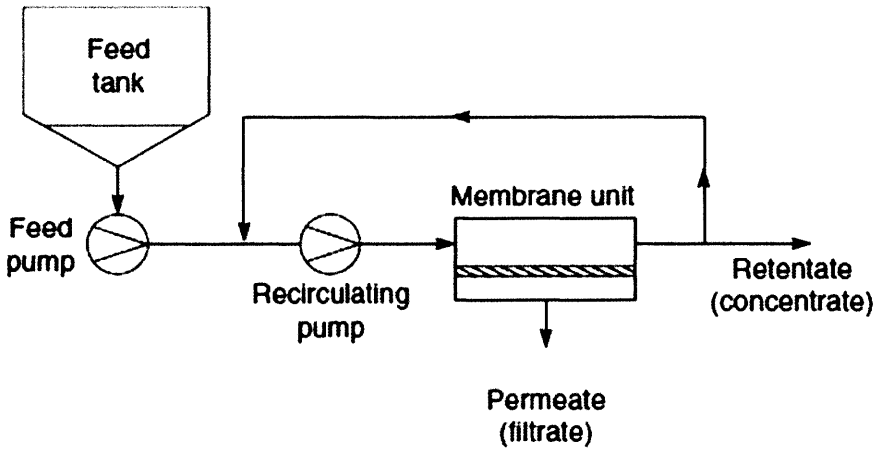

Figure 4-5: Feed-and-bleed system often used in large filtration plants. A large volume of solution is circulated through membrane modules. Concurrently, a small volume of feed solution enters the recirculation loop while an equivalent volume of more concentrated solution is removed (or bled) from the recirculation loop (reproduced from Baker 2012).

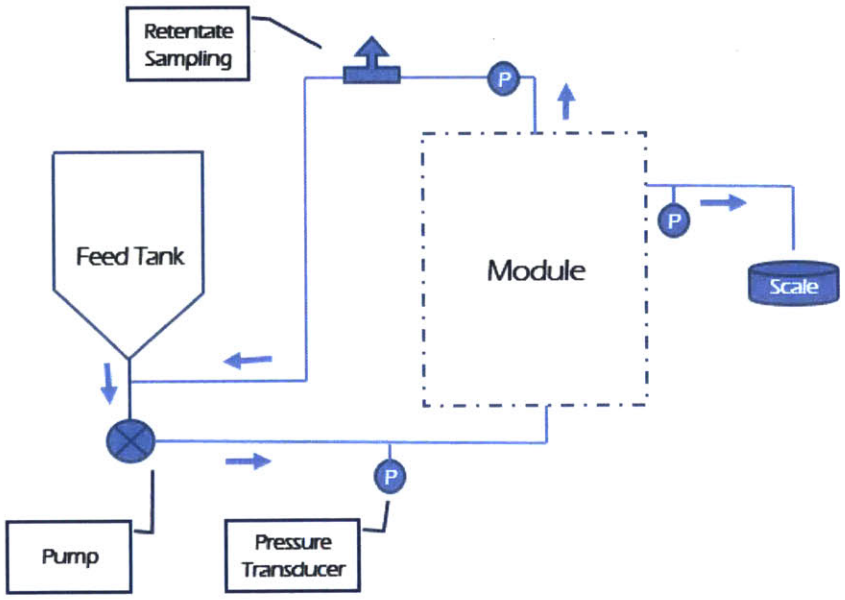

Figure 4-6: Diagram for the system flow process in the concentrating experiment.

4.6 Membrane Cleaning

4.6.1 Flux-Pressure Tests

After each run, to ensure thorough cleaning, the membrane is usually washed with 0.5 M NaOH solution (and possibly around 1 ppm of NaClO if needed) at a high cross-flow velocity to ensure the maximum shear effect to remove any deposited layer (as instructed by the membrane module cleaning manual from the manufacturer of the membranes). The wash usually lasts 30 min to 1 hour. Then, if the membrane permeability still has not returned to the desired level in comparison with the original permeability, a backwash where the feed enters through the permeate port at a relatively low pressure and exits from the original feed or retentate port will also be carried out. After the backwash, foulant deposits may come off from the membrane surface again and another high cross-flow velocity flush will be required. Pure water permeability will be tested after the wash to determine whether the membrane can return to the initial permeability.

4.6.2 Continuous Tests

For the continuous tests, both mechanical washes and chemical washes will be conducted. For mechanical washes, a similar high cross-flow velocity wash + backwash + high cross-flow velocity wash cycle is conducted, but the wash solution is either pure water or the permeate solution (or solutions with similar composition of the permeate solution), which is generally the common practice in industries for backwashing (Davis 2010). Over longer periods of operation, membrane

fouling cannot be entirely cleared up through the physical cleaning process, and chemical cleaning is required. Chemical cleaning follows similar physical processes but with the addition of higher levels of NaOH (~0.5 M) and NaClO (~1 ppm) if necessary for dissolving the foulants. Generally, chemical cleaning is considered to be more cumbersome and costly and requires the shutdown of several systems and the addition of extra levels of chemicals (Crozes et al. 1997). Chemical cleaning may also negatively impact the quality of the membrane (Kimura et al. 2004). Consequently, it would generally only be kept at a minimum and conducted when mechanical cleaning is insufficient. The flux that can be recovered by chemical cleaning is still considered reversible fouling. However, any remaining change in permeability (both for water and black liquor) is considered irreversible flux, suggesting that the membrane is permanently damaged. The rate of reversible changes in membrane flux observed through the continuous run experiments after mechanical cleaning cycles helps predict the cleaning frequency and membrane cleaning cost. The rate of irreversible changes observed after chemical cleaning cycles helps predict membrane life.

4.7 Summary

In summary, the experiment will be carried out in hollow-fiber membrane modules, and both fresh Indian black liquor and synthesized black liquor will be processed in the same setup. The general experimental operations in sequence include:

- System preparation through washing and hydraulic compaction of membrane;
- Flux-pressure test for selection of optimal operating pressure and cross-flow velocity;
- Constant feed mode run or concentrating feed mode run at optimal operating parameters;
- Membrane cleaning and observation of membrane permeability change.

5 Experimental Results from Fresh Black Liquor

Results from experiments using fresh Indian black liquor are described in this chapter. Results from the flux-pressure tests and the optimal operating parameters determined through the tests are described in Section 5.1. Flux variation results and lignin retention results from the constant-composition feed runs are described in Section 5.2 and 5.3 respectively. Irreversible fouling of the membrane is discussed in Section 5.4.

5.1 Flux-pressure Test: Optimum Parameter Selection

Fresh black liquor directly from the Bindlas Duplux paper mill have been utilized in this experiment. While a general snapshot of the black liquor quality was provided in Chapter 3, the characteristics of the black liquor still vary from experiment to experiment. There was also some slight addition of water to assist the prefiltration process due to clogging of the vacuum filters. In general, the black liquor used for the 3, 5, 10 kDa membrane experiments are still consistent with each membrane type, and the characteristics are shown in Table 5-1. All the black liquor was pre-filtered as described in Chapter 4.

Table 5-1: Different characteristics of black liquor for experiments with the different membranes

Experiment	10 kDa run	5 kDa run	3 kDa run
pH	10.07	10.05	9.98
Total Solids (w/w)	6.8%	7.3%	7.7%
Lignin (mg/L)	27120	33055	38440
COD (mg/L)	67320	80000	88000

The same 3,5, and 10 kDa membrane were used throughout all the experiments with fresh black liquor.

Results from the flux-pressure test are shown in Figure 5-1 - Figure 5-3. Due to limited available time, the tests in India were only conducted for a feed flow rate of 165 mL/min, which creates a cross-flow velocity of 0.39 m/s and 6200 s^{-1} shear rate at the membrane surface.

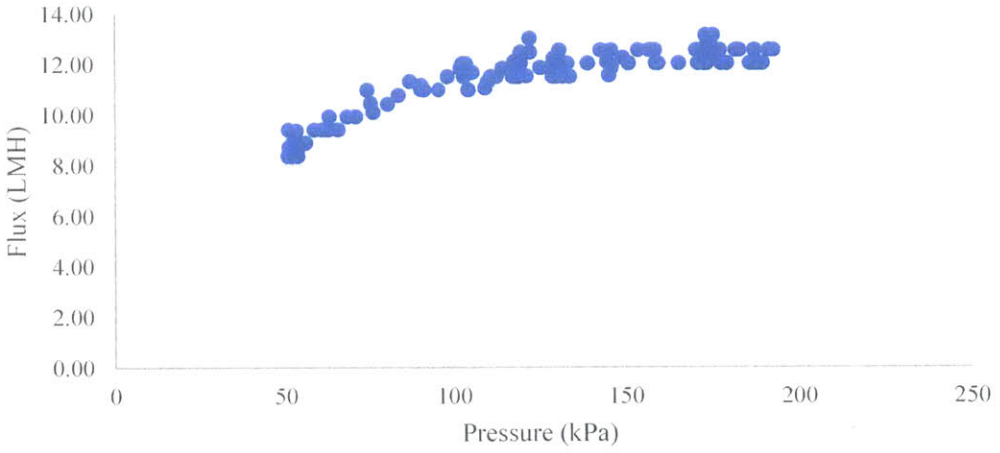

Figure 5-1: The change in flux across the 10 kDa membrane as pressure increases in a flux-pressure test. The slope of the flux-pressure curve decreased more significantly around 110 kPa.

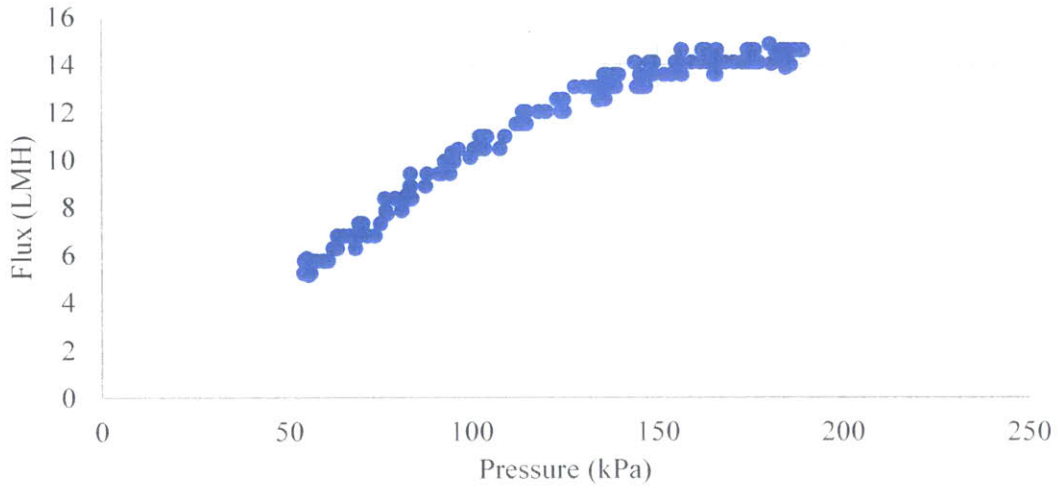

Figure 5-2: The change in flux across the 5 kDa membrane as pressure increases in a flux-pressure test. The decline in the flux-pressure slope became more significant after 151 kPa.

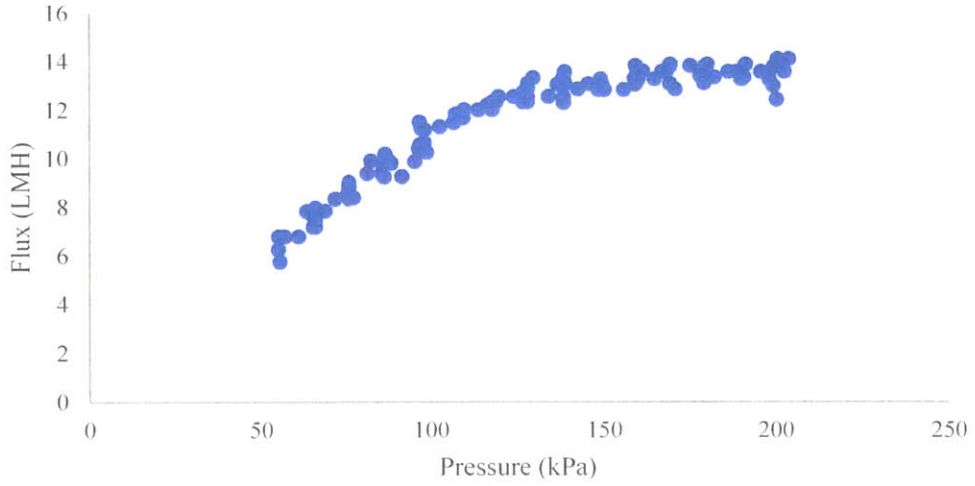

Figure 5-3: The change in flux across the 3 kDa membrane as pressure increases in a flux-pressure test. The decline in the flux-pressure slope became more significant after 159 kPa.

As shown in the above figures, the decline in the marginal increase of flux can be observed for all three membrane types, indicating the formation of gel layers at higher pressures. Critical flux and pressure can be readily determined at the given feed flow rate by comparison of the figures above to Figure 4-3 (standard flux-pressure test figure in Chapter 4). The optimal pressure selected based on the critical pressure ranges are shown in Table 5-2. The constant pressure tests would be conducted at these pressures.

Table 5-2: Optimal operating pressures for membranes determined by flux-pressure tests

Membrane MWCO (kDa)	10	5	3
Optimal Transmembrane Pressure (kPa)	110	151	159

5.2 Constant Feed Mode Run: Permeate Flux Decline

Constant pressure and constant-composition feed runs were conducted at the pressures in Table 5-2 for each of the membranes. The black liquor quality for each of the membranes was still the same as in Table 5-1. The black liquor quality may vary slightly after the flux-pressure test due to permeate sample being taken. However, the overall variation of the black liquor total solids content is still less than 5%, suggesting that the black liquor quality for each membrane run is overall consistent.

Due to the limited in time in India, the constant pressure experiments were only conducted over approximately 1.5 hours to observe the variation in flux. Nevertheless, the flux variation was observable even within the short run, as shown in Figure 5-4 - Figure 5-6. The recovery ratio, which is the ratio of the permeate flow rate over the feed flow rate, is proportional to the flux and is shown by the same data set correspondingly on the secondary axis.

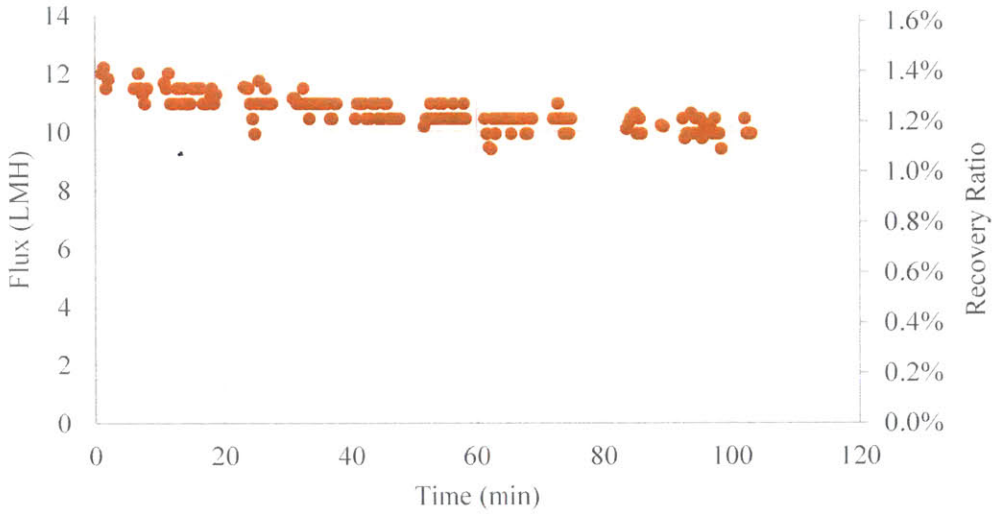

Figure 5-4: Flux variation over a period of 1.5 hours for 10 kDa membrane operating at 110 kPa transmembrane pressure. Flux is plotted on the primary axis. Recovery ratio is directly proportional to flux, and the recovery ratio corresponding to the flux is plotted on the secondary axis.

For the 10 kDa membrane run at 110 kPa TMP, the flux declined from the initial 12.2 LMH to around 9.9 LMH at the end of the experiment. The recovery ratio declined from 1.4% to 1.1% in correspondence. The rate of decline, as shown, decreased during the course of the experiment, but the decline still seems to extend beyond the course of the experiment.

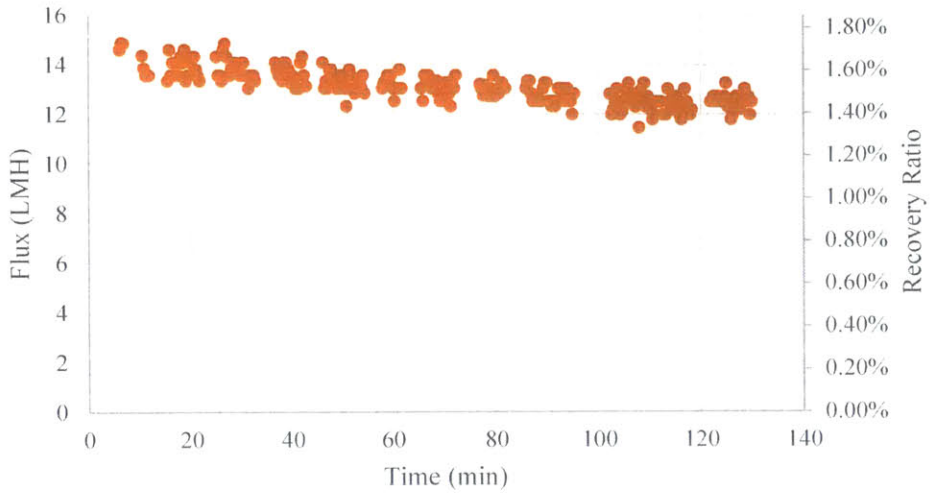

Figure 5-5: Flux variation over a period of 2 hours for 5 kDa membrane operating at 151 kPa transmembrane pressure. Flux is plotted on the primary axis. The recovery ratio that the flux is corresponding to is plotted on the secondary axis.

For the 5 kDa membrane operated at 151 kPa TMP, the flux declined from 14.9 LMH to around 12 LMH, and the recovery ratio declined from 1.7% to 1.4% over the course of the experiment. The rate of decline decreased over time, especially around 100 min, showing signs of a steadier flow rate afterwards. Longer experiments may help demonstrate whether the flux started to level off after this initial flux decline, or whether the decline would continue on further.

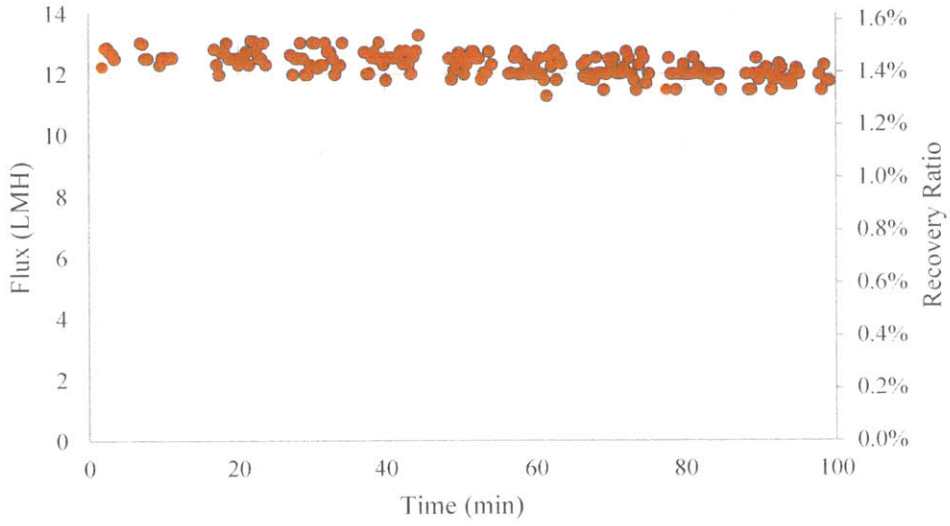

Figure 5-6: Flux variation over a period of 1.5 hours for 3 kDa membrane operating at 159 kPa transmembrane pressure. Flux is plotted on the primary axis. The recovery ratio corresponding to the flux is plotted on the secondary axis.

For the 3 kDa membrane operated at 159 kPa, the flux declined from 13 LMH to around 11.5 LMH, and the recovery ratio declined from 1.5% to 1.3% over the course of the experiment. The rate of

decline is comparatively lower than for the other two membranes, and the decline rate seemed to be relatively steady throughout the course of the experiment. Longer experiments may help determine if the steady rate of decline would continue over a longer time.

Over the 1.5 – 2 hour experiments, the flux decline rate in the three sets of experiments are show in Figure 5-3.

Table 5-3: The rate of flux decline for the different membranes when treating fresh black liquor

Membrane MWCO	10 kDa	5 kDa	3 kDa
Initial Flux (LMH)	12.20	14.88	13.04
Average rate of decline (LMH/h)	0.95	0.89	0.56
Average percent decline (%/h)	7.8	6.0	4.4
Overall percent decline (%)	18.7	19.7	12.0

5.3 Lignin Rejection and Passage

During the constant feed tests, the lignin concentration in the permeate stream is measured every 20 minutes starting from 10 minutes into the experiments. The amount of lignin in the permeate can help determine the percentage of lignin that was concentrated into the retentate stream and how much passed through the membrane. Their variation over time is also recorded to determine if the functionality of the membrane has changed over time due to fouling or other changes affecting the membrane performance.

The lignin concentration at different time into the constant feed mode experiments are shown in Table 5-4.

Table 5-4: Lignin concentration in the permeate stream at different times into the three constant-pressure experiments for the three different membranes.

Lignin concentration (g/L)		Feed	Time into the experiment					
			10 min	30 min	50 min	70 min	90 min	110 min
Membrane MWCO	10 kDa	27.2	7.9	9.2	9.3	8.9	9.4	8.4
	5 kDa	33.1	9.1	8.7	9.0	8.8	8.8	9.1
	3 kDa	38.4	9.4	9.2	9.5	9.4	9.5	9.6

The lignin concentration in the permeate stream can also be plotted over time to observe the trend of the permeate level, as shown in Figure 5-7. Due to the limitations of the UV spectrophotometer process and the range of the UV Spectrophotometer in India, the lignin solution usually has to be diluted over 300 times to obtain an accurate absorbance reading within the proper range, and the dilution process would increase the potential operational random errors for the results. Thus, the error bars are plotted with these lignin concentration results.

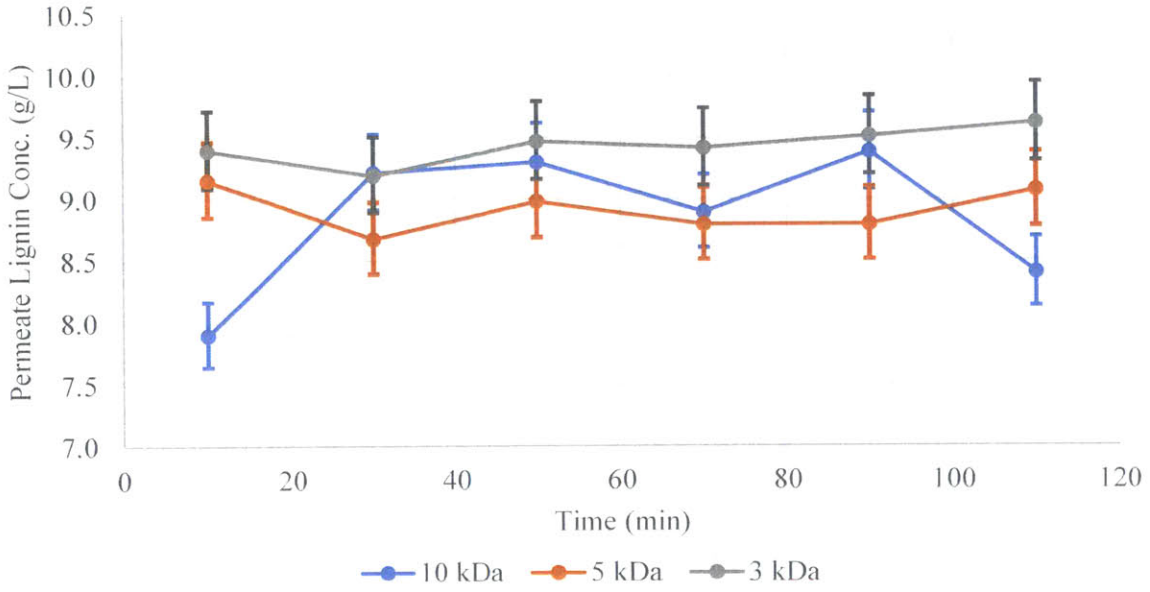

Figure 5-7: Lignin concentration in the permeate stream and its variation over time since the start of the experiment.

While permeate lignin concentration level dropped from the initial value measured at 10 min for the 3 and 5 kDa membranes, the concentration level jumped up for the 10 kDa membrane. For the 3 and 5 kDa membranes, while there is a slowly increasing trend in the permeate lignin level, especially after 70 minutes into the experiments, the trend is still unclear if the errors are taken into consideration. For the 10 kDa membrane, the concentration fluctuates quite a bit and there is also no clear trend of the lignin concentration over time. It may also be possible that the experiments have not been conducted over a long enough period for significant trends to be observed.

To compared the results among the three membranes, instead of just plotting the concentration level in the permeate stream, we would like to plot the lignin passage ratio, which is the ratio of lignin concentration in the permeate stream to the feed stream. Considering that the initial concentration of black liquor in the feed differs among each experimental run, a percentage comparison may be more appropriate, as shown in Figure 5-8.

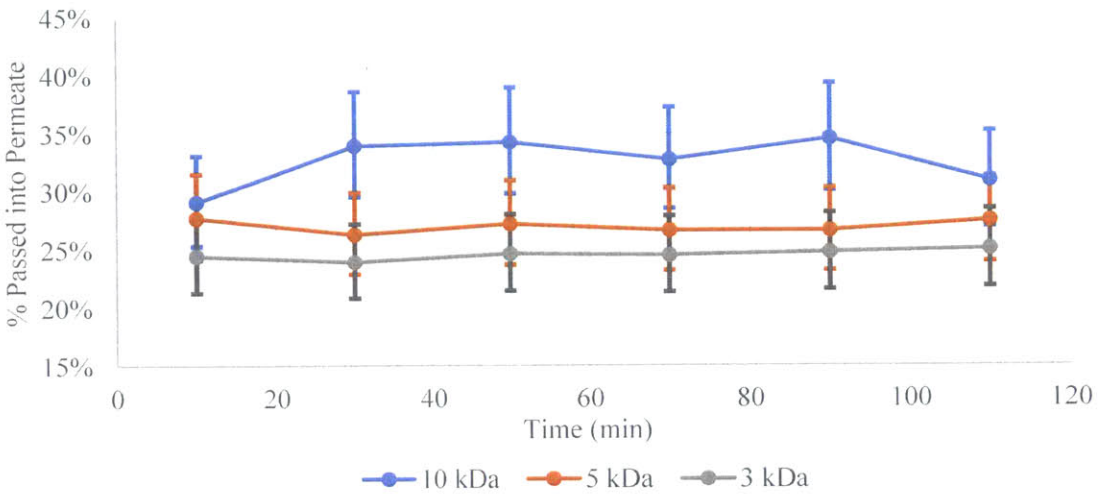

Figure 5-8: Lignin concentration in the permeate as a percentage of lignin concentration in the feed, as a function of time into the experiment for the different membranes.

As Figure 5-8 shows, the filtration capability of the membrane increases as the pore size decreases, which is expected. In fact, within this range, the permeate lignin percentage is relatively linear to the pore size of the membrane as shown in Figure 5-9. Considering that the intercept is not at (0,0) for the linear fit, which would be expected in theory, this result is merely empirical and only helps to roughly predict the lignin rejection and lignin passage ratio, and would likely not extend to membrane of other pores sizes unless further experimentation confirms so.

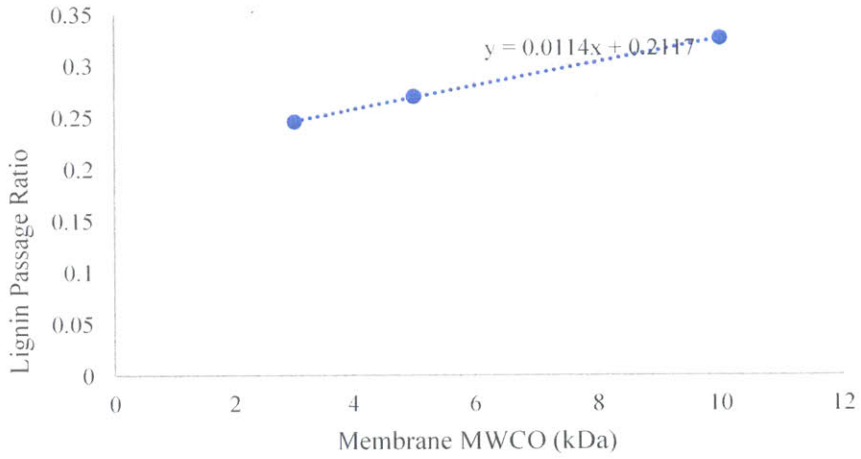

Figure 5-9: Lignin passage ratio is directly proportional to the membrane MWCO within the selected range of membranes.

The average lignin passage and rejection ratio, along with the COD removal level are shown in Table 5-5.

Table 5-5: Summary of the membrane filtration capability for lignin and other organics in general (as

indicated by the chemical oxygen demand removal level). The permeate level is still significantly higher than the discharge standard of 200 mg/L in India.

Membrane MWCO	Average Lignin Rejection	Average Lignin Passage	Permeate COD Level (mg/L)	COD Removal from the Feed
10 kDa	67%	33%	27,720	59%
5 kDa	73%	27%	26,660	67%
3 kDa	75%	25%	30,666	65%

5.4 Irreversible Fouling

For fresh black liquor, constant pressure experiments were not operated over multiple cycles where reversible fouling can be recovered by backwashing between the cycles and irreversible fouling can be observed. However, irreversible fouling can still be observed by measuring the water permeability change between experiments after membrane cleaning has been thoroughly conducted. These results, while unable to give a definitive answer relating to the membrane lifetime, can give a qualitative understanding of the level of irreversible fouling and the effect of membrane cleaning.

The change in permeability of the 10 kDa membrane between the various experiments conducted are shown in Table 5-6, together with the details of each experiment. The variation of the permeability is also shown in Figure 5-10.

Table 5-6: Water permeability variation between consecutive experiments with the 10 kDa membrane

Experiment	water permeability (LMH/kPa)	recovered permeability from previous experiment	Experiment details			
			duration (min)	TMP (kPa)	Black liquor content	note
Initial	1.67					
Exp 1	1.46	87.7%	50	0-110	unfiltered, 50%	
Exp 2	1.28	87.5%	40	0-83	unfiltered, 100%	membrane channel clogging observed
Exp 3	1.15	89.9%	30	0-124	unfiltered, 75%	membrane channel clogging observed
Exp 4	1.11	96.5%	55	0-207	filtered, >80%	
Exp 5	1.04	93.6%	100	110	filtered, >80%	

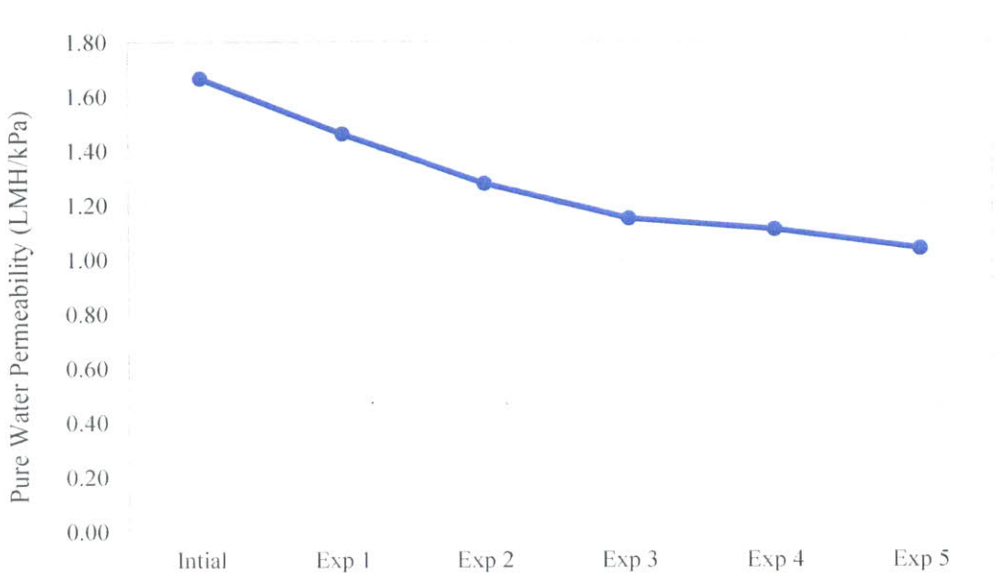

Figure 5-10: Permanent change in membrane permeability of the 10 kDa membrane between experiments after sufficient membrane cleaning. In this case, decline in permeability is most likely due to irreversible fouling of the membrane.

Continuous decline in the water permeability can be observed for the 10 kDa membrane, even after sufficient membrane cleaning through backwashing and chemical washing. The recovery of flux increased up to 96.5% in the last two experiments, but no full recovery was observed. Overall, there was still a continuous increase in irreversible fouling of the membrane, but the rate of decline showed signs of decrease as the experiments went on.

The change in water permeability of the 5 kDa and 3 kDa membranes between experiments are similarly shown below in Table 5-7 and Table 5-8. Only the flux-pressure test and constant pressure tests were performed on these two membranes in India.

Table 5-7: Water permeability variation between consecutive experiments with the 5 kDa membrane

Experiment	Water Permeability (LMH/kPa)	Recovered Permeability	Experiment Details		
			Duration (min)	TMP	Black Liquor Content
Initial	0.62				
Flux-Pressure Test	0.54	86.9%	74	0-30	filtered, >80%
Constant Pressure Test	0.53	98.1%	129	22	filtered, >80%

Table 5-8: Water permeability variation between consecutive experiments with the 3 kDa membrane

Experiment	Water Permeability (LMH/kPa)	Recovered Permeability	Experiment Details		
			Duration (min)	TMP	Black Liquor Content
Initial	0.57				
flux-pressure test	0.47	81.9%	70	0-30	filtered, >80%
constant pressure test	0.41	88.3%	100	23	filtered, >80%

The variation in permeability is also demonstrated by Figure 5-11 and Figure 5-12.

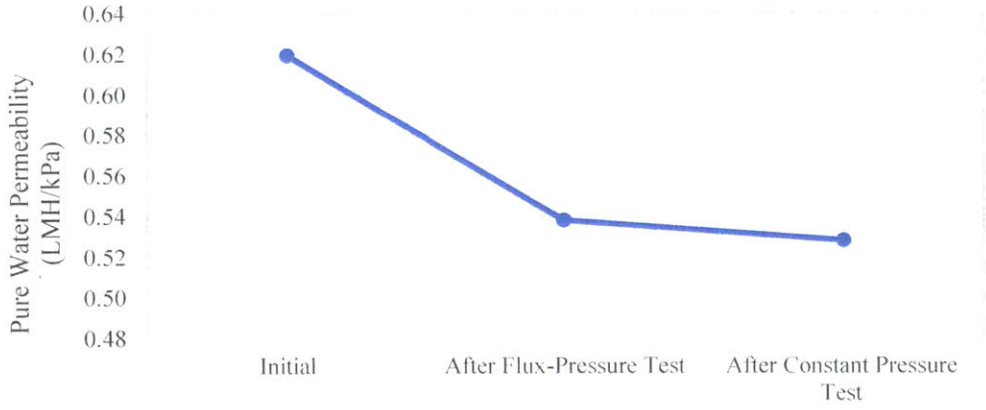

Figure 5-11: Permanent change in membrane permeability of the 5 kDa membrane between experiments after sufficient membrane cleaning.

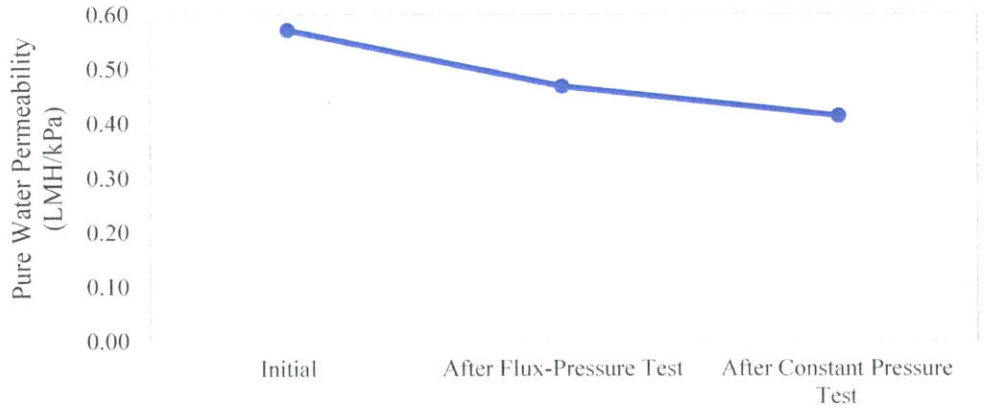

Figure 5-12: Permanent change in membrane permeability of the 3 kDa membrane between experiments after sufficient membrane cleaning.

Similarly, both membranes showed irreversible changes of membrane permeability after each

experimental run. The flux recovery increased between the experiments, even though the constant pressure test lasted for longer and was at a higher pressure, suggesting that rate of irreversible fouling may decrease as the experiments go on.

Overall, the irreversible fouling of the membrane seems to happen at a relatively quick rate, creating a 38% decline in water permeability of the membrane in less than 5 hours of black liquor operation in the case of the 10 kDa membrane. However, the rate of fouling increase declines over time, and eventually when the permeability declined beyond a certain level, the decrease may become minimal. This would still allow a substantial membrane lifetime when treating black liquor.

5.5 Summary

We can summarize our findings as the following based on results from fresh Indian black liquor experiments:

- According to the flux-pressure tests, the optimum operating transmembrane pressure for 3, 5 and 10 kDa membranes at 0.39 m/s cross-flow velocity are 110, 151 and 159 kPa respectively.
- According to the continuous-composition constant-pressure tests, flux declines ranges from 0.56 - 0.95 LMH/h or 4.4 – 7.8%/h over the course of the 1.5 h experiment. Overall flux decline levels ranging from 12% to 19.7% are observed.
- Irreversible fouling of the membrane is quite significant based on the water permeability decline of the membrane. Over the course of five 1-2 hour experiments, a water permeability decline from 1.67 LMH/kPa to 1.04 LMH/kPa is observed for the 10 kDa membranes.
- According to the lignin rejection results, lignin passage ratios of 25%, 27% and 33% were observed for 3, 5 and 10 kDa membranes respectively. Lignin passage fluctuated over the course of the experiments, but no clear trend over time was observed.

6 Experimental Results from Synthesized Black Liquor

Results from experiments using synthesized black liquor are described in this chapter. Results and from the flux-pressure tests and the optimal operating parameters determined by the tests are described in Section 6.1. Reversible and irreversible fouling results along with lignin retention results from the constant-composition feed runs are described in Section 6.2, while results from concentrating feed runs are described in Section 6.3.

6.1 Flux-pressure Test: Optimum Parameter Selection

Black liquor synthesized from lignin and sodium hydroxide was utilized in this set of experiments. A general snapshot of the synthesized black liquor quality was provided in Chapter 3, and again the crucial variables are shown in Table 6-1 below.

Table 6-1: Synthesized black liquor characteristics for flux-pressure tests

	Synthesized Black liquor
pH	10.07
Total Solids	3.90%
NaOH (mg/L)	2400
Lignin (mg/L)	38300

Despite the variability in the lignin level of the fresh black liquor from India paper mills that we worked with, we synthesized the black liquor according to the highest lignin concentration. This helps ensure that we are not underestimating the fouling capabilities of the black liquor and can realistically estimate the lifetime of the membrane. During the experimental process, sometimes contents of the black liquor are lost to the membrane or lost to the sampling in the permeate stream. Consequently, the lignin content in the black liquor is measured after each experimental run to ensure that the lignin concentration is still within 5% of the original concentration as expected in Table 6-1.

Nine flux-pressure experiments, as shown in Table 6-2, were carried out for the hollow fiber membranes of three different MWCO (10 kDa, 5 kDa and 3 kDa) at three varying flow rates (165 mL/min, 300 mL/min and 450 mL/min which corresponds to the respective cross-flow velocity (CFV) as shown in Table 6-2) to determine the optimum pressure and optimum flow rate for the membrane system. Although fouling over time may increase some uncertainty of the results, the length of the experiments was generally kept to around 1 hour to minimize the potential effect of fouling on the flux-pressure curve.

Table 6-2: Flux-pressure tests are conducted for the three different membranes at three different cross-flow velocities by adjusting the feed flow rate. Nine total flux-pressure tests are conducted.

Membrane MWCO	Feed Flow Rate (mL/min)	Cross-flow Velocity (m/s)	Shear Rate (s^{-1})
3, 5, 10 kDa	165.00	0.39	6228
	300.00	0.71	11323
	450.00	1.06	16985

Results from the flux-pressure test for 3 kDa membranes at the three different cross-flow velocities are shown in Figure 6-1, Figure 6-2 and Figure 6-3.

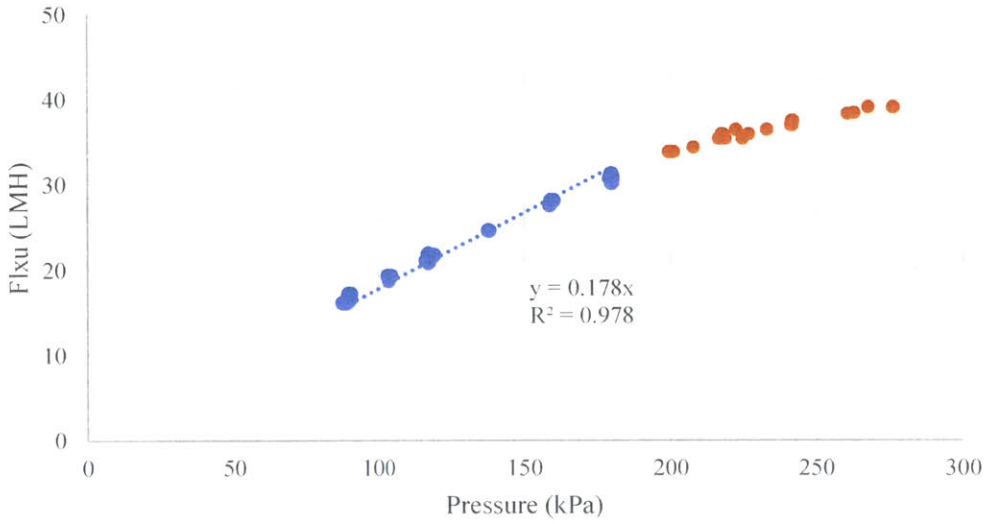

Figure 6-1: Flux – pressure curve for 3 kDa membrane at 165 mL/min feed flow rate and 0.39 m/s CFV. The curve remained linear until the critical pressure of 172 – 207 kPa where a layer of foulant started forming and the slope slowly declined as the pressure increased. A linear fit was made for the linear section (blue) of the flux-pressure curve, and the rest of the curve is in orange.

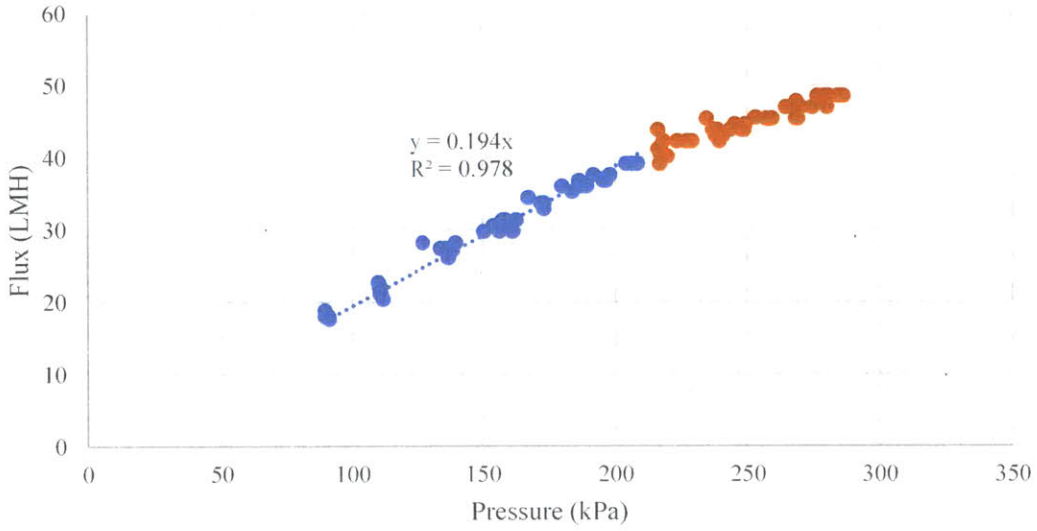

Figure 6-2: Flux – pressure curve for the 3 kDa membrane at 300 mL/min feed flow rate and 0.71 m/s CFV. The curve remained linear until the critical pressure range of approximately 220 – 255 kPa, which is above the recommended maximum operating pressure of the membrane. A linear fit was made for the linear

section (blue) of the flux-pressure curve, and the rest of the curve is in orange.

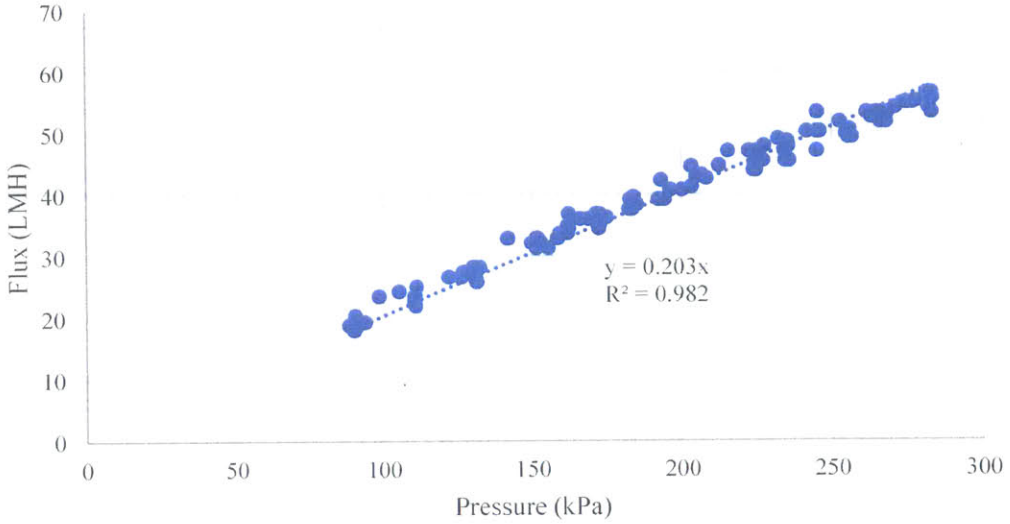

Figure 6-3: Flux – pressure curve for the 3 kDa membrane at 450 mL/min feed flow rate and 1.06 m/s CFV. The curve remained linear beyond the pressure range that was tested for, and much beyond the recommended maximum operating pressure of the membrane. A linear fit was made to the flux-pressure curve.

The flux-pressure curves show a general linear trend until the critical pressure range. The critical pressure range should help determine the optimum operating transmembrane pressure at the respective cross-flow velocities.

To determine the optimal operating cross-flow velocity, the slopes of the linear section of the flux-pressure curve are plotted over the cross-flow velocity to determine how flux varies with cross-flow velocity at constant pressures below the critical pressure range, as shown in Figure 6-4.

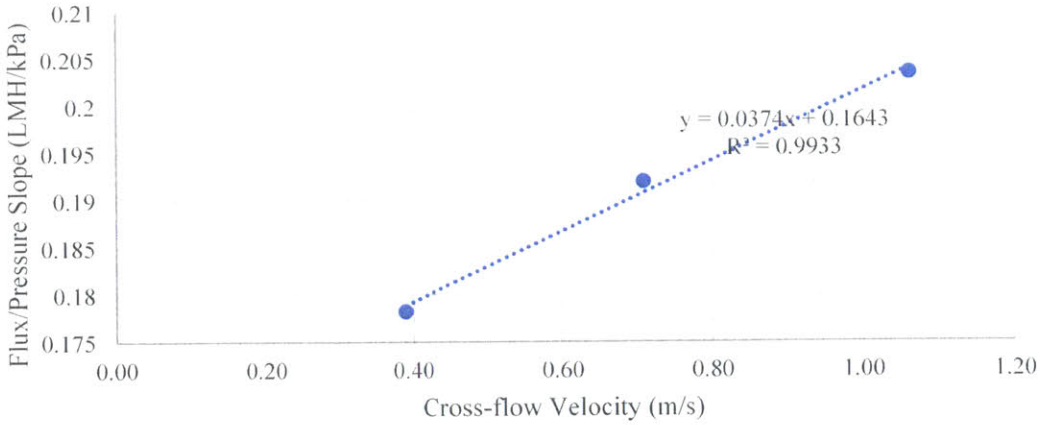

Figure 6-4: The flux/pressure slope variation with cross-velocity for the 3kDa membrane. Below a certain threshold, permeate flux would vary linearly with cross-flow velocity when operating at constant TMP (or in other words, the flux/pressure slope varies linearly with cross-flow velocity). For 3 kDa membrane, the

linear trend seems to hold true within the range that was tested for.

Figure 6-4 suggests that no marginal decline in the flux/pressure slope has occurred within the selected range of cross-flow velocity. Consequently, the maximum cross-flow velocity should be selected as the optimum operating cross-flow velocity. The cross-flow velocity is also similar to other literature studies with cross-flow velocity values between 0.1 – 4 m/s (Choi et al. 2005). Higher cross-flow velocities may have also been effective, but the upper limit of the cross-flow velocity of the pump is 1.13 m/s (feed flow rate of 480 mL/min). Consequently, the optimum operating cross-flow velocity based on the system's limitation, would be 1.06 m/s, which corresponds to a feed flow rate of 450 mL/min.

At 1.06 m/s cross-flow velocity, the critical pressure of the 3 kDa membrane is beyond the maximum operating pressure of 207 kPa. Thus, the optimum pressure for the membrane module would be 207 kPa.

Similarly, flux-pressure curves were plotted for 5 kDa membranes, as shown in Figure 6-5.

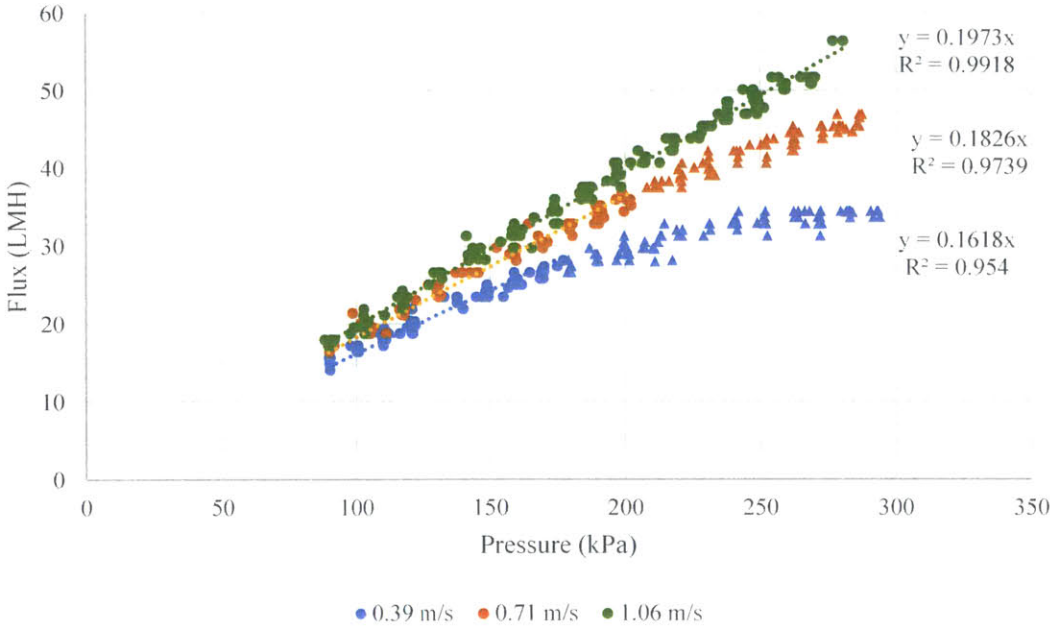

Figure 6-5: Flux – pressure curve for the 5 kDa membrane at 0.39 m/s, 0.71 m/s and 1.06 m/s cross-flow velocity. A linear fit was made to the linear portion of each of the flux-pressure curve, where the data are labeled with round points. Beyond the linear range, the data are labeled with triangular points. The critical pressure range is 179 – 207 kPa at 0.39 m/s CFV, 228 – 262 kPa at 0.71 m/s and beyond the tested pressure range at 1.06 m/s.

The flux/pressure slopes are also plotted against the cross-flow velocity for the 5 kDa membrane in Figure 6-6.

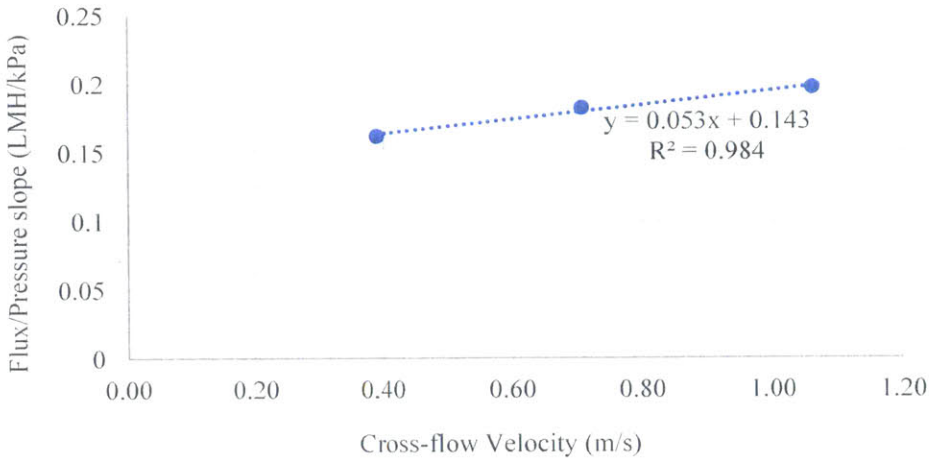

Figure 6-6: For the 5 kDa membrane, the flux/pressure slope is proportional to the cross-flow velocity within the range that was tested for.

Similarly, the linear increase in flux was observed throughout the cross-flow velocity ranges that were tested for. Consequently, the optimum cross-flow velocity is again 1.06 m/s, corresponding to 450 mL/min feed flow rate. At this cross-flow velocity, the optimum pressure for the membrane module, as shown in Figure 6-5, is again the maximum operating pressure of 207 kPa, because the critical pressure range is beyond the maximum recommended operating pressure.

For the 10 kDa membranes, the flux-pressure curves are shown below in Figure 6-7.

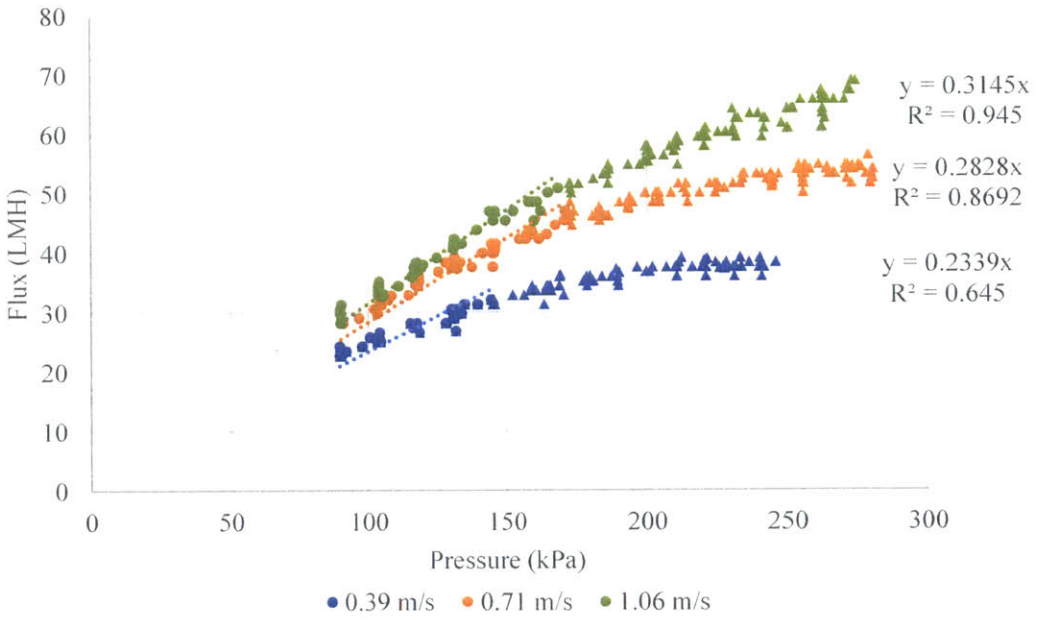

Figure 6-7: Flux – pressure curve for the 10 kDa membrane at 0.39 m/s, 0.71 m/s and 1.06 m/s cross-flow velocity. A linear fit was made to the linear portion of each of the flux-pressure curve, where the data are labeled with round points. Beyond the linear range, the data are labeled with triangular points. The critical

pressure range is 138-172 kPa at 0.39 m/s CFV, 159-193 kPa at 0.71 m/s and 172-207 kPa at 1.06 m/s, but there are large uncertainties within this range due to the comparatively lower R-square values for the linear fit.

In comparison to the previous flux-pressure curves and the linear fit at pressure range below the critical pressures, the linear fit for the 10 kDa membrane have a lower R-squared value. Instead of the theoretical linear flux-pressure curve that should pass through the origin, the experimental data seem to instead suggest a curve that has an intercept larger than 0, and one that is less steep than the linearly fitted curve. There is more uncertainty in the linear fit for the 10 kDa membrane, and more uncertainty for the critical pressure range and optimum pressure selection.

The flux/pressure slopes are again plotted against the cross-flow velocity for 10 kDa membranes in Figure 6-8.

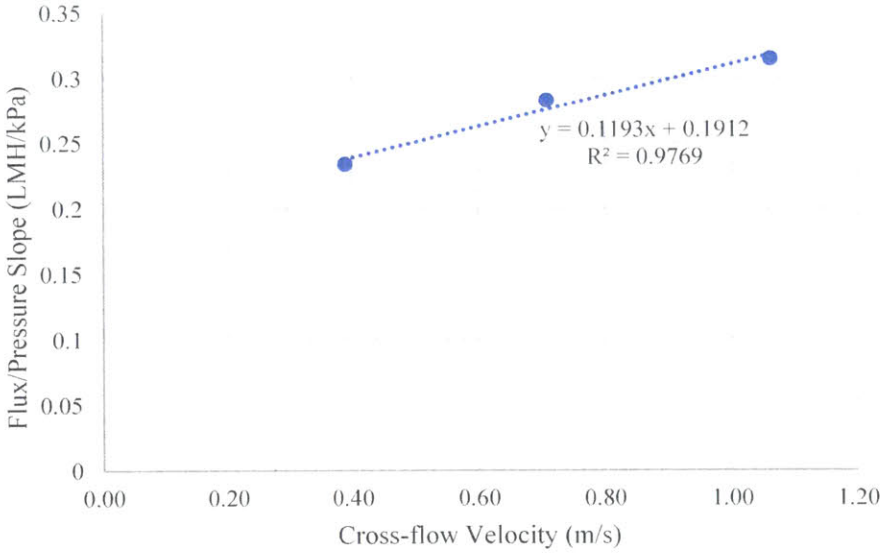

Figure 6-8: For the 10 kDa membrane, the flux/pressure slope is proportional to the cross-flow velocity within the range that was tested for.

The linear increase in flux was still observed throughout the cross-flow velocity ranges that were tested for and the optimum cross-flow velocity is again 1.06 m/s, corresponding to 450 mL/min feed flow rate. At this cross-flow velocity, the optimum pressure for the membrane module, as shown in Figure 6-7, would ideally be within the critical pressure range of 172 - 207 kPa. There may be more uncertainty regarding this range due to the uncertainty of the flux-pressure linear fit as described in Figure 6-7.

Consequently, the optimum operating cross-flow velocity and the optimum transmembrane pressures at the selected cross-flow velocity can determined based on the results above. The results are shown in Table 6-3.

Table 6-3 Optimum operating cross-flow velocity and transmembrane pressure for the membranes.

Membrane MWCO	10 kDa	5 kDa	3 kDa
Optimum Cross-flow velocity (m/s)	1.06	1.06	1.06
Optimum transmembrane pressure (kPa)	172 - 207	207	207
Flux/pressure slope (LMH/kPa)	0.315	0.197	0.203

6.2 Constant Feed Mode Run

6.2.1 Flux Decline and Reversible Fouling

Constant pressure and constant-composition tests would be conducted at the optimum feed flow rate and TMP, as shown in Table 6-3. A new batch of synthesized black liquor was made for the constant feed run, with its characteristics shown in Table 6-4. The composition is identical (< 0.3% difference) to the composition of the batch for the flux-pressure tests as shown in Table 6-2. There is variation of the black liquor composition during the course of the experiment due to sampling from the permeate stream, but the difference in composition was generally kept below 5% from the original composition. If there were any indication that the composition deviated more than 5%, the flux and other related data would be omitted from the results and no longer considered as valid.

Table 6-4: Synthesized black liquor characteristics for constant pressure tests

	Synthesized Black liquor
pH	10.03
Total Solids	3.90%
NaOH (mg/L)	2400
Lignin (mg/L)	38200

Even though ideally each run should continue until the flux declines approximately 40% before the backwash, the flux in these experiments generally did not decline more than 40% within a reasonable time frame, and the decline became relatively slow towards the end of each experiment. Because of the manual process in remixing the permeate to ensure the feed consistency, the experiment require constant supervision when it is running, and it would affect the quality of the results if the experiments were stopped in the middle and restarted again later. Hence, the constant pressure experiments were carried out in approximately 24-hour cycles followed by mechanical backwash, considering the challenge to be constantly monitoring the experiment for longer than 24 hours. Even though a 40% decline cannot be observed, the frequency of mechanical cleaning can still be estimated through observing the decline in flux during each of runs. The backwash is usually conducted for a sufficiently long period of time so that minimal further recovery of flux can be observed with longer time. We generally ended with backwashing cycles of 3-5 hours after each run.

In addition, over time and continuous accumulation of fouling materials on the membranes,

sometimes physical cleaning procedures such as backwashing can no longer effectively clean up the fouled membranes, and the changes to the membrane can only be reduced by chemical washing processes (Kimura et al. 2004). However, chemical processes should generally be minimized due to its higher costs (more chemicals are added and the process is less automatic in comparison to backwashing) and its potential to affect membrane life (Kimura et al. 2004). Comparing the flux across the runs may roughly indicate the level of fouling that cannot be cleared through mechanical washing and the need for chemical cleaning, which is also important in determining membrane lifetime and treatment cost. A final chemical wash is conducted at the end of the four cycles.

Due to the length of the continuous tests and the constraint of time, only 5 kDa membranes were tested with continuous constant-pressure operation. 5 kDa membranes were selected because in theory it would be a good compromise between having higher rejection ratio of lignin (where 3 kDa membranes would have been preferred) and higher flux at the optimum pressure (where 10 kDa membranes would have been preferred). In addition, variables such as pressure and feed flow rate, apart from affecting the flux, also directly relates to the pumping power, which contributes directly to the cost of membrane system. On the other hand, the pore size of the membrane is only related to the flux, which is then contributes to the membrane area and system cost. Membranes of different pore sizes are similar in cost. Consequently, the membrane pore size is then considered as a secondary factor in determining the cost-effectiveness of the membrane system, and the optimization of other primary factors such as pressure and pumping rate (feed flow rate) are prioritized instead. Thus, considering that the ultimate goal of the experiments is to estimate the cost-effectiveness of a membrane system in treating black liquor, we will only look at the 5 kDa membrane for the purpose of this research. The results can be roughly extended to 3 kDa, 10 kDa and even membranes of other MWCO based on their flux-pressure results and lignin rejection ratio.

Results from the first 25-hour cycle of constant pressure test at 207 kPa is shown in Figure 6-9.

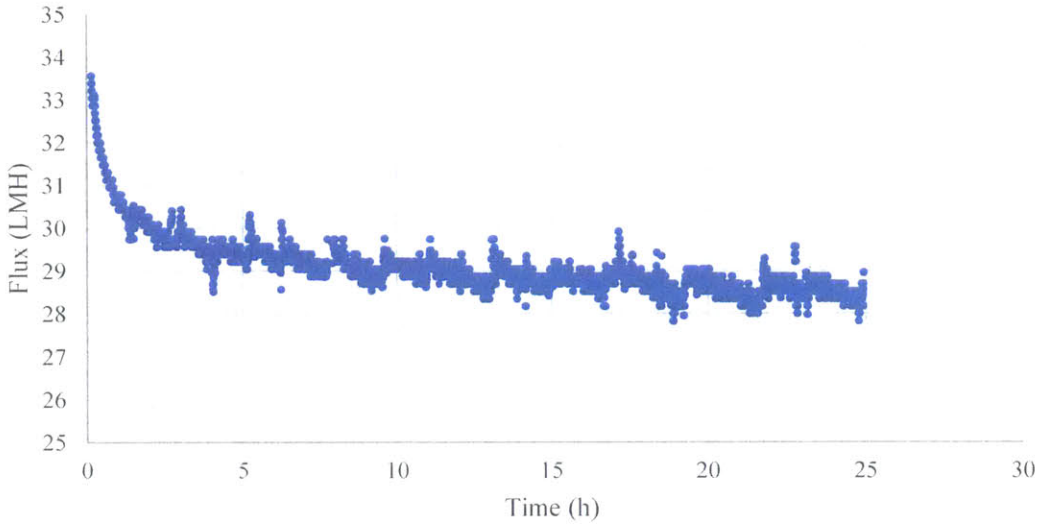

Figure 6-9: Flux decline over Run 1 - the first 24-hour cycle for the 5 kDa membrane.

As shown in Figure 6-9, a sharp decline in the flux level happened within the first 4-5 hours, and afterwards the decline became relatively slow and steady. The end flux was between 28 and 29 LMH after the 25-hour run. The small periodic fluctuations in the flux are due to the change in the feed concentration. The permeate stream is collected and measured on a scale for flux calculation, and the permeate is then returned to the feed to ensure that less than 5% change in concentration occurs in the feed. It seems that even such small changes in feed concentration affected the flux, but the overall trend in the flux is still observable despite the fluctuations. The subsequent cycles showed similar trends in the decline in flux.

Results from the next 16-hour cycle is shown in Figure 6-10.

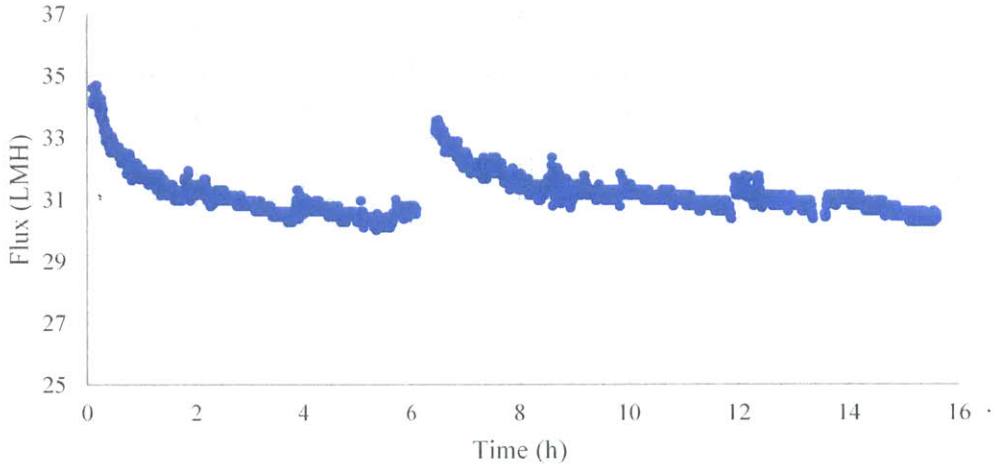

Figure 6-10: Flux decline over Run 2 - the second 16-hour cycle for the 5 kDa membrane. The two segments occurred because the experiment had to be paused for approximately 11 hours in between, but no washing occurred. The pump was stopped and the pressure was also alleviated during the pause of

experimentation.

Similarly, a sharp decline can also be observed at the first 4-5 hour of the experiment. Interestingly, the pause in the experiment caused a large increase in the flux, increasing it almost to the initial level. The flux was able to be recovered through a pause in the experimentation, without any membrane cleaning process. The pause almost served a similar purpose to membrane cleaning. This cycle was relatively short compared to the first 25-hour cycle, and with the pause causing significant flux recovery, the flux didn't decline nearly as much as it did in the first cycle.

Results from the third cycle which is approximately 27 hours are shown in Figure 6-11.

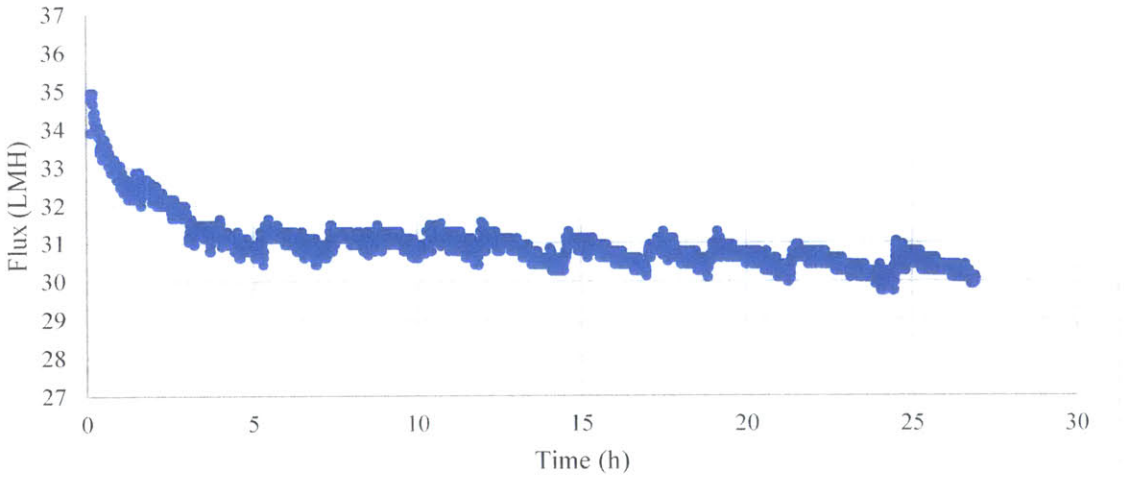

Figure 6-11: Flux decline over Run 3 - the third cycle of 27 hours for the 5 kDa membrane. The slight discrepancy at around 3 hours into the experiment is due to the continuous rise in the feed concentration due to infrequent mixing of the permeate solution back into the feed. Thus, the system has to be stopped for mixing to ensure the feed stream concentration was back to the initial level. Overall, the trend was very similar to the first cycle, with a rapid drop in the first 5 hours and slow and steady decline afterwards.

The sharp initial decline is still observable in the first few hours, followed by a steady and relatively slow decline. The flux also didn't decline as much as it did in the first run, dropping to around 30 LMH after 26-27 hours of black liquor treatment, as opposed to 28-29 LMH in the first run.

Results from the last cycle are shown in Figure 6-12.

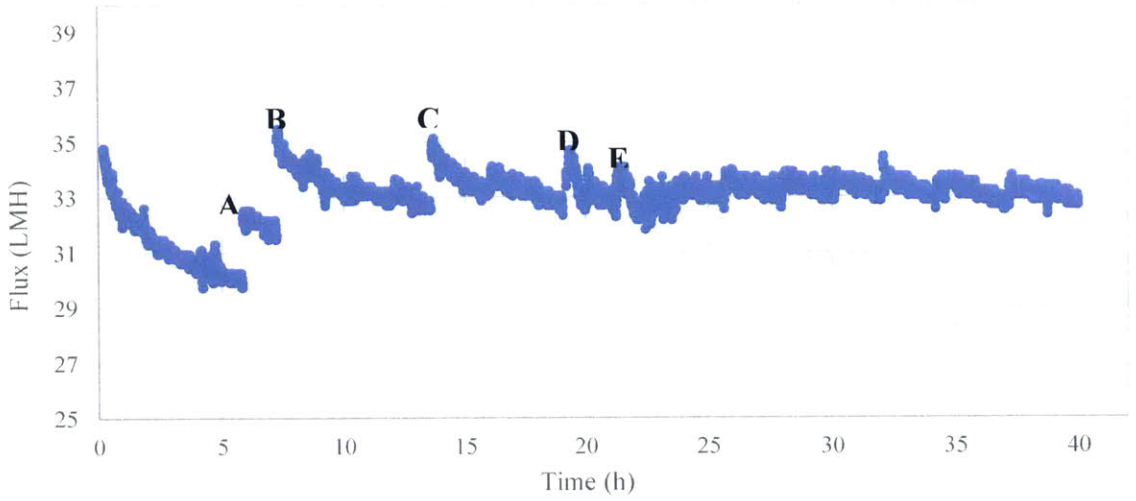

Figure 6-12: Flux decline over Run 4 - the fourth cycle of 40 hours for the 5 kDa membrane. Flux data has been left out where the concentration of the feed solution deviated more than 5% from the original feed concentration due to the infrequency of pouring the permeate back into the feed. There are many disruptions in the flux for this particular run, and the most prominent ones are labeled as A-E in the figure.

There are a few more operational complications that caused disruptions in the flux curve, and the disruptions are labelled above. At point A, the system had problems with maintaining a constant TMP, and the pressure was fluctuating and increased above the threshold inlet pressure, which caused the pump to shut down to protect the integrity of the membrane. The pump stopped, and the pressure across the membrane was also alleviated temporarily. The system was restarted very quickly again after the shutdown, and the initial flux quickly jumped up to 32.3 LMH as opposed to the 30 LHM flux level right before the pump was automatically shut off. However, the flux didn't recover to the initial level of approximately 35 LMH. At both B and C, the experimentation was shut off manually for a few hours and restarted without any washing. This pause in the experimentation also caused the flux of black liquor to fully recover, similarly to the results in the second run. While the flux only partially recovered at A with a short experimentation pause (< 30 minutes), the flux has generally fully recovered at B and C after a much longer pause (1 – 2 days). The disruption at D was caused by returning the permeate stream into the feed to ensure that the concentration is consistent. However, while a slight increase due to the remix of the permeate stream is expected, the flux almost returned to the initial level at D, which is unexpected. This is followed by some turbulence in the flux for about 3 – 4 hours, exhibiting a relatively irregular flux pattern that has not been seen in any previous runs. After another permeate remix at E, the flux increased slightly again but quickly declined afterwards. The irregular turbulence after E is not as observable anymore, and soon afterwards the flux slowly started to show only regular turbulences due to the remix of the permeate back into the feed. After point E, however, the flux only showed very minimal decrease over the next course of almost 20 hours. The flux at the end of the 40-hour run was around 32.9 LMH, which is the highest of all four runs conducted.

To determine the need for chemical washing, the general trend of reversible flux over the different

runs can also be observed by plotting the different runs on the same timeline, as shown in Figure 6-13.

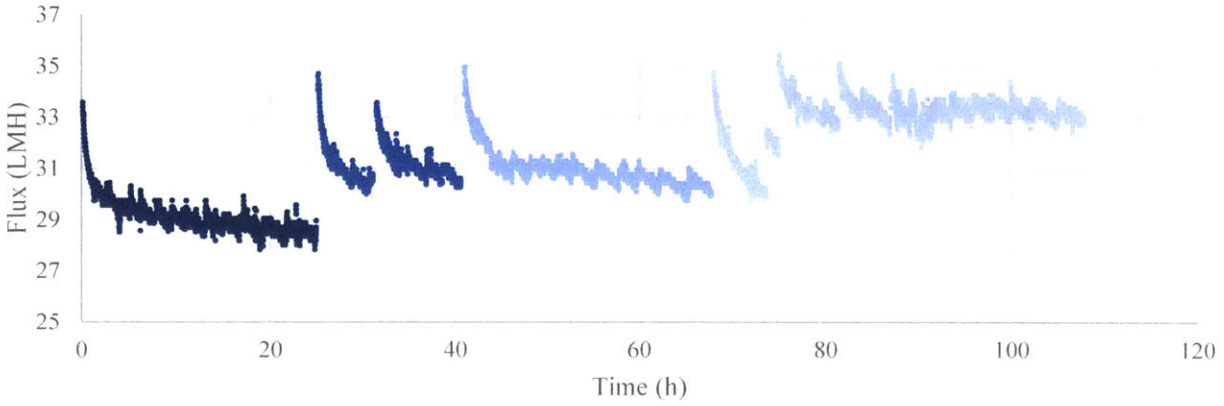

Figure 6-13: Flux decline over the four consecutive runs. The different runs are shown in different shades of blue. The regular mechanical backwash was conducted between the four runs of experiment experiments. The mechanical washes are usually conducted for a sufficiently long period of time to recover as much of the flux as possible, which is usually around 3-4 hours of washing.

The flux decline is relatively rapid at the beginning of the experiment, but declines quickly after about 5-10 hours of experimentation. Over the four different runs, the average flux decline for the first 5 hours of the experiment and the last 5 hours of the experiment is documented in Table 6-5. The rate of decline of the last 5 hours is consistently higher than the rate of decline over the first 5 hours.

Table 6-5: Rate of flux decline for the different runs

		Run 1	Run 2	Run 3	Run 4
Experiment Duration (h)		25	16	27	40
Initial Flux (LMH)		33.3	34.3	34.8	34.7
First 5h	Rate of decline (LMH/h)	0.80	0.78	0.780	0.92
	Percent decline (%/h)	2.39	2.27	2.29	2.56
Last 5h	Rate of decline (LMH/h)	0.038	0.12	0.048	0.047
	Percent decline (%/h)	0.13	0.38	0.16	0.14
Overall percent decline (%)		14.4	11.2	13.8	5.5

Even though the flux declines within each of the separate run is significant, the flux of synthetic black liquor through the membrane generally rises back up with sufficient mechanical washes. If we take a close look at the variation of the initial flux over time as shown in Figure 6-14, the initial flux was not showing signs of decline during the experiment. In fact, there was a rising pattern over the first three runs. The rise was relatively small, so the rising pattern may only be results of slight variations in some of the experimental setup between the different runs, rather than a significant increasing pattern. Overall, the initial flux was relatively stable around 33-35 LMH, with a small rising trend among the first three runs.

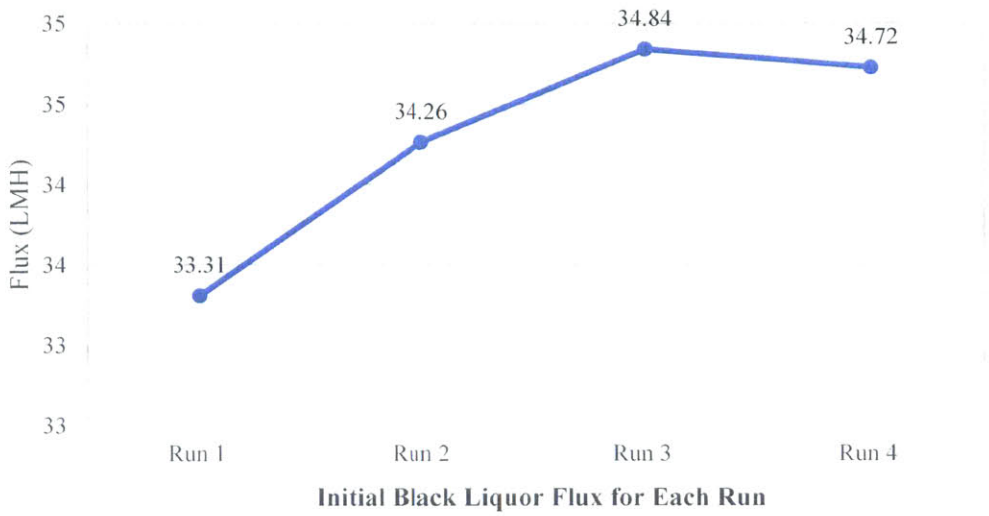

Figure 6-14: Variation of initial flux of across the different runs

However, the condition of the membrane permeability should be best determined by observing the water permeability of the membrane, instead of the black liquor permeability. For pure water permeability (flux/pressure ratio), the changes across the different runs are shown in Figure 6-15.

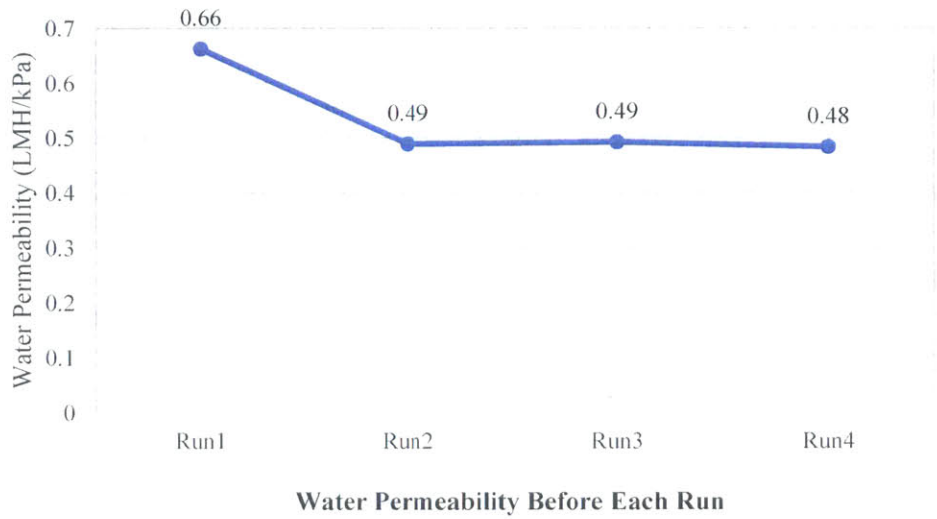

Figure 6-15: Variation of water permeability across the different runs.

Despite the fact that the initial black liquor flux was almost constant across the runs, the figure above suggests that the water permeability has indeed decreased from its initial level after the black liquor runs. Specifically, after run 1, only around 74% of the water permeability was recovered after the mechanical backwash. However, for most of the subsequent runs, little further drop in water permeability was observed. Only the first black liquor run sufficiently fouled the membrane to a degree that mechanical washing could not completely clean up.

It is useful to note that the backwash cleaning was first conducted by only water after run 1.

However, water wash was only able to get the water permeability back to around 53% of the initial water permeability. A cleaning solution with composition similar to the permeate was then used as the backwashing solution, which was able to return the initial water permeability back to 74%, as shown previously. In the subsequent runs, all the mechanical backwash cleaning used a composition similar to the permeate.

Overall, while black liquor flux declines significantly over the course of each run, the mechanical backwash is almost always able to restore all of the black liquor permeability, suggesting that the fouling in the process of the runs are generally reversible. Interestingly, the backwash slightly increased the initial black liquor flux, which departs from our expectation. On the other hand, water permeability can only be restored back to around 74% through backwash, suggesting that the flux was not fully reversible through mechanical backwash cleaning alone.

6.2.2 Irreversible Fouling

Over the time, physical cleaning procedures such as backwashing can no longer effectively clean up the fouled membranes, and the changes to the membrane can only be reduced by chemical washing processes, a generally costlier procedure (Davis 2010). In the four runs of the reversible flux experiments, even though there was little variation in the initial black liquor flux, the 26% decline in pure water flux of the washed membranes still represents fouling that cannot be cleaned up by mechanical processes alone. After the four runs, the initial black liquor flux or water permeability were staying relatively stable, so due to the limit of time, the runs stopped and a chemical wash was conducted to observe how effectively it can clean up the fouling that was not able to be removed by mechanical cleaning. The chemical wash was conducted for more than 8 hours until no further improvements in water permeability can be observed. Any fouling that still cannot be removed by chemical washing at this point would be considered irreversible fouling, or in other words, permanent damage to the membrane. The level of irreversible fouling observed from the experiment can effectively predict the lifetime of the membrane, and the membrane replacement cost.

The run after the chemical wash was not a full-day run, and it was only operated for approximately five hours to observe the general pattern of the initial and flux decline, as shown in Table 6-6.

Table 6-6: Overview of the flux decline patterns for the run after the chemical wash

		Run after chemical wash
Experiment Duration (h)		5
Initial Flux (LMH)		38.58
First 5h	Rate of decline (LMH/h)	0.921
	Percent decline (%/h)	2.39
Overall percent decline (%)		11.5

If we look at the overall flux pattern with the addition of the cycle after the chemical wash, as shown in Figure 6-16, we can observe a significant increase in black liquor permeability after the chemical wash. The comparison of the initial flux after the chemical wash in Figure 6-17 also confirms at least a 10% increase in the initial flux after the chemical wash, compared to the previous run. The initial flux of black liquor after the chemical wash is also larger than the initial flux at the beginning of the experiment when the membrane was still in pristine state. This is interesting because irreversible fouling was expected to occur, and the black liquor initial flux was expected to decrease in comparison to the initial flux at the beginning with a pristine-state membrane, as shown in Figure 2-12. However, in our case, we actually observed the opposite where the initial flux increased over the different runs, and increased even more significantly after the first chemical wash. It's also useful to note that even though the initial flux was higher than before, the rate of flux decline over the first five hours was also slightly higher in comparison to the previous runs before the chemical wash. The percentage decline in flux over the 5 hours of this run was even more than the percentage decline in run 2 over 16 hours. So despite the initial high flux after the chemical, the rate of decline also seemed to be more significant.

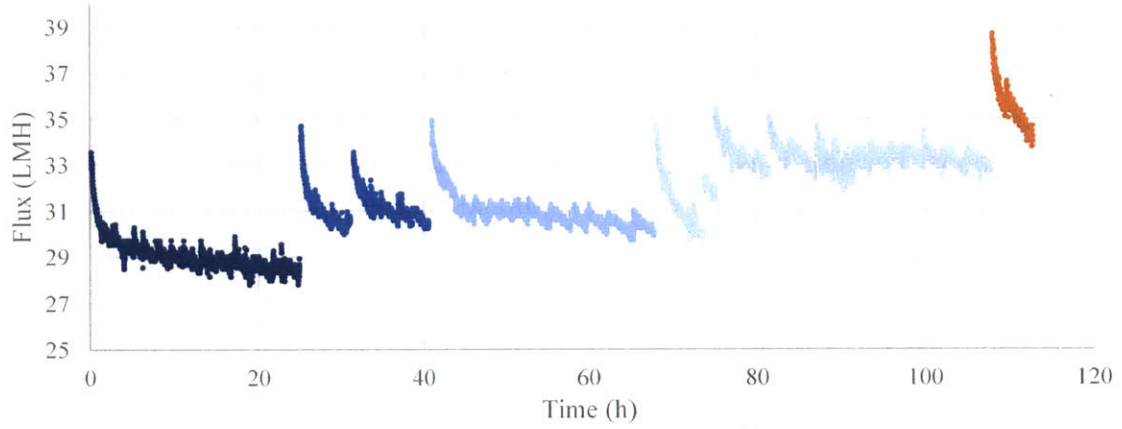

Figure 6-16: Flux decline over the four consecutive runs and after the chemical wash. The different runs are shown in different shades of blue, while the short 5-hour run after the chemical wash was shown in orange.

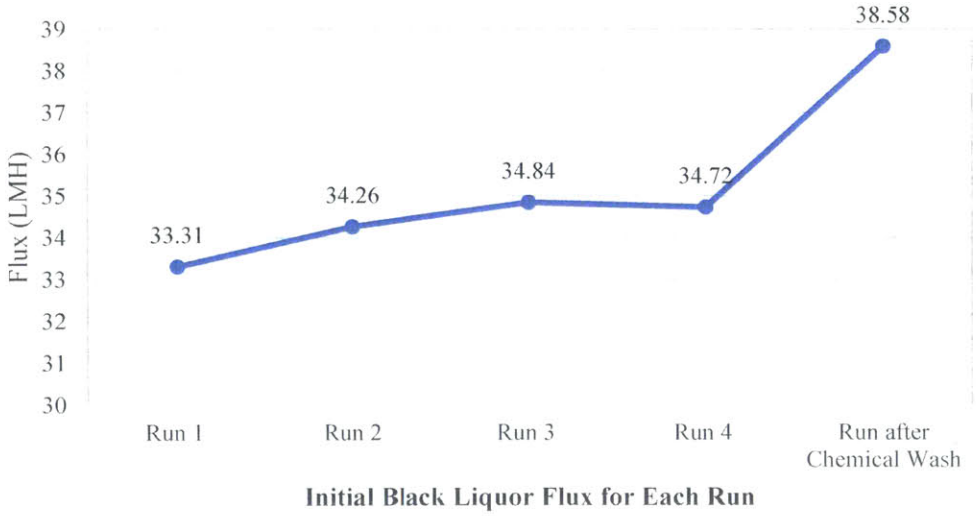

Figure 6-17: Variation of initial flux across the different runs, including the last run right after the chemical wash. A significant increase can be observed in the black liquor flux right after the chemical flux.

On the other hand, if we look at the water permeability, the results do not align with the results from black liquor filtration. As shown in Figure 6-18, water permeability did not recover after the chemical wash, and even decreased approximately 10% after the chemical wash, even though it was quite stable before when only mechanical backwashes were conducted. This also deviates from our expectations, because it is generally expected that chemical wash would be able to recover some level of water permeability of the membrane. Instead, in this case, no restoration of permeability can be observed.

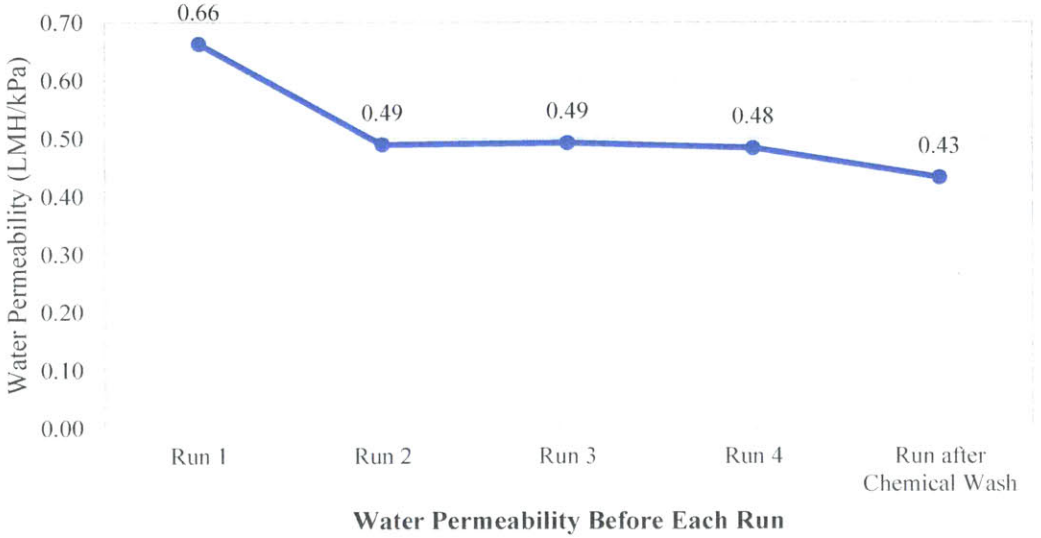

Figure 6-18: Variation of water permeability across the different runs and after the chemical wash.

An overview of the variation in permeability of the membranes over the different runs can be summarized in the table below.

Table 6-7: Black liquor and water permeability variation between consecutive experiments after backwash and lastly, chemical wash. All recovered permeability ratios are comparing to the previous experiment, except after the chemical wash, where the recovered is calculated comparing to the initial permeability at run 1. Generally, a flux recovery of more than 100% is not expected, so when the recovery is larger than 100%, it is only marked as >100% and the actual percentage is noted on the side.

Experiment	Water permeability before run (LMH/kPa)	Recovered permeability	Initial black liquor permeability (LMH/kPa)	Recovered black liquor permeability
Run 1	0.66		0.161	
Run 2	0.49	73.7%	0.166	>100% (102.9%)
Run 3	0.49	>100% (100.6%)	0.168	>100% (101.7%)
Run 4	0.48	98.2%	0.168	99.7%
Run after chemical wash	0.43	65.2%	0.187	>100% (116.2%)

Overall, based on the experimental results from constant-composition black liquor filtration processes, little irreversible changes to the black liquor flux was observed after the four continuous runs of black liquor. In fact, the initial flux under the same conditions increased instead of decreasing, and increased even more significantly after the chemical cleaning to almost 111% of the previous flux in run 4 and 116% of the original initial flux during the first run of black liquor. Based on the water permeability change, however, fouling that was irreversible under mechanical cleaning still remained irreversible under chemical cleaning. Only 65% of water flux was recovered when comparing the final water permeability to the initial water permeability before any black liquor runs, indicating a relatively high level of irreversible fouling. Hence, despite the fact that few irreversible changes were observed when processing black liquor, the water permeability indicated relatively heavy levels of irreversible fouling. The irreversible fouling may not necessarily affect black liquor flux during the filtration process.

6.2.3 Lignin Rejection and Passage

During the flux pressure tests, the lignin concentration in the permeate stream is measured at the beginning of the experiments where the pressure is low, and at the end of the experiments where the pressure becomes as high as 276 kPa. The concentration of lignin in the permeate helps determine the level lignin passage into the permeate, as well as the level of lignin retention in the concentrate, which is directly related to the effectiveness of the filtration and concentration of black liquor process.

A general overview of the lignin concentration in the permeate stream is shown in Table 6-8.

Table 6-8: Lignin concentration in the permeate stream for the various flux-pressure tests of the different membranes at different feed flow rates. Generally, due to the dilution process to measure lignin concentration, the lignin concentration has an error range of approximately 1.5%, or around +/- 0.02 g/L.

Membrane MWCO	Feed Flow Rate (mL/min)	Cross-flow Velocity (m/s)	Initial Permeate Concentration (g/L)	End Permeate Concentration (g/L)	Average Lignin Rejection	Average Lignin Passage
3 kDa	165	0.39	1.52	1.47	96.2%	3.8%
	300	0.71	1.43	1.33	96.5%	3.5%
	450	1.06	1.22	1.05	97.2%	2.8%
5 kDa	165	0.39	1.33	1.10	97.0%	3.0%
	300	0.71	1.07	1.02	97.4%	2.6%
	450	1.06	1.10	0.97	97.5%	2.5%
10 kDa	165	0.39	1.44	1.39	96.3%	3.7%
	300	0.71	1.46	1.36	96.4%	3.6%
	450	1.06	1.62	1.51	96.1%	3.9%

The permeate lignin concentration decreases over the course of each flux-pressure tests, likely due to the fact that with increasing pressure there is more fouling (potentially blocking the passage of lignin) and also more water passage through the membrane, which would amount to a decreasing lignin concentration. The lignin passage level also generally decreases with increasing cross-flow velocity (apart from the 10 kDa membrane at 1.06 m/s), because again increasing cross-flow velocity would suggest a higher flux with higher water passage, potentially decreasing the concentration of the permeate. Even though we expect lignin passage to decrease with decreasing membrane pore size, the 3 kDa membrane in fact had a higher average lignin passage overall in comparison to the 5 kDa membranes. It's useful to note that the flux vs. pressure slope of 3 kDa membranes was in fact slightly higher than 3 kDa membranes, which aligned with results from Liu et al. suggesting that flux didn't necessarily increase with membrane pore size. The lower flux level of 5 kDa potentially indicates more fouling, which could result in less lignin passage.

Overall, the lignin passage was low and was around 2-4%, and the retention rate was as high as 96-98%.

In the continuous test, the concentration of lignin in the permeate stream is generally tested every 1 – 1.5 hours to obtain the trend of lignin concentration over the course of the runs.

The general trend of the lignin concentration over four runs and the short run after the chemical wash is shown in Figure 6-19. The lignin level started from around 1.67 g/L and ended at around 1.03 g/L before the chemical wash. Interestingly, these permeate lignin concentration levels were generally higher than the permeate lignin concentration levels of the flux-pressure tests of the 5 kDa membranes at similar feed concentration and the same cross-flow velocity (1.06 m/s) as shown in Table 6-8. This is potentially because the flux-pressure test membranes have gone through previous runs of black liquor at higher pressures and lower cross-flow velocities (the previous 0.39 and 0.71 m/s pressure-flux tests and a few pervious trials as well), causing more fouling and changes to the membrane, while the membrane for constant-composition runs is

pristine when first utilized in this set of experiments. It may also be because the inherent differences in the different membranes, as well as the slight compositional differences in the different black liquor feed.

Due to the comparatively low levels of lignin and the moderate dilution ratio, the measurement errors of the data are relatively low, also around 0.02 g/L, similar to the level suggested in Table 6-8. However, there are other systematic errors such as potential changes to the permeate sample during sample storage and so on, which could be avoided in the future by improved experimental procedures such as immediate testing of lignin after sampling.

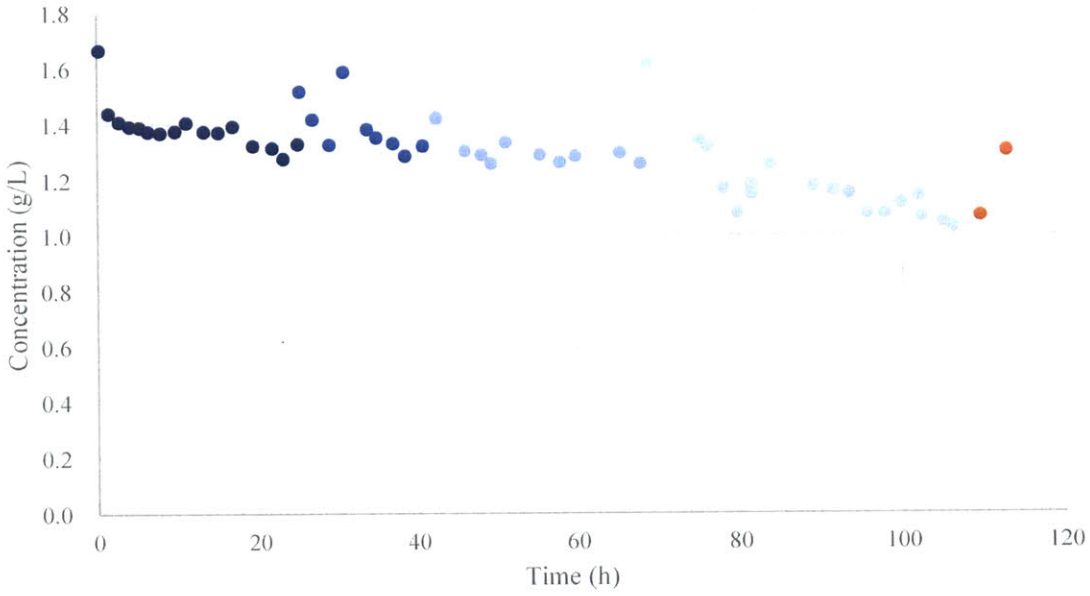

Figure 6-19: The variation of lignin in the permeate stream over the four continuous runs and the last run after the chemical wash. The colors for the different consecutive runs are in different shades of blue, and the run after the wash is in orange. The color scheme is identical to the one utilized in Figure 6-16.

The general composition of the feed solution has varied minimally across the different runs, so the concentration of lignin in the permeate stream is comparable across the different runs. Overall, there are some spikes in the figure at the beginning of each run, similar to the spikes of the flux at the beginning of each run. The spikes generally dropped after the first few points and the flux became steadier afterwards in each run. In contrast to the overall increasing trend of the permeate flux rate, there is also an overall decreasing trend of the lignin concentration in the permeate stream across the different runs, and even the chemical wash at the end was not able to raise the lignin passage ratio significantly (the last point after the chemical wash is unexpectedly high, but it may not be exactly accurate because it was taken after the system was shut off and restarted again so it is not included in the discussion here). This aligns with the previous conclusion that the membrane has been irreversibly fouled and its rejection ratio of lignin has been permanently affected, even though the permeate flux did not show a declining pattern.

If we align the permeate stream lignin concentration with the permeate flux rate as shown in Figure

6-20, we can see that within each run, the increasing and decreasing patterns of permeate lignin concentration almost exactly mimics the permeate flux rate. For example, in Run 2, the two separate peaks followed by a sharp decrease pattern is demonstrated in sync in both the permeate flux level and the permeate lignin concentration level. However, as suggested previously, while the flux shows a rising pattern across the different runs, the permeate lignin concentration shows a continuously declining pattern.

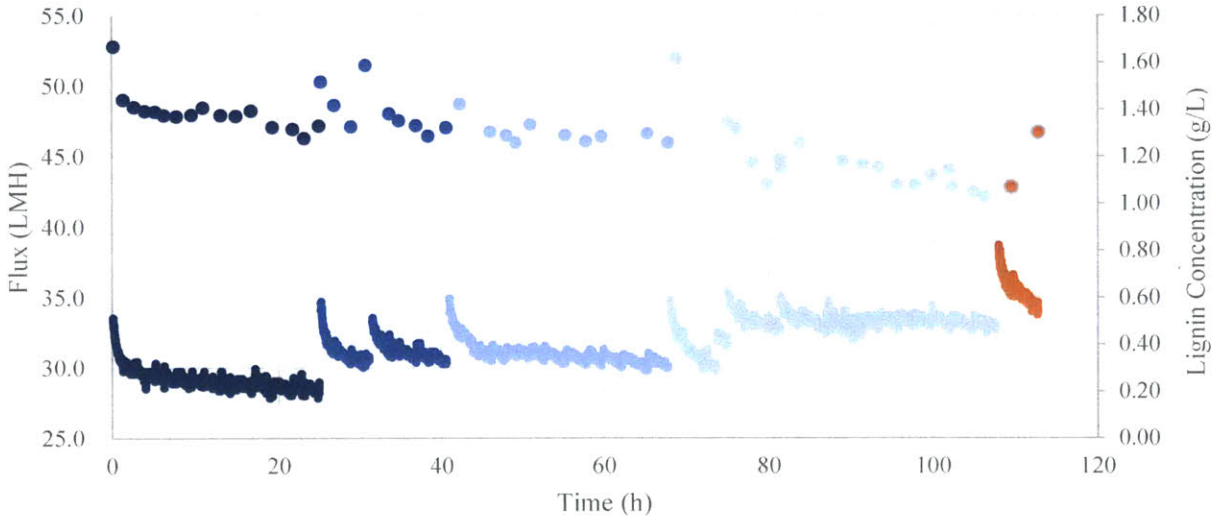

Figure 6-20: The variation of lignin concentration in the permeate stream plotted together with the variation of permeate flux. The flux is plotted on the bottom with more continuous dotted lines with values corresponding to the primary axis on the left, while the lignin concentration is plotted on top with the dotted scatter plot with values corresponding to the secondary axis on the right. The color scheme is the same as the ones in Figure 16 and 19..

Overall, the trend of the lignin rejection ratio within each run bears a strong resemblance to the trend of permeate flux. Across the different runs, the membranes showed a generally increasing capability of lignin rejection that was not reversed by chemical washing, which also indicates that permanent changes to the membranes is likely to have happened, and permanent fouling may have decreased the passage of lignin over the course of the runs.

6.3 Concentrating Feed Mode Run

6.3.1 Flux Decline

The same batch of synthesized black liquor was utilized in the concentrating run of the experiment. Although the lignin content has varied slightly in the batch due to the remixing and permeate sampling processes in the previous constant-composition feed experiments, the variation in composition is generally less than 2%. The current feed composition characteristics is reported in

Table 6-9.

Table 6-9: Synthesized black liquor characteristic for the feed of the concentration run

	Synthesized Black liquor
pH	10.0
Total Solids	3.85%
NaOH (mg/L)	2400
Lignin (mg/L)	37600

Unlike the previous experiment using black liquor of relatively constant composition by continuously remixing the permeate and retentate and adding them back into the feed. In this case, a system mimicking the feed-and-bleed system is established as indicated in Chapter 4, and while the retentate is returned to the feed line, the permeate is not returned, resulting in an increasing feed concentration over time. The concentrating feed experiment continued for approximately 3 hours until the permeate flux was minimal due to the high concentration and high levels of fouling of the membrane. Only 5 kDa membranes are used for this experiment to offer a comparison between the results from the constant composition experiments also run with 5 kDa membranes only. The 5 kDa membrane used in this experiment is a new membrane that has not been fouled by black liquor, different from the 5 kDa membrane that was continuously used in the previous run. The pressure is still constant at the optimum pressure of 207 kPa.

Results from the 3-hour cycle of concentrating feed run is shown in Figure 6-21.

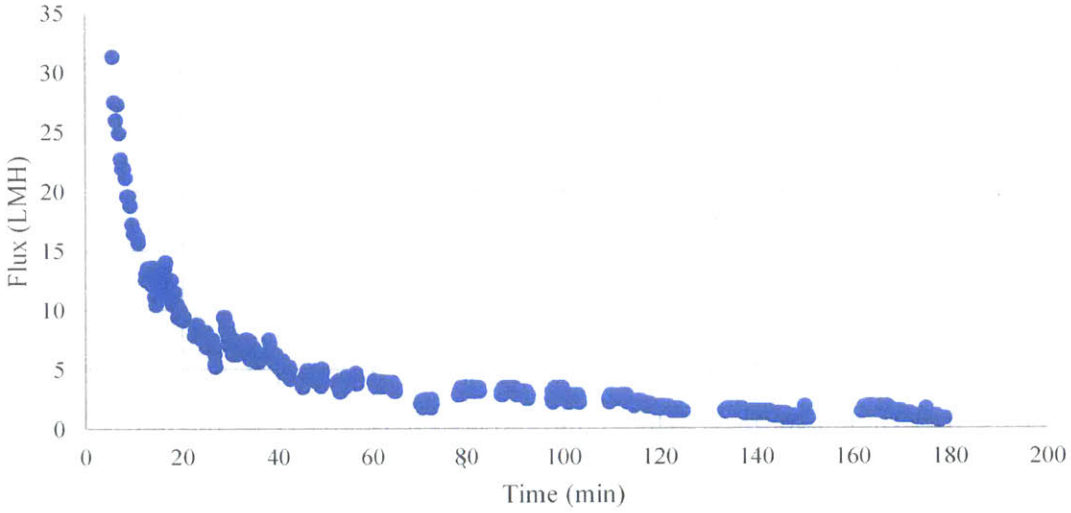

Figure 6-21: Flux decline over the 3-hour concentrating feed mode run for the 5 kDa membrane. The data is not continuous at certain time point due to the time needed to collect permeate samples. The time to collect a sufficiently large sample for lignin analysis became longer as the flux decreased, so the gap between the data increased significantly as the flux declined over time.

As shown in Figure 6-21, a rapid decline in the flux happened within the first hour of the experiment, after which the decline became steadier and less than 5 LMH decline was observed in the last two hours (the flux was less than 5 LMH). The initial flux was around 31.30 LMH, which was at a slightly lower level to the flux in the previous constant-composition feed runs. This is likely because the initial flux in this experiment was recorded after the pressure has stabilized around 207 kPa, which took about 5 minutes after the experiment started. Considering the rapid decline and rapid concentration of the feed at the beginning of the experiment, this initial flux most likely dropped within the 5 minutes when the system TMP was still being adjusted to reach the target constant pressure of 207 kPa. Thus, the flux of 31.30 LMH after 5 minutes into the experiment is considerably lower than the actual initial flux, and would still comparable to the initial flux of 33.3 LMH in Run 1 of the constant-composition feed runs. With the concentration of black liquor increasing significantly towards the end of the experiment, the flux at the end dropped to a minimal level of around 0.83 LMH.

Empirically, the flux decline over time demonstrates a strong exponential pattern as shown below.

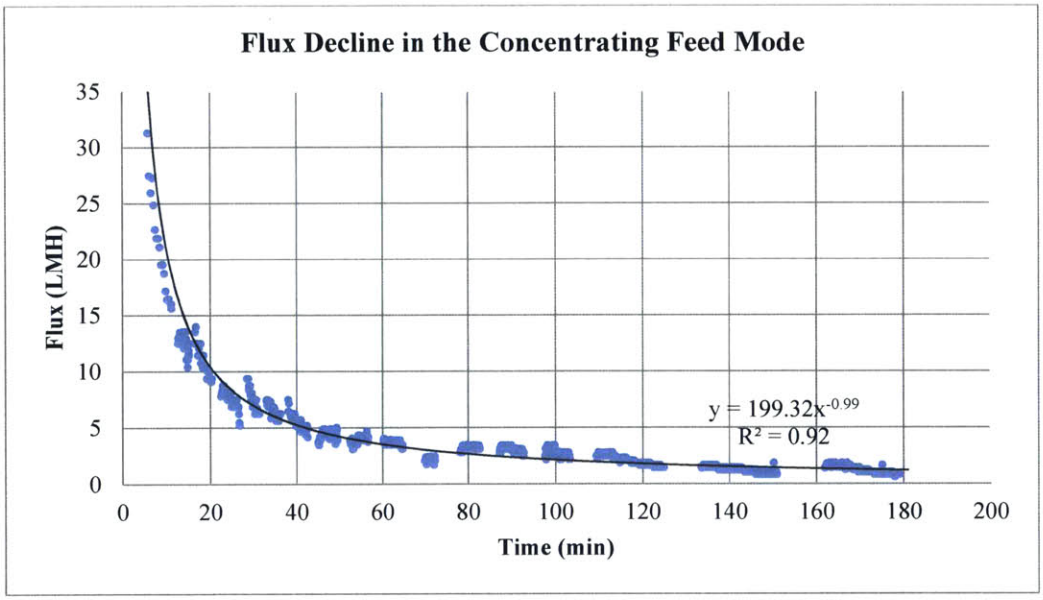

Figure 6-22: Fitted version of the flux decline pattern over the 3-hour concentration feed mode run

The length of the experiment was less than 5 hours, so instead of observing the rate of decline over five hours, the general flux decline pattern can be observed through the first hour of the run and the last hour of the run, as shown in Table 6-10.

Table 6-10: Overview of flux decline patterns for the concentrating feed mode run

		Concentrating Feed Run
Experiment Duration (h)		3
Initial Flux (LMH)		31.3
First 1h	Rate of decline (LMH/h)	28.2
	Percent decline (%/h)	90
Last 1h	Rate of decline (LMH/h)	1.043
	Percent decline (%/h)	55.6
Overall percent decline (%)		97.3

As shown in the table, the rate of flux decline is significantly higher than the constant-composition experiments, with a 90% decline in the first hour and a 97.3% decline over the course of the 3-hour experiment. In comparison, in the first constant-composition feed runs, the flux only declined around 2.39% in the first hour, and the overall decline throughout the 25-hour experiment was 14.4%. The increasing concentration significantly increased the fouling of the membrane, and the flux decline was rapid.

6.3.2 Reversible and Irreversible Fouling

After the concentrating feed experiment, backwash was conducted first, and the black liquor and water flux were measured afterwards to observe the level of flux recoverable through mechanical backwash. Chemical wash was then conducted immediately after, followed by another measurement of black liquor and water flux to observe the level of flux recoverable through chemical wash, as well as the level of irreversible fouling that cannot be recovered.

The trend in initial black liquor flux and water permeability are shown in the figures below.

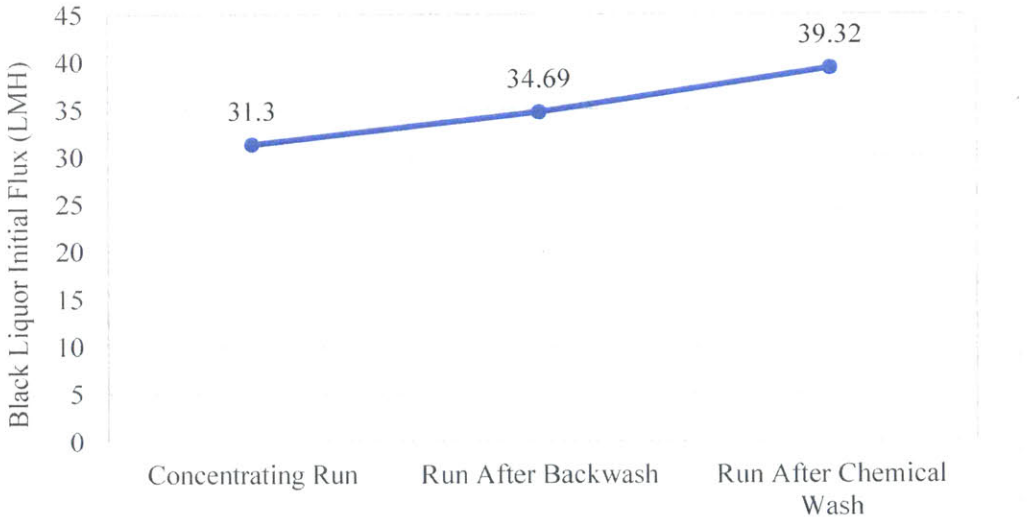

Figure 6-23: Change in the initial flux for each run - during and after the concentration feed run, with different membrane cleaning mechanisms. Note the initial black liquor flux of 31.3 LMH for the

concentrating run may be lower than the actual value, as explained previously.

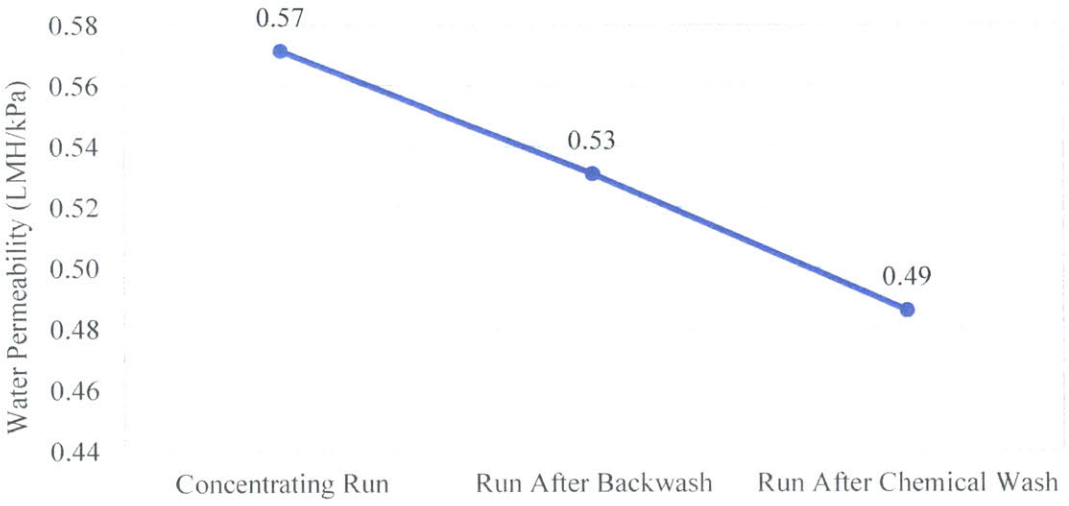

Figure 6-24: Variation of water permeability before each run (before and after the concentration feed run, with different membrane cleaning mechanisms).

Despite the strong fouling at the end of the experiment and the significant decrease in flux, the flux recovery is still very similar to the recovery patterns demonstrated in the constant-composition runs. The initial black liquor flux increased with backwash and increased further with chemical wash, again deviating from our expectation that the black liquor initial flux would decline due to membrane fouling that cannot be recovered through membrane cleaning. The water permeability, on the other hand, still showed levels of decline despite the backwashing and chemical washing. The chemical washing process only recovered 85% of the permeability, less than the permeability recovered by backwash, which is also unexpected.

Although the concentrating feed run has caused the membrane to foul much more heavily due to the increasing concentration of the feed, causing the flux to almost decrease to 0, the flux was surprisingly recovered over 90% only after backwash. Also, it is useful to note that the water permeability was better recovered after the concentrating feed run (with 92.9% recovery) just after backwash, while the water permeability was only recovered 73.7% after the constant-composition feed run. This is likely because the constant-composition run was conducted over a much longer period of time and more irreversible changes have occurred to the membranes. It may be possible to conclude that high-level fouling over a short period of time may not be as detrimental to the membrane as low-level fouling over an extended period of time.

A summary of the flux recovery is show in Table 6-11.

Table 6-11: Black liquor and water permeability variation after backwash and chemical washes. All

recovered permeability ratios are comparing to the initial permeability at the beginning of the experiment.

	Water permeability (LMH/kPa)	Recovered permeability	Black liquor permeability (LMH/kPa)	Recovered permeability
Beginning of run	0.57		0.15	
After backwash	0.53	92.9%	0.17	>100%
After chemical wash	0.49	85.0%	0.19	>100%

Overall, based on results from the concentrating mode filtration process, even though the flux declined significantly during the course of the experiment to almost 2.7% of the initial flux, the flux of black liquor was easily recovered after backwashing processes. Even though flux recovery of more than 100% is not expected, the chemical wash process even increased the initial black liquor permeability to a level that is 126% of the initial black liquor flux at the beginning of the experiment, a result similar to the constant-composition run and remains to be further explained. On the other hand, 92.9% recovery of the water permeability was observed after the backwash. Hence, despite the increasing levels of black liquor permeability, the water permeability still shows that irreversible fouling has occurred to the membrane. This irreversible fouling would not necessarily affect the black liquor flux during the filtration process.

6.3.3 Lignin Rejection and Passage

During the concentrating feed mode test, the lignin concentration in both the retentate and the permeate stream is recorded approximately every 10 minutes, with the interval increasing at the experiment went on due to the decreasing flux rate. The retentate stream, along with the permeate stream, was increasingly becoming more concentrated as the permeate streams are not returned back into the system in the feed-and-bleed experimental setup. Generally, per our conversation with the local paper mill engineers, black liquor that has been roughly concentrated to 20-40% total solids level would greatly help with the evaporation process and greatly enhance the efficiency of the evaporators. With our current total solids level at 3.85%, a 5-fold concentration, or an 80% volume reduction, would increase the level to around 20%. For India black liquor, the total solids level starts out higher initially due to other smaller compositions of inorganic and organic components not accounted for in the synthesized black liquor, so the 5-fold concentration would increase the total solids level to an even higher rate. The 80% volume reduction level is also generally the level recorded in literature for other concentrating feed experiments (Wallberg, Jönsson, and Wimmerstedt 2003a). Consequently, the concentrating experiment was run until the permeate flux was minimal while ensuring that at least a 5-fold increasing in concentration was achieved.

In the end, the change in retentate and permeate concentration is documented in The retentate and permeate stream concentration variation along the run is plotted below in Figure 6-25. Generally, both streams followed a similar pattern where the lignin concentration increased drastically within

the 30 minutes of the experiment, and then the increase rate dropped and there was a much slower and steadier rise afterwards.

Table 6-12 below. The missing retentate concentration was due to an error in the dilution, but due to the limited amount of sample taken to not affect the black liquor concentration in the experiment, there was not sufficient sample left for another accurate dilution. The missing permeate concentration was because at the end the permeate flux was too small to collect a sufficiently large sample for analysis.

The retentate and permeate stream concentration variation along the run is plotted below in Figure 6-25. Generally, both streams followed a similar pattern where the lignin concentration increased drastically within the 30 minutes of the experiment, and then the increase rate dropped and there was a much slower and steadier rise afterwards.

Table 6-12: Variation of lignin concentration in the feed and permeate stream along the course of the concentrating feed mode experiment, and the corresponding rejection ratio and concentrating ratio. The experiment ended around a concentration ratio of 5 and a volume reduction of 80%.

Time (min)	Retentate lignin concentration (g/L)	permeate lignin concentration (g/L)	lignin rejection ratio	lignin passage ratio	concentration ratio	volume reduction
5	51.8	1.1	97.9%	2.1%	1.4	27%
11	66.7	2.1	96.9%	3.1%	1.8	44%
15	102.1	2.4	97.7%	2.3%	2.7	63%
20	127.8	2.7	97.9%	2.1%	3.4	71%
27	143.2	2.9	98.0%	2.0%	3.8	74%
31	162.8	3.0	98.2%	1.8%	4.3	77%
36	160.6	3.0	98.1%	1.9%	4.3	77%
43	160.8	3.4	97.9%	2.1%	4.3	77%
57	172.3	3.2	98.1%	1.9%	4.6	78%
75	185.7	3.6	98.0%	2.0%	4.9	80%
84	-	3.2	-	-	-	-
94	183.9	3.2	98.3%	1.7%	4.9	80%
129	190.9	4.0	97.9%	2.1%	5.1	80%
152	184.9	4.5	97.6%	2.4%	4.9	80%
179	199.2	-	-	-	5.3	81%

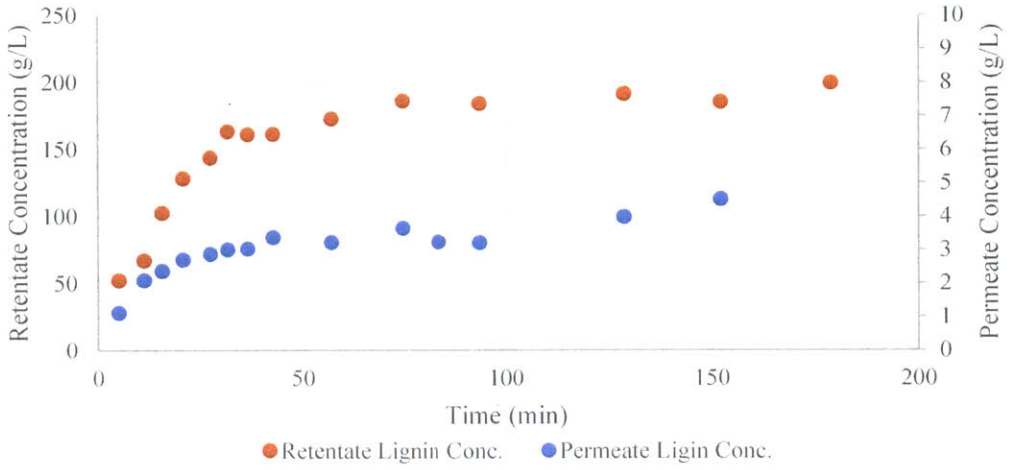

Figure 6-25: The retentate (which directly becomes the feed, so it is the same as the feed concentration) and permeate concentration variation along the course of the concentrating feed mode experiment. The retentate concentration (in orange) is plotted on the primary axis on the left while the permeate concentration (in blue) is on the right.

The retentate concentration ended almost around 200 g/L of black liquor, and the viscosity was very high, as shown in the image in Figure 6-26. It was also expected that lignin may have already started depositing as the concentration rose. Both factors are likely to cause heavy fouling within the membrane, resulting in a dramatically decreasing flux.

Figure 6-26: At the end of the concentrating feed run, the concentrated black liquor was collected from the retentate line (the white tube in the picture) into the beaker below. The concentrated black liquor from the retentate stream can be seen in the beaker. Strong viscosity and thickness of the solution can be observed in the pictures.

While both the retentate solution and the permeate concentration increased, the lignin passage ratio, as shown in Figure 6-27, exhibited a slight decrease at the beginning of the experiment. This is expected because the lignin passage is likely to drop as the fouling increased significantly.

However, after around 30 minutes into the experiment, the lignin passage ratio became relatively steady with some slight fluctuations, indicating that the increasing fouling of the membrane after that did not strongly affect the membrane's rejection function after that. There is also a slight increase in the passage ratio at the end of the experiment, but the data was relatively sparse due to the limited permeate samples amount as the flux decreased, so the pattern is unclear and it may also have been an erratic data point at the end of the experiment.

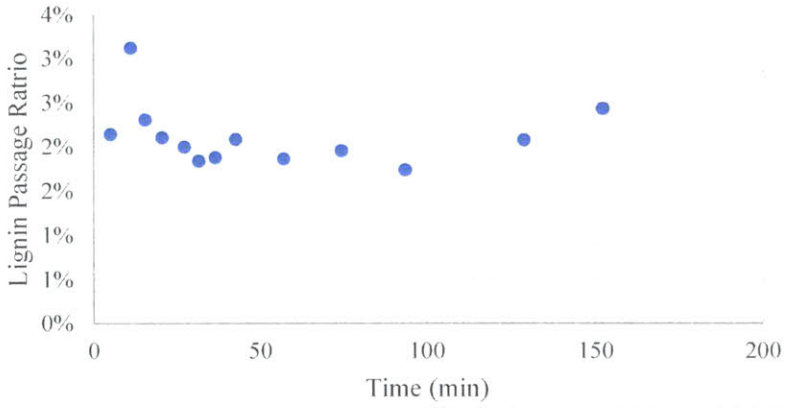

Figure 6-27: Lignin passage ratio variation over the course of the concentrating feed mode experiment

To better understand the concentrating feed mode process, and utilize this to predict the average flux in the process of concentrating black liquor to the desired concentration for further processing, it is also useful to understand how flux relates to the concentration ratio. Flux was plotted against both volume reduction ratio and feed lignin concentration in

Figure 6-28 and Figure 6-29 to observe the trend of flux variation as black liquor feed becomes concentrated.

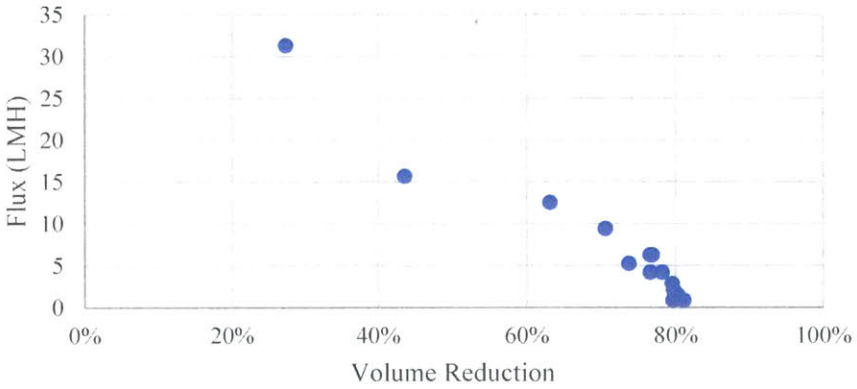

Figure 6-28: Flux vs. volume reduction ratio over the course of the concentrating feed experiment.

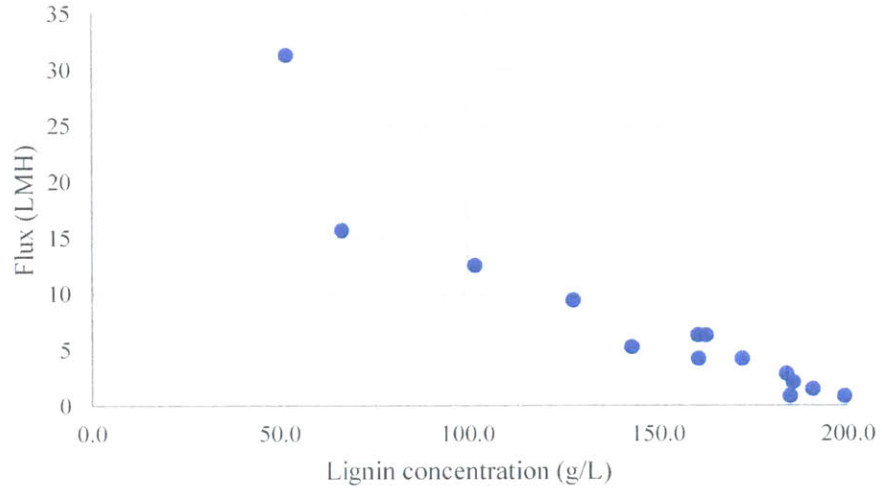

Figure 6-29: Flux vs. feed lignin concentration over the course of the concentrating feed experiment.

In both figures, the downward slopping trend is relatively clear. Apart from the second point that slightly deviates from the general trend of the curvature, the flux vs. volume plot shows a slightly concave function while the flux vs. feed plot shows a generally linear function. It's again important to note that while the flux decreased to almost 0 when the lignin concentration increased 5-fold to around 200 g/L, the flux was quite effectively recovered to more than 90% of the orginal flux after only backwashing, as shown in Section 6.3.2.

Because of the quickly rising feed concentration at the beginning of the experiment, the lignin concentration data collected over relatively fixed intervals were more centered at the higher feed concentrations, and there were too few data at the lower end of to make out a discernable pattern, or to analyze whether the second data point is an outlier. However, with the existing pattern, we can still reasonably predict the resulting flux pattern if we are interested in concentrating black liquor to a certain level of concentration, and this information can be highly effective in predicting the amount of black liquor that can be processed daily per unit membrane area, and eventually help determine the cost effectiveness of the membrane filtration system for concentrating black liquor.

6.4 Summary

The following summary can be made of the results from the synthesized black liquor experiments:

- According to the flux-pressure tests, the optimal operating cross-flow velocity is 1.06 m/s or higher for all the membranes, and the optimal operating transmembrane pressure is 172 – 207 kPa for the 10 kDa membrane, and 207 kPa or higher for the 3 and 5 kDa membranes.
- According to the constant-composition constant-pressure runs, there is always a significant flux decline around the first 5 hours into the experiment, with an average decline between 2.39% - 2.56% per hour. The decline slows down as the experiment goes on, ending at a decline rate

of around 0.13 - 0.38% per hour. However, the flux across the different runs did not show a sign of decline.

- The lignin passage ratio was around 2-4%, and it declined over the course of each constant-composition runs, as well as across the different runs.
- The concentrating feed mode run was able to concentrate the black liquor to as high as 200 g/L. The permeate lignin concentration increased proportionally, maintaining a relatively stable rejection ratio. The flux declined from 34 LMH to less than 1 LMH over the 3 hours of the run. Over 90% of the water permeability and 100% of the black liquor flux was quite effectively recovered after only backwash, which is more than the flux recovery of constant-composition runs. This suggests that heavy fouling over short periods of time may create less irreversible change than light fouling over long periods of time.
- Overall, the water permeability change of the membrane indicates irreversible fouling of the membrane, declining to only around 74% of the initial flux after the four 24 h constant-composition runs and around 85% after the 3 h concentrating feed run.. However, the initial flux of black liquor was not affected and showed no sign of irreversible decline.

7 Discussion

This chapter discusses results produced from both fresh Indian black liquor and synthesized black liquor to conclude on general optimal operating parameters (including pressure, cross-flow velocity and membrane pore-size), as well as filtration results (including flux, membrane change and lignin concentration) for treating black liquor from small-scale paper mills. Following the overview in Section 7.1, optimal parameters are discussed and compared with literature results in Section 7.2 while filtration results are discussed and compared in Section 7.3. The implications of these results on cost and benefit of the membrane treatment system are also discussed and summarized in Section 7.4.

7.1 Overview

As suggested in Chapter 4, the results produced both in India with fresh black liquor and in the U.S. lab with synthesized black liquor can help realistically determine:

- Optimal operating parameters: transmembrane pressure, cross-flow velocity, membrane pore size
- Experimental results: flux rate, long-term reversible and irreversible changes of membrane function, and effectiveness in concentrating lignin.

We are focusing on these variables to estimate the cost and benefit the system. Cost of black liquor membrane treatment have been studied in literature and the traditional categories of cost factors including capital cost, operating power cost and membrane cleaning and replacement costs have been estimated through general cost assumptions (such as electricity cost, membrane module cost and so on) as well as experimental information (Jönsson and Wallberg 2009). Experimental results including cross-flow velocity, transmembrane pressure, flux rate, frictional pressure drop and lignin concentration were feed into the calculation of total cost (Jönsson and Wallberg 2009).

Consequently, parameters and results obtained through our studies are analyzed and compared to literature results on the same key variables used in cost estimates, to eventually determine the viability of the membrane treatment system.

We focus on literature results by Wallberg et al. because they have done a reasonable cost-benefit estimate that indicated a potentially profitable model for their membrane processes. Based on the analysis and comparisons, it can be then determined whether membrane systems are viable solutions for the treatment of fresh black liquor in India, and under what conditions.

7.2 Optimal Operating Parameters

7.2.1 Transmembrane Pressure

The optimal operating transmembrane pressure for processing fresh black liquor in India was successfully found through the flux-pressure tests, and is generally below 207 kPa. However, in India, due to the limit of time, the experiments were only conducted at a relatively low cross-flow velocity of 0.39 m/s. In comparison to results from fresh Indian black liquor, results from synthesized black liquor generally showed a higher optimal pressure at the same cross-flow velocity. Results from synthesized black liquor also showed a trend of increasing optimum pressure as the cross-flow velocity increased, as shown in Figure 6-5 and Figure 6-6. The optimal pressure for the three differently sized membranes at the highest cross-flow velocity for the

synthesized black liquor is usually beyond 207 kPa. This suggests that in India, even with high-fouling fresh black liquor, the optimum operating pressure at a higher cross-flow velocity would approach or even extend beyond 207 kPa. It is also likely that the fouling of the membrane over time may have affected the accuracy of the optimal pressure estimate, especially for the flux-pressure tests at lower cross-flow velocities. It may remain to be explored whether the fouling at higher pressure is caused only due to the raised pressure, or also due to fouling over time. At higher cross-flow velocities, however, the flux-pressure curve is still linear toward the end of the 1-hour experiment, suggesting minimal effects of fouling over time.

This pressure range is reasonable compared to the studies of Wallberg et al., where the pressure generally ranges from 69 – 414 kPa, but much lower than the pressure ranges of studies from Arkell et al. where the pressure went up as high as 4000 kPa (Wallberg, Jönsson, and Wimmerstedt 2003b; Wallberg and Jönsson 2006; Arkell, Olsson, and Wallberg 2014). This could be because that the experiments by Wallberg et al. generally utilized ceramic membranes with the lower pressure range because it is less prone to fouling, and could produce high flux despite the lower pressures. However, with the synthesized black liquor and hollow fiber mPES membranes, a reasonable flux around 30 LMH (comparable to that of ceramic membranes) was already achieved around 207 kPa of transmembrane pressure.

For synthesized black liquor, if the hollow fibers membranes allowed for a higher pressure cap above 207 kPa, the system can then be operated at the optimum pressure (which according to Figure 6-5, is likely above 280 kPa) instead of the maximum allowed pressure of 207 kPa. However, the pressure around 207 kPa is still relatively reasonable. For fresh Indian black liquor, the optimum pressure was all reached below 207 kPa, so it would not be realist to increase the operating pressure because the flux generally plateaus after the optimum pressure due to formation of a heavy fouling layer. To increase the optimum pressure and achieve higher flux, fouling should first be minimized through higher cross-flow velocity or more pre-filtration.

7.2.2 Cross-flow Velocity

As mentioned in the previous section, cross flow velocity was set at 0.39 m/s for fresh Indian black liquor filtration, while set at three different levels of 0.39 m/s, 0.71 m/s and 1.06 m/s for synthesized black liquor filtration. Increasing cross-flow velocity decreases the level of fouling, and generally increases the optimum pressure for the filtration process as again evidenced by Figure 6-5 and Figure 6-6. The flux-pressure slopes for the three different membranes were all still relatively linear up to 1.06 m/s of cross-flow velocity, suggesting that the optimum operating cross-flow velocity is likely higher than 1.06 m/s. Again due to the limit of the pump, the cross-flow velocity only goes up to 1.13 m/s, so the optimum cross-flow velocity was not reached.

This conclusion is similar to results from Arkell et al. (2014), where the ideal range of cross-flow velocity was between 2 - 4 m/s, slightly higher than the operating cross-flow velocity in the synthesized black liquor experiment. The ideal cross-flow velocity range may also be within the 2 - 4 m/s range. Nevertheless, due to limit of the maximum operating pressure of the membrane,

even with a higher cross-flow velocity and increased optimum transmembrane pressure, the operating pressure still could not exceed 207 kPa.

For the synthesized black liquor experiments, the 10 kDa membranes, which has an optimum pressure below 207 kPa at 1.06 m/s, can benefit from an increased cross-flow velocity, while the benefit for the 3 and 5 kDa membranes may be limited because their optimum pressure already exceeded the maximum allowed pressure. For the fresh Indian black liquor experiments, all optimal pressures at 0.39 m/s cross-flow velocity were below the maximum pressure, so experiments conducted at higher cross-flow velocities would have been helpful in raising the optimum pressure while keeping the fouling at a minimum and effectively raising the flux rate. The flux rate range in the India black liquor experiment was generally low at only around 10 – 15 LMH, and the situation may have been significantly improved if higher cross-flow velocity tests were also carried out. The ability to carry out tests above 1.13 m/s may also be helpful, because considering the more serious fouling with fresh black liquor, it is likely that more shear is needed to allow for an optimum operating pressure of around 207 kPa. However, because no tests were done above 0.39 m/s, it remains unclear what the ideal cross-flow velocity would be.

Overall, with the limit of the experimental system, the cross-flow velocity of 1.06 m/s was the most ideal in the experiment with synthesized black liquor. Higher cross-flow velocity capacity is likely to enhance the performance of the system, especially if the maximum operating pressure of the membranes can also be increased as well. The ideal cross-flow velocity for the experiment with fresh Indian black liquor is higher than 0.39 m/s, and operating the system at higher cross-flow velocities would have improved the performance of the filtration process.

7.2.3 Membrane Pore Size

3, 5 and 10 kDa membranes were used in both the fresh Indian black liquor experiments and synthesized black liquor experiments. The range was selected according to the literature where the membranes process black liquor are generally within the 1 - 60 kDa range (Arkell, Olsson, and Wallberg 2014; Liu et al. 2004).

It is generally expected that the lignin rejection ratio will be higher for membranes with lower MWCO, which would be ideal in producing cleaner permeate streams while increasing the concentration in the retentate stream, likely speeding up the black liquor concentration process. On the other hand, lower MWCO is likely to result in stronger fouling, which would result in a comparatively lower flux rate, as shown by the flux rate of different membranes in Figure 2-6 and Figure 2-7. A lower flux rate would slow down the filtration process, and to process the same amount of black liquor, more membranes have utilized, which would increase the system cost. Thus, selecting the right size of the membrane is highly dependent on the balancing of these two factors.

Overall, lignin rejection ratio has been shown to increase with smaller pore sizes in the fresh Indian black liquor experiments. In fact, lignin passage showed a strong linear correlated with membrane

MWCO in Figure 5-9, but the sample size is too limited to confirm any substantial correlation. Experiments with synthesized black liquor, however, showed a higher rejection ratio with 5 kDa membrane in comparison 3 kDa membranes, but with another 5 kDa membrane, the rejection ratio was lower than 3 kDa membranes as expected. The first 5 kDa membrane has been utilized to filter black liquor briefly in other experiments before, which may have caused pre-existant fouling and increased the rejection ratio. As for the flux rate, 10 kDa membranes generated a higher permeate flux in comparison to 3 kDa and 5 kDa membranes under the same transmembrane pressure, but the flux for 3 kDa membranes was overall higher than 5 kDa membranes with both types of black liquor. This might have been because the 5 kDa membranes, while allowing more lignin to pass through the membrane, also became more fouled in the process. This result is also reasonable because while a number literature showed increasing flux with increasing MWCO, Liu et al. also showed no correlation between flux and pore size when processing black liquor (Liu et al. 2004).

With the fresh Indian black liquor experiments, the same set of experiments were repeated on all three membranes. With the synthesized black liquor, due to the length of the continuous experiments, only one type of membrane had to be selected. 5 kDa membranes were selected as a compromised between higher flux and higher rejection ratio of lignin. However, as the results suggest, 3 kDa membranes sometimes have an even higher flux. 3 kDa membranes may have also been a reasonable choice for comparison if time allowed. In general, membrane pore size is a secondary determinant factor in estimating the cost of the membrane treatment system, so working with only one type of membrane initially would still be effective in giving a generation cost-benefit estimate. However, membrane pore size still relates directly to the flux level and the rate of lignin concentration, and if more varieties of pore sizes could be tested, it would help with finding the optimal pore size in treating black liquor.

7.3 Experimental Results

7.3.1 Flux

Generally, the flux is shown to effectively increase with pressure up until the optimum pressure indicated in the flux-pressure tests. Holding the pressure constant below the optimum pressure, the flux also increases linearly with increasing cross-flow velocity, and it is linear at least up to 1.06 m/s. However, unlike the flux-pressure linear fits, this linear fit does not start at the origin as shown in Figure 6-4, Figure 6-6, and Figure 6-8, suggesting that the curve may no longer be linear at very cross-flow velocities, potentially due to a very rapid decline in flux when the cross-flow velocity decreases below a certain point. On the other hand, the flux pattern with membrane pore sizes are not as clear. Even though it is expected that 10 kDa membranes would generate a higher flux than 3 and 5 kDa membranes, it was shown to have the lowest flux rate with fresh Indian black liquor. This is also likely because the 10 kDa membrane has already been utilized previously to process

black liquor, and even though it was only for a short period of time and was thoroughly washed afterwards, there is still likely to have been permanent effects on the membrane flux. Hence, the results may not have been exactly comparable. On the other hand, with synthesized black liquor, 3 kDa membranes also showed a slightly higher level of flux in comparison to 5 kDa membranes, as explained in section 7.2.3. From the results, it seems that generally membrane pore sizes are generally not as well correlated to flux as pressure and cross-flow velocity, which is also reflected in some literature when little correlation has been discovered between flux and membrane pore sizes (Liu et al. 2004). Overall, with the existing patterns discovered through the current sets of experiments, it would be possible to estimate the flux of black liquor when filtering with 3, 5 or 10 kDa mPES hollow fiber membranes, given a reasonable transmembrane pressure and cross-flow velocity.

With the optimum operating parameters, the flux for the fresh Indian black liquor experiments are around 10 – 15 LMH, while the results for the synthesized black liquor under the same conditions are as high as 30 – 40 LMH, almost three times as high. This indicates a much stronger level of fouling with the fresh black liquor. While the lignin concentration is generally the same between the fresh and synthesized black liquor, the total solids level of fresh black liquor is more than twice the solids level of synthesized black liquor. As suggested in Chapter 3, a number of other compositions are in the fresh black liquor apart from sodium hydroxide and lignin, such as inorganic components including sodium sulfide and organic components including hemicellulose. In theory the inorganic components are sufficiently small so that they are not filtered by ultrafiltration-range membranes, and should not have significant effects on the flux. The additional organic components should be relatively small in comparison to the concentration of lignin. However, these organic components, even though in small components, may have affected the viscosity of black liquor, which may potentially have a large impact on fouling. In addition, significant precipitation of lignin and other solids from the fresh black liquor was observed according to Figure 3-11 and Figure 3-12. Lignin is likely very saturated in fresh black liquor, especially considering the higher total solids content. Hence, it may be likely that lignin could precipitate onto the membrane over the course of the experiment due to changing pressures and temperatures in the experimental environment. Lignin and other solids may also precipitate in the feed tank, and remixing could stir up the precipitated lignin, raising the level of suspended solids in the feed solution. As a result, the increasing levels of precipitated lignin and other solids in the membrane module system can significantly impact its operation, and heavily foul the membrane. On the other hand, with the synthesized black liquor, lignin was very well dissolved into the solution through extensive magnetic stirring. The black liquor solution has also sat still for a period of time for sedimentation, and then separated from any precipitation of lignin to ensure minimal suspension of solids during the course of the experiments. With a much lower total solids level, lignin is also likely to have been better dissolved in the synthesized black liquor, so little precipitation is expected during the course of the experiment. These factors combined together can result in a much more fouled membrane for fresh black liquor in comparison to synthesized black liquor. While the synthesized black liquor is a close attempt at mimicking field results through

simplifying the black liquor composition to only focus on the key components, the addition of some other fresh black liquor components may greatly enhance the capability of the synthesized black liquor to simulate fresh Indian black liquor results.

With the synthesized black liquor results, we have seen an increase of the flux at the same transmembrane pressure with increasing cross-flow velocity. More specially, when increasing the cross-flow velocity from 0.39 m/s (the only cross-flow velocity utilized in India) to 1.06 m/s, the flux for synthesized black liquor increased approximately 14% for the 3 kDa membranes, 22% for the 5 kDa membranes and 34% for the 10 kDa membranes for the same transmembrane pressure (at or below the optimum operating pressure). Assuming that these rates also hold for the fresh Indian black liquor, the flux would go up to around 17, 18 and 15 LMH, when operating at optimum pressure and 1.06 m/s cross-flow velocity with 10, 5 and 3 kDa membranes respectively. In literature results, while the flux frequently rises up to as high as 100 – 200 LHM for treating black liquor, that is generally with membranes with large pore sizes (sometimes even going into the microfiltration range) at higher pressures and sometimes with black liquor of higher temperatures. If we only compare with membranes of similar pore sizes and systems operated at a comparable pressure and cross-flow velocity, Liu et al. (2004) recorded a flux of around 20-30 LMH with 6 kDa membranes operating at 207 kPa and 2.3 m/s (as shown in Figure 2-8), while Wallberg and Jonsson (2005) obtained a flux of around 25 LHM with 5 kDa membranes operating at 207 kPa and 4.2 m/s. These flux results are very comparable to the flux results that we have obtained with both the fresh black liquor and synthesized black liquor. Despite the fact that the fresh Indian black liquor flux results are still below 20 LMH and on the lower end of the results in comparison to literature records, this is reasonable considering that there is generally a much higher cross-flow velocity in literature.

All of the results discussed above are for constant-composition runs. While constant-composition results are a good way to estimate the characteristics of the membranes in the filtration process, to actually simulate the process of concentrating the black liquor to an ideal level of total solids for further processing, a concentrating feed mode experiment is needed. The concentrating mode feed test was only conducted with synthesized black liquor. The flux decline vs. volume reduction results are generally comparable to literature results as shown in Figure 7-1. The flux decline vs. feed lignin concentration results were also in a relatively linear pattern, identical to results by Wallberg et al. (2005), as suggested in Figure 7-2. Apart from the second point in the series, which seems relatively low in comparison to the general trend, the overall patterns generally aligned. More data collected in the earlier section of the experiment would have helped clarify if the point was an outlier or showing a different trend altogether. However, concentration process was already fairly quick, and the data was taken only 5 minutes apart, and more frequently data may interfere with the flux results as well. A better setup to collect permeate samples more frequently without interfering flux measurements on the permeate scale, or a slightly slower process of concentration where the permeate stream may be slowly and partially returned to the system, are all potential solutions to better resolution of data during the earlier section of the experiment.

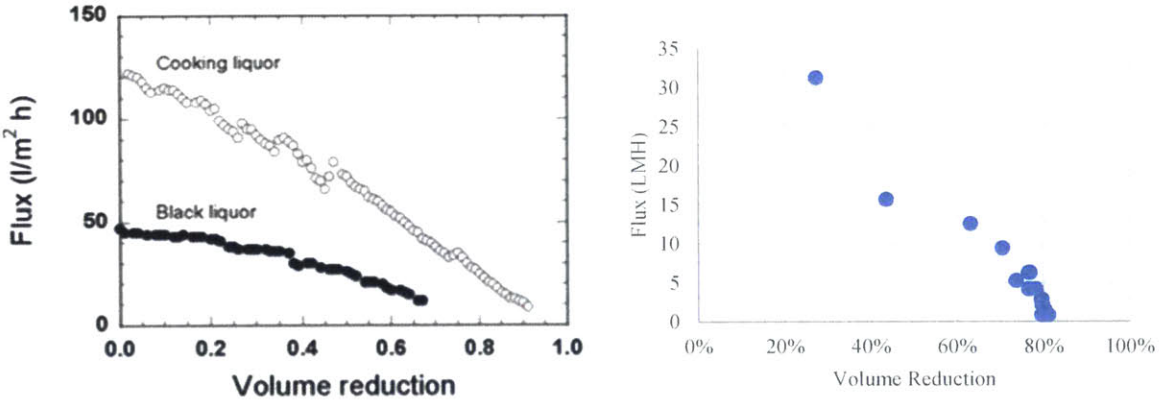

Figure 7-1: Comparable results for flux variation across increasing volume reduction (Jönsson and Wallberg 2009).

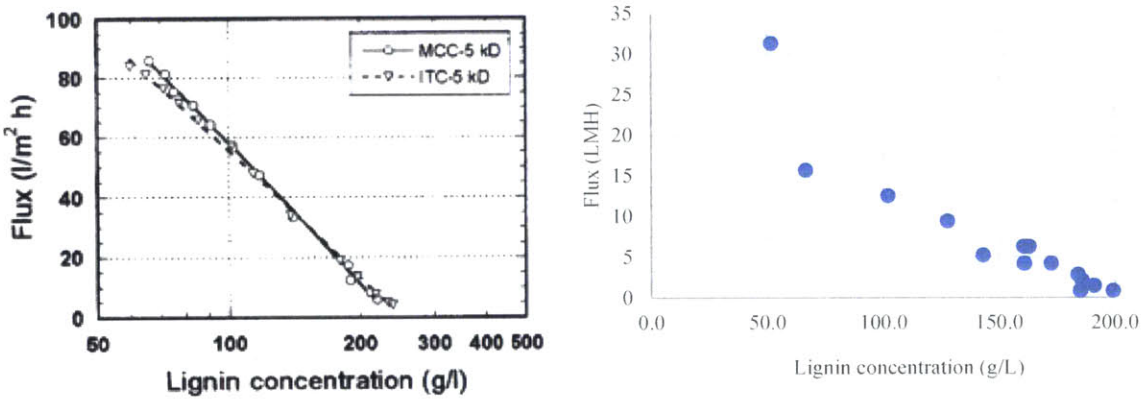

Figure 7-2: Comparable results for flux variation across increasing feed lignin concentration (Wallberg, Holmqvist, and Jönsson 2005).

In the literature results, the flux is generally much higher than our initial flux around 30 – 40 LMH. Again, this is due to the variation in operating parameters – for example, in Figure 7-1, the literature results are for 15 kDa membranes and in Figure 7-2, the system described in the literature was operated at around 414 kPa (Jönsson and Wallberg 2009; Wallberg, Holmqvist, and Jönsson 2005).

When conducting cost estimates, the average flux over a certain volume reduction is generally used, and it is usually considered more realistic. For example, the average flux of concentrating black liquor in the process as shown in Figure 1 to a volume reduction ratio of 0.66 is 33 LMH. This is calculated through fitting the flux-volume reduction results through a polynomial equation (Wallberg and Jönsson 2003):

$$J = a + b * VR + c * VR^2 + d * VR^3 \quad (1)$$

where J is the flux, VR is the volume reduction and a,b,c,d are the polynomial coefficients for the fit.

The average flux is then calculated through integrating the equation as shown in Equation 2 below

(Wallberg and Jönsson 2003):

$$J_{av} = \frac{\int_0^{VR} J\, dVR}{VR} = a + \left(\frac{b}{2} * VR\right) + \left(\frac{c}{3} * VR^2\right) + \left(\frac{d}{4} * VR^3\right) \quad (2)$$

where J_{av} is the average flux between volume reduction from 0 up to VR.

Because our first flux data point was already at a volume reduction of 27%, to obtain a better polynomial fit, the initial flux with no volume reduction is estimated to be 33.31 LMH, which is the initial flux from the continuous-composition runs operating under the exact same conditions with 5 kDa membranes. With this initial point, the polynomial fit is shown as below in Figure 7-3, and the average flux between 0 and 80% volume reduction is around 21 LMH. This is a reasonable value, considering that 15 kDa membranes in left figure in Figure 7-1 had an average flux of 33 LMH.

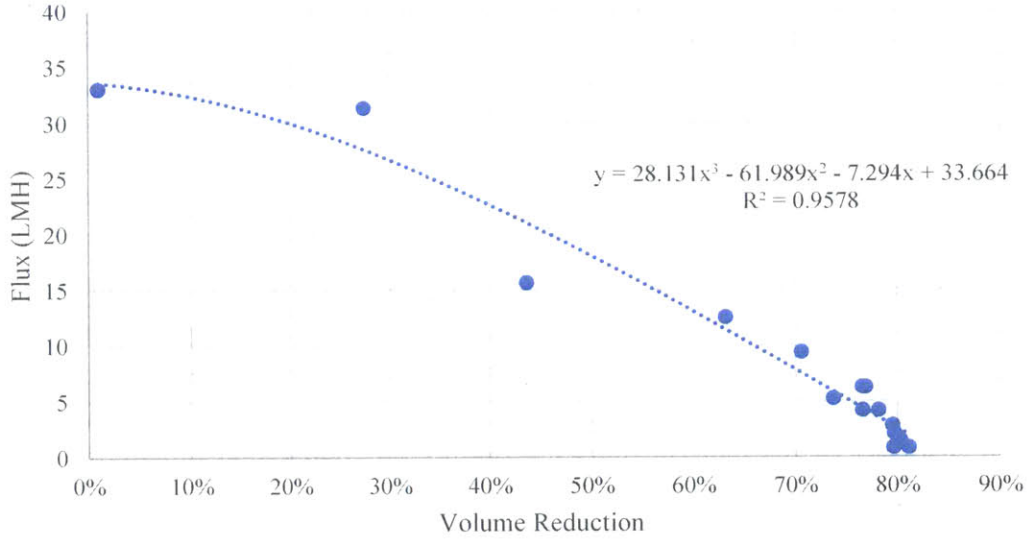

Figure 7-3: Flux variation across volume reduction (with polynomial fit) for the concentrating feed run.

Of course, it would be much more useful to conduct the concentrating experiment with fresh Indian black liquor. With the more intensive fouling, it is expected that the flux may decrease more rapidly with increasing concentration, and the average flux may be much lower. As shown in the previous, the flux results from India black liquor may be as low as 1/3 of the flux results from synthesized black liquor under the same operating conditions. Consequently, the average flux rate for fresh black liquor may be as low as 7 LMH, but the rate is likely to rise if the fresh black liquor can be better pre-treated with effective sedimentation or filtration.

Overall, permeate flux rate for processing continuous constant-composition fresh Indian black liquor (at optimal pressure of around 207 kPa and cross-flow velocity of around 1 m/s) is likely to be in the range of 15 – 18 LMH for membranes with MWCO of 3, 5 and 10 kDa. For concentrating black liquor up to 5 times the original concentration, the average flux for synthesized black liquor

is around 21 LMH and the results for fresh black liquor is likely to be much lower. These results are comparable to the flux rates in literature, but generally on the lower end. The average flux rate result is directly related the required membrane area to process all produced black liquor, and in turn the capital cost of the system. Even though the black liquor is generally much lower in concentration in our case, the flux results in our experiment did not show a drastic advantage over black liquor flux results in the literature. It would not be a significant drawback either, because the results are generally in the same range as literature results, although experimental results from India is frequently on the lower end of the spectrum. As we suggested above, the reason that fresh black liquor is fouled more along the membranes could potentially be the precipitation and re-suspension of solids and lignin in the process, which would be resolved by longer sedimentation for the black liquor as well as better pre-filtration. More experiments to explore the effects of better pre-filtration and better sedimentation of black liquor would be useful in exploring optimal pre-treatment setups to enhance the flux. More results on the concentrating feed mode process for fresh Indian black liquor would also help to more realistically assess the membrane area required and the capital cost. All in all, based on the current experimental results, flux level is at a moderate rate and the the capital cost should be similar to or slightly higher than Jönsson and Wallberg's results, which as discussed by Jönsson and Wallberg, should be reasonably affordable considering the potential benefits (Jönsson and Wallberg 2009).

7.3.2 Changes in Membrane Function

The reversible and irreversible changes to the membrane is also crucial in determining the cost-effectiveness of the system, because they directly relate to the frequency required for cleaning and replacing membranes. When we communicated with local industries, fouling and the need for frequent cleaning of membranes is also one of the key concerns of implementing membrane solutions. It is also one of the gaps in literature due to the challenging process of running the experiment for a sufficiently long procedure and repeated cycles to observe the patterns of reversible and irreversible changes.

First, it is useful to learn about how frequently membranes are required to be cleaned through the continuous feed experiments. While continuous concentrating feed cycles are ideal for a more realistic estimate of fouling through the filtration process, the system would require constant monitoring and feed replacement to ensure a continuous run, which is not realistic with the current setup. Instead, continuous constant-composition runs are carried out to given an estimate of the fouling rate, because with constant-composition runs, while the remix of the permeate and concentration still needs to happen every 2 hours, it still requires much less monitoring and would allow continuous cycles up to 24 hours. The constant-composition runs are carried out with the understanding that the results would overall be an underestimate of the level of fouling because realistically the concentration of black liquor would increase over the course of each concentrating cycle, and it is more likely to induce fouling than black liquor of constant composition.,

From the constant-composition run results with synthesized black liquor, while the initial decline

is rapid, the decline after around 5 hours becomes significantly slower. Hence, we focus on the rate of decline at the last 5 hours instead to predict the future declines. Among the 4 separate runs, run 1 and run 3 had fewer issues during the operation process and hence showed the more typical patterns - run 2 paused and restarted in the middle, so the second segment of run was actually only around 9 hours, which is why the rate of decline in the last five hours of the experiment was significantly higher than the other 3 runs, and run 4 had many pauses and restarts, and had a curious rising flux after the first pause in the experiment so its patterns may also be atypical. Between run 1 and run 3, run 1 was carried with a pristine membrane that has not been used before, so the results from run 3 may be a more realistic estimate of flux decline and the frequency of membrane cleaning. As shown in Figure 7-4: Flux decline rate of the last 5-6 hours of synthesized black liquor continuous-composition Run 3, if we conduct a linear fit to the last five hours of the experiment, we can see that the decline rate is approximately 0.0475 LMH/h, as also indicated in Table 6-5.

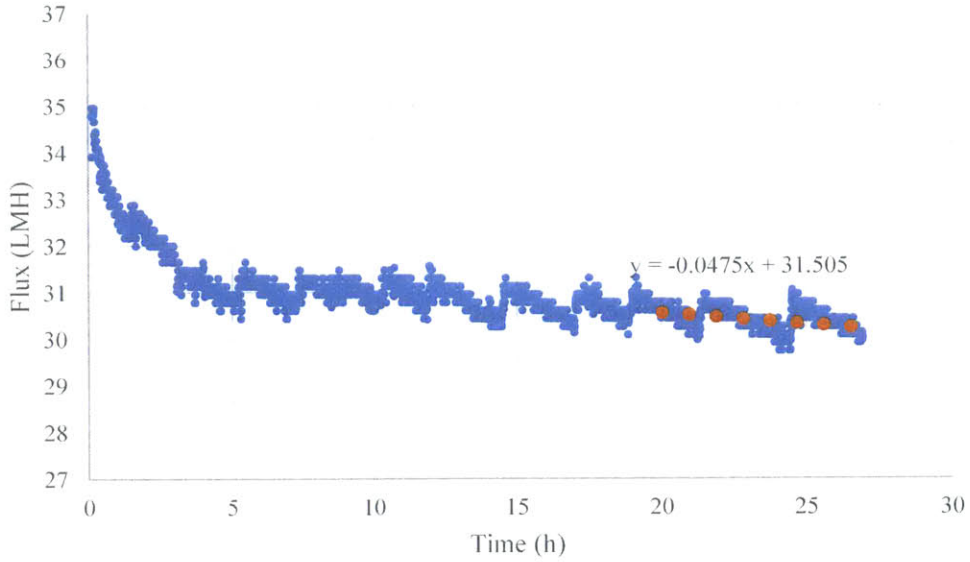

Figure 7-4: Flux decline rate of the last 5-6 hours of synthesized black liquor continuous-composition Run 3

With this flux decline rate, and the end flux rate of 30 LMH or Run 3 at 27 hours into the experiment, we can effectively predict that it would take approximately another 80 hours before the flux declines to 25% of the initial flux of 34.8 LMH, totally around 107 hours to achieve 25% decline. If we consider backwashing when achieving 40% flux decline, then it would be approximately 216 hours, or 9 days before backwash is needed. As we suggested before, the fouling rate is likely underestimated because the increasing feed concentration is not accounted for, so the actual interval required for backwash cleaning would be shorter. Also, the flux decline rate may vary as the filtration process goes on, which would also affect the estimate. In comparison, Liu et al. observed a decline of 25% in flux after 374 hours of black liquor filtration operation. The longer interval is expected because they were using 0.2 μm microfiltration inorganic membranes, which has less fouling due to the characteristic of ceramic membranes and the larger pore sizes. Overall, the literature results match our estimates based on synthesized black liquor.

With fresh Indian black liquor, the estimates would be less accurate because the experiment length is much shorter. As demonstrated through experiments with synthesized black liquor, the decline of the flux is generally more rapid at the beginning of the experiments and slows down as the experiment goes on, so the decline at the first 90 minutes of the experiment (length of the constant-composition runs in India) may not be a good predictor of future flux trend. As shown in Table 6-3, the rate of decline over the 1.5-hour experiment is 1.4 LMH/h for the 5 kDa membranes, which is almost twice as high as the rate of decline of around 0.8 LMH/h observed in the first five hours of the synthesized black liquor experiments. For 5 kDa membranes, while the flux declined around 14% over the course of 25-hour runs for synthesized black liquor, the flux already declined 9.4% within the first hour for fresh Indian black liquor run. Even though we expect the trend to slow down, the flux decline trend over the 1.5 hours has not yet showed such signs. As show in Figure 7-5, following the general decline trend (0.015 LMH/min or 0.89 LMH/h) of the flux, a 25% decline happens around 4 hours into the experiment, while a 40% decline happens around 6.5 hours. This indicates a required frequency of backwashing of 3-4 times a day, which is much more frequent than the several-day intervals estimated by synthesized black liquor. However, this is likely an over-estimation because the decrease is slowing down at the tail end of the flux-time curve and the decrease rate may drop as the experiment continues. On the other hand, as suggested above, this frequency may also be an under-estimation because the concentration of black liquor was not taken into account. In general, the estimated frequency of cleaning required for fresh Indian black liquor, likely up to several times a day, is much higher than the values estimated by synthesized black liquor. The membranes are generally cleaned once a day for around an hour according to Jönsson and Wallberg's cost calculations, so this frequency of several times a day may pose a significant maintenance cost (Jönsson and Wallberg 2009).

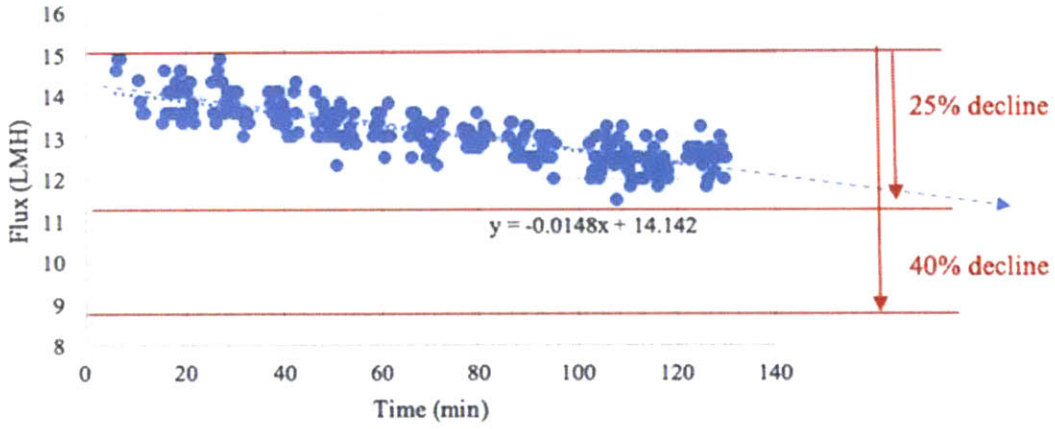

Figure 7-5: Flux decline rate over the fresh Indian black liquor run with 5 kDa membrane, and the projected time for 25% and 40% decline.

Apart from the frequency required for backwash, it would also be useful to understand the frequency required for chemical cleaning when backwashing is no longer sufficient. Chemical cleaning is generally more expensive and carried out over much longer intervals in comparison to backwashing. However, is should be effective in removing fouling that backwashing can no longer

remove. The need for mechanical backwashing and chemical cleaning were tested for separately only in the synthesized black liquor experiments. The results did not show extra recovery of flux through chemical cleaning, which was unexpected. In fact, with chemical cleaning, water flux through the membrane dropped in comparison to just backwash cleaning, and black liquor flux rose but rose to a level that was higher even than the initial flux before black liquor was filtered through the membrane, both of which are highly surprising. One potential explanation is that due to the strong chemical wash, a lot of sodium hydroxide is soaked into the system and into the membranes and even the water flushing process after the chemical wash were not able to completely clean it up. Consequently, with an additional layer of sodium hydroxide on the membrane, the water flux is likely to decrease due to the increased resistance. In addition, more sodium hydroxide surrounding the membrane can better dissolve lignin, the main component of the foulant on the membrane surface, which may decrease the fouling level significantly and strongly increased the initial flux of black liquor after the chemical wash. Apart from this explanation, it could also be that some of the membrane chemical or physical characteristics were affected through long periods of chemical washing. The hollow fiber membranes, while relatively strenuous for lab settings (with the manufacturer stating that it has last for over a year under continuous usage for some labs), are still disposable membranes for single use. It is possible that they are not as stable as industrial membranes, which are designed for continuously chemical processing. Their compositions may have changed over the chemical washes, causing the erratic increase in black liquor flux after the chemical wash. In summary, the frequency required for chemical washing could not be accurately determined through the continuous runs with synthesized black liquor and would require further clarification through additional experiments.

The water permeability decline of the membranes shows that some of the membrane fouling was not reversible through either mechanical or chemical cleaning. For example, in Figure 5-10 and Figure 6-18, the flux of water for the same membrane continuously declined after each run despite long periods of chemical and mechanical cleaning. These irreversible changes to the membrane helps determine the ideal length of membrane replacement. With larger irreversible declines in the flux, the overall concentration process of black liquor would slow down significantly and more membrane area would be needed to process the same amount of black liquor. With the same logic for the frequency of membrane cleaning, we can also assume that a membrane is likely in need of replacement if its flux declines below 40% of the initial flux. From the general trend of water permeability decline when processing fresh Indian black liquor with 10 kDa membranes, as shown in Figure 7-6, 40% decline in water permeability has already been reached after only 5 experiments with fresh black liquor, each lasting shorter than 2 hours. The permeability with 3 and 5 kDa membrane processing fresh Indian black liquor is not too optimistic either as shown in Figure 5-11 and Figure 5-12, already reaching around 15 – 20% decline after 2 experiments each lasting around 2 hours. The declining trend did slow down as the experiments went on. In particular, the 3 kDa membrane showed only a further 2% decline in permeability after the second set of experiments. One theory considers the fact that fouling is usually a blockage in some of the pores, and due to the shapes and patterns of some of the pores, they may be more easily blocked than others. As the

fouling goes on, the most easily blocked pores are fouled already, and over time this would decrease the general rate of fouling, which is reflected in our result. Overall, the declines are still quite significant, and the 40% threshold for membrane replacement may be reached within days, if not hours of fresh black liquor filtration.

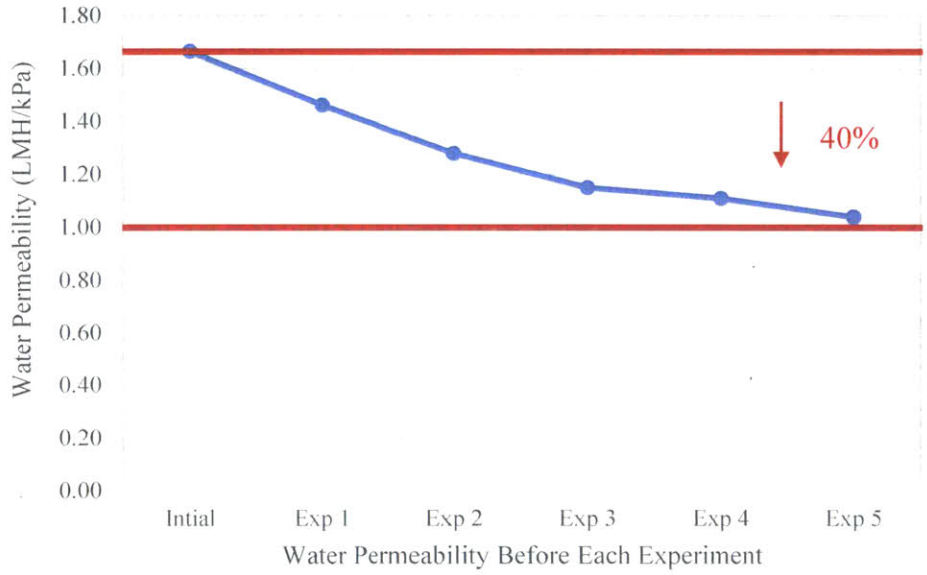

Figure 7-6: Permanent membrane permeability decline of 10 kDa membrane over the different sets of experiments for treating fresh Indian black liquor, and the time for projected flux decline of 40% (the general membrane replacement threshold).

The experiments with synthesized black liquor yield more positive results. If we are not taking into account of the erratic declined caused by chemical washing (which is likely due to factors other than permanent membrane fouling, as explained before), after the initial 26% decline after the first run, little further decline was observed. Considering that the four runs are already totaling up to 5 days of continuous black liquor run (assuming that the system is running nonstop every day), the results would predict a time frame of least several weeks up to a few months before the 40% threshold would be reached, as shown in Figure 7-7. The prediction is with high uncertainty because no decline trend has shown beyond Run 2. Again, this decline is an underestimate because we are leaving out the consideration for the concentrating feed. As the concentrating feed experiment showed, even only after 3 hours of concentrating feed mode run, 8% flux was unable to be recovered.

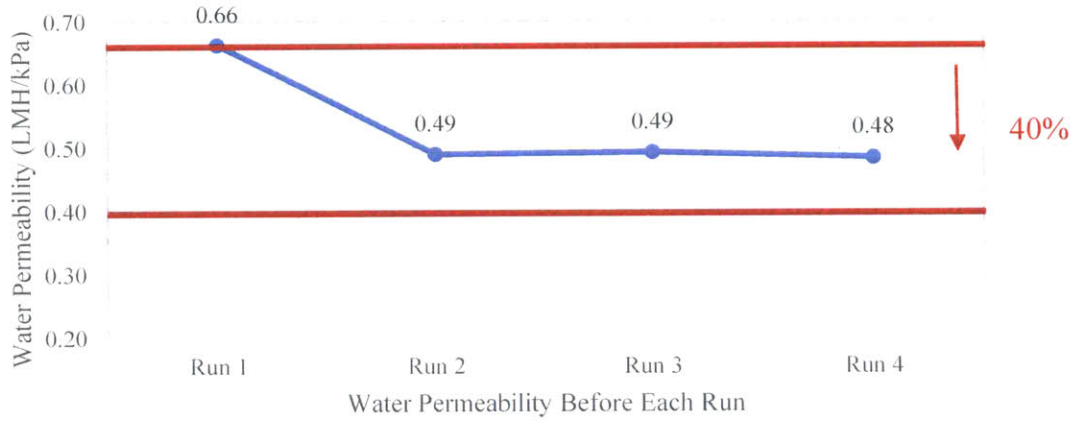

Figure 7-7: Permanent membrane water permeability decline over the different runs of synthesized black liquor with 5 kDa membrane, and the time for projected decline of 40% water permeability (the general membrane replacement threshold).

The characteristic difference between synthesized black liquor and fresh black liquor can help explain the difference in their fouling tendency and their required frequency of membrane backwashing. In comparison to synthesized black liquor, fresh black liquor is more complex and heterogeneous in its composition, and with additional solid suspension and lignin deposition occurring in the filtration process, it is much more likely to cause permanent fouling of the membrane. For example, when the 10 kDa membrane was processing fresh and unfiltered black liquor, severe clogging happened repeatedly where the inlet pressure increased dramatically above the threshold pressure whenever the pump was turned on, as recorded in

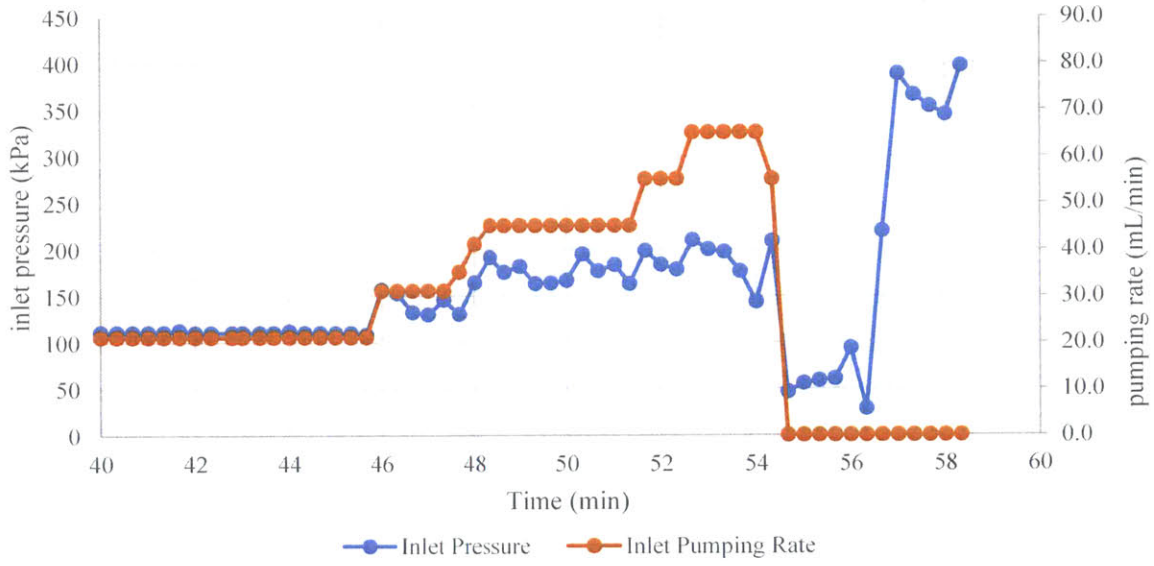

Figure 3-13. The 0.5 mm hollow fiber channels are very sensitive to suspended solids, and any particulates may permanents get stuck inside the channels and simply block out one of the fiber channels. While continuous flushing with high pressure may clean up some of the blockages, this

is still likely to have been partially responsible for the continuously declining permeability of the membranes when treating India black liquor. Hollow fiber channels with wider diameter, or tubular membranes may have been more effective in resisting fouling. This is also inline with Wallberg and Jönsson's conclusion that a channel larger than 3.5 mm is preferred, suggesting that our narrow channels may have been a limiting factor of performance (Wallberg and Jönsson 2006).

On the other hand, while the water permeability continuously declined, the initial black liquor flux did not show a decline over different filtration runs of synthesized black liquor. The backwash was always able to return the flux back to 100% or even more. Hence, even though the water permeability showed significantly drops in membrane functionalities, the membrane's ability to concentration black liquor was actually intact, suggesting a much longer life span for the membrane than what is predicted by the water permeability variation. But it is also important to note that while the mechanical cleaning process was very effective in flux recovery, it was not as effective when we only used water as the cleaning agent. Instead, to ensure a more thorough cleaning process, we added sodium hydroxide in water to match the concentration of sodium hydroxide in the permeate stream and used this solution for backwashing to mimic the process of backwashing with the permeate solution. While the sodium hydroxide solution mimicked the permeate stream, it did not have the lignin content of the original permeate stream (we could not use permeate from the experiment because they were all remixed with the retentate stream and returned to the feed solution). This enhanced the solution's capability to clean up the lignin foulants, in comparison to realistic permeate solutions. The mechanical backwash process may have been more effective than the realistic backwash processes at the industrial scale. Nevertheless, the 100% black liquor flux recovery is still much higher than water permeability recovery. This also suggests that the 40% decline in water permeability when processing fresh Indian black liquor may not be directly correlated to a decline in fresh black liquor flux, and the life time of the membrane when processing fresh black liquor may much higher than the few days as predicted by water permeability decline.

Generally, literature results suggested a 70-80% restoration of water permeability through backwash and over 98% recovery of permeability through chemical washes, which was not observed in our case. Full water permeability was never resumed, even when processing the cleaner and more homogenous synthesized black liquor (Liu et al. 2004; Wallberg et al. 2003 – frac; Wallberg et al. 2005; Holmqvist et al. 2005; Bhattacharjee and Bhattacharya 2006). A permanent decline of water permeability of 20% or more is frequently observed. This is likely because many of the experiments worked with diluted or well-pre-filtered black liquor, which would produce a more much optimistic estimate of membrane lifetime. In general calculations of membrane lifetime, 1 to 1.5 year is used for synthetic membranes (Jönsson and Wallberg 2009). Based on our estimates with black liquor in India, even though the lifetime would likely be higher than the few days, likely up to several weeks, the 1-year lifetime still seems to be an overestimate based on our observations of the changing characteristics of the membrane. Of course, our membrane may not be as strenuous as industrial scale membranes because they are generally designed for disposable uses in the lab. We would also require more data from fresh Indian black

liquor to observe the actual trend of initial black liquor flux to better determine the lifetime, because water permeability variation has shown not to be as effective in determining the membrane's black liquor permeability variation. Declines in pure water flux may not necessarily mean that the filtration of black liquor is in any way affected. Nevertheless, the 1-year lifetime still seems challenging to achieve with our current membrane module.

Overall, our results with fresh black liquor showed that the required washing frequency and the life time of the membrane, when processing undiluted and coarsely filtered black liquor, is generally not as optimistic as what the literature suggests. While the literature used the average membrane lifetime of 1 to 1.5 year, and the daily washing frequency, the strong fouling nature of black liquor and the likelihood of lignin and other solids depositing during the filtration process seems to make this estimate slightly unrealistic. More fouling resistant membranes, such as ceramic membranes or coated membranes, may have produced better results. Hollow fiber membranes with larger fibers might also have decreased the likelihood of clogging by suspended particles in black liquor, and these are future improvements to the experimental process that remains to be further explored. Based on our current results, the washing frequency and the lifetime of the membrane remains to be the most challenging cost factor due to heavy membrane fouling.

7.3.3 Lignin Concentration

The lignin concentration level in the feed and permeate stream can help determine the effectiveness of the membranes in concentrating black liquor and filtering out lignin from the permeate solution. The results can help estimate the potential profit of the membrane filtration process in comparison to the more traditional recovery boiler process of treating black liquor (or in some cases, the process of just dumping the black liquor away). For example, it is possible that black liquor with a concentration around 30-40% could be an effective raw material for road making, due to its high viscosity (communicated in person by engineers of the local factory). It is also possible that the membrane concentration of black liquor could be a more cost-effective replacement of the concentration process by multiple effect evaporators. With a better understanding of the rejection ratio of lignin, we can determine if membrane treatment is an effective substitute for other evaporative methods in processing black liquor. On the other hand, due to the relatively high levels of caustics and COD that is still leftover in the permeate, it would not be possible to simply discharge the stream. Instead, it was expected to be reused in the cooking process so that the caustics can be recycled to save costs as well, as illustrated in Figure 1-3. However, to ensure that the permeate can be effectively reused in the cooking process, the lignin level cannot be too high because the lignin in the black liquor may affect the extraction of lignin from the agro-waste materials and reduce the efficiency of the cooking process. Thus, understanding the lignin concentration in the permeate stream can also help determine if the permeate stream can be reused.

Based on our results from synthesized black liquor, a lignin passage ratio of generally 2-4% is observed for the 5 kDa membranes, giving a permeate concentration of around 1-2 g/L. In comparison, for fresh Indian black liquor is around, the lignin passage ratio would go up to

approximately 25 – 30%, giving a concentration of around 9g/L in the permeate. The values for fresh black liquor aligns much better with literature results, where an 80% rejection ratio of lignin is observed for 4 kDa membranes, and a 66% rejection ratio for 5 kDa membranes (Wallberg, Jönsson, and Wimmerstedt 2003b; Wallberg, Jönsson, and Wimmerstedt 2003a). This could be because the synthesized black liquor does not have the additional organic components such as hemicelluloses, and the existence of other organics may affect the passage ratio of lignin for fresh black liquor. In addition, with a heavier fouling layer for the fresh black liquor, it is likely that the permeate would carry more lignin across the membrane when it passes through the foulant cake formation on the membrane. Lastly, as described in Chapter 3, while Indulin-AT lignin, the lignin used for synthesizing black liquor in the lab, and lignin extracted from fresh black liquor have similar CHNS compositions as shown in Table 3-4, the molecular weight range of the mixtures organic molecules might still differ significantly because the source of these lignin are different. Indulin-AT lignin was extracted from hardwood black liquor while fresh black liquor in India are produced from agro-waste. Based on the passage ratios, it is likely that lignin from hardwood has fewer organic molecules below 5 kDa in comparison to lignin from agro waste. Tolbert et al. has suggested an average molecular weight of around 8000 g/mol for lignin isolated from Birchwood in comparison to 2000 g/mol for lignin from wheat straw, which supports the theory that Indulin-AT lignin may have a higher average molecular weight that lignin from argo-based black liquor. much fewer molecules in the lower range that would pass through the membrane into the permeate (Tolbert et al. 2014).

Lignin concentration for the flux-pressure tests with synthesized black liquor showed a clear pattern where the lignin concentration decreased as each of the experiment went on (where pressure is increasing), as shown in Table 6-8. This is likely because as the pressure increases, the fouling also increases. At the end of the experiment, generally a cake formation of foulant layer would be on the surface of the membrane. The increasing foulant layer and blocked pores are likely to prevent lignin from passing into the permeate, so it is reasonable that the lignin concentration decreases in the permeate as the flux-pressure experiment goes on. Apart from results from the 10 kDa membrane, the permeate concentration also decreased as the cross-flow velocity increased. With the increasing cross-flow velocity, concentration polarization is likely to decrease, which also decreases the possibility of solute leakage, and increasing the rejection ratio (Blatt et al. 1970). This would eventually result in decreasing lignin concentration in the permeate stream. As for the 10 kDa membrane, it may be likely that the increasing cross-flow velocity decreased the blocked pores, allowing more lignin molecules to pass through. This process may have dominated instead of the decreasing concentration polarization, and resulted in an overall increasing lignin passage ratio with increasing cross-flow velocity.

In the continuous runs of synthesized black liquor, the concentration of lignin in the permeate solution also decreased within each run as the experiment went on as shown in Figure 6-19, likely for similar fouling and pore blockage reasons that also caused a decrease in permeate lignin concentration in flux-pressure runs. The flux decrease was also evident across the four different runs, potentially due to a continuous fouling process that was not recovered by mechanical

cleaning. This aligns with water permeability results, but black liquor flux results, on the other hand, showed a sign of increase flux instead. As suggested in the previous sections, this may have been due to accumulation of caustics on the surface of the membrane, which increases the dissolution of lignin foulants as the black liquor passes through the membrane. This may enhance the flux and at the same time decrease the lignin passage as lignin becomes more dissolved neared the surface of the membrane, resulting in a simultaneous increase in flux and decrease in lignin passage ratio. Lastly, the chemistry of the membrane may have been affected by the long-term exposure to solution with a slightly high pH, resulting in the trend in permeate lignin concentration and permeate flux.

As for the concentration runs, it is important to note that despite some slight fluctuations, the lignin passage ratio did not change with the increasing feed concentration. This means that the permeate lignin concentration increased along the retentate lignin concentration, generally at the same pace. The increase in both retentate and permeate concentration was significant at the beginning, but was minimal after around 80 minutes into the experiment when the retentate concentration became as high as 185 g/L, suggesting that this should be the ideal target of concentration beyond which the process would be highly inefficient. When the retentate lignin concentration increased almost 5-fold to 185 g/L, the permeate lignin concentration also increased around 4-fold to 3.6 g/L at the end.

Despite the slight increase at the end, the lignin passage ratio still generally remained within the range of 1.5% - 3%. Hence, as the feed lignin concentration increases, we know that the permeate lignin concentration would also start increasing, and would eventually increase up to a point where the permeate stream needs to be re-filtered again because it would contain too much lignin to be reused in the cooking process. This is especially true considering the permeate concentration of fresh Indian black liquor of 9 g/L without any concentration of the feed. If there is a 5-fold increase in the feed and retentate stream concentration, then the permeate concentration may also increase 4-5 fold, going up to 40 g/L, even higher than the initial feed concentration. This need for refiltration as concentration happens would also decrease the overall speed of filtration, and more membrane area would likely be required to ensure that all black liquor can be effectively separated into a concentrated stream and a permeate stream with sufficiently low lignin levels so that the caustics can be reused. This suggests a higher capital cost due to the need for more membrane area, and a higher operational cost with more pumping processes needed for the extra membranes.

The fresh Indian black liquor results did not show patterns as clear as the ones for synthesized black liquor. There is not a very clear pattern of permeate lignin concentration variation along the course of the constant-composition runs, according to Figure 5-8. The trend in lignin passage ratio did not follow the flux decline pattern closely like how it did with synthesized black liquor runs. First of all, this may be because there is a higher uncertainty range for the data with India's black liquor. Only a very old UV Spectrophotometer was available in one of the pesticide factories nearby. The machine has not been operated for a long time, so its exact accuracy cannot be immediately verified. Also, its range was lower in comparison to the one used in the lab. The

samples needed to be diluted much more to ensure that the absorption falls within the range. The increase dilution level and the low quality of the machine would likely to raise the uncertainty of the data, so even if there could be a trend over the course of the experiment, it may not be observable due to the high level of uncertainty associated with the data, as indicated by the error bars in Figure 5-8. In addition, the black liquor in India is much more complex and heterogeneous. The flux rate may be affected by fouling of materials other than lignin, and the passage of lignin could also be affected by other compositions of black liquor, so the two variables may no longer be directly follow each other as they did with synthesized black liquor where the only component of concern is just lignin. The results from fresh Indian black liquor showed a relatively consistent lignin passage ratio for each of the membranes despite the significant decline in flux, suggesting that even though fouling strongly affected flux, the filtration capability of the membrane was not affected.

Overall, lignin rejection results are relatively consistent with the results shown in literature. Over courses of continuous runs, while some level of lignin passage ratio decline may be observed, the decline is generally not significant. Two separate streams of concentrated lignin solution and reusable permeate solution can be generated constantly at adequate quality. This suggests that the benefit associated the lignin concentration and caustic reuse is reasonable and beneficial. However, the cost calculations of the system rarely took into account the concentrating permeate stream in the concentration process. The concentration of the permeate stream can largely affect the reusability of the permeate stream and affect the potential benefits that may be gained from the stream. As suggested above, additional capital cost for more membrane area and additional operation cost for increased pumping would need to be taken into consideration if we are looking at the more realistic process of concentration, which was not factored into Jonsson and Wallberg's cost estimation. These large increases in cost would be a great challenge for the implementation of the membrane filtration process for filtering black liquor.

7.4 Summary

The discussions above, especially comparisons with literature results and general cost-effectiveness evaluations, may be summarized as follows:

- The optimal operating parameters selected are an operating pressure of 207 kPa or more and a cross-flow velocity of 1.06 m/s or more for 5 kDa membranes. The limit of the experimental set-up limited our scope to search for parameters that would be more accurate. The results are generally in line with expected values from literature.
- According to flux results, the average flux of 7-21 LMH are reasonable comparable to flux rates reported in literature, but did not show any expected advantage, despite the lower concentration of the fresh black liquor from Muzaffarnagar. This is potentially due to heavier fouling.

- According to the results of the reversible and irreversible fouling of the membranes, the required washing frequency is likely higher than the 1-day washing cycles, and the membrane lifetime would go up to a few weeks, which is far from the 1-year lifetime estimate. The associated maintenance and membrane replacement costs are expected to be high, and further exploration on black liquor pretreatment or more fouling resistant membranes may reduce these cost factors.
- According to the lignin concentration results, the lignin rejection ratio is generally consistent across the experiments and consistent with literature results for membranes of similar pore sizes. However, in the concentrating feed runs, the constant rejection ratio would indicate that permeate lignin concentration can go up to 40 g/L and would require retreatment before it can be reused. This affects the benefit of reusing the permeate stream, and adds to the cost of reprocessing the permeate stream. These increases in costs are generally not taken into account in the literature, suggesting an over-optimistic estimate of cost-effectiveness in this aspect.

8 Conclusion

The conclusions from this study are summarized in this chapter. Based on the discussions of each key experimental variable and comparison with literature results in Chapter 7, the overall cost-effectiveness of membrane systems for treating fresh black liquor from India small-scale brown paper mills is summarized in Section 8.1. The uncertainties of the results and conclusions are briefly discussed in Section 8.2, followed by proposals of future work for improved cost and benefit evaluations in Section 8.3.

8.1 Cost-effectiveness of Membrane Treatment System

According to the discussion in Chapter 7, we can come to the following conclusions about the key experimental variables estimates that relate to the cost and effectiveness of the membrane system, as shown in Table 8-1. These experimental variables are generally estimated values for 5 kDa hollow fiber membranes based on the combination of results from fresh Indian black liquor and synthesized black liquor, as discussed in the previous chapter.

Table 8-1: Key variables related to the cost and benefit of membrane treatment of black liquor

Cost/Benefit category		Key Experimental variables	Values
Costs	Capital cost	Average flux	7-21 LMH
	Operational cost	Pumping pressure	207 kPa
		cross-flow velocity	1.06 m/s
	Maintenance cost	Membrane cleaning frequency	4-6 hours
	Membrane replacement cost	Time for substantial membrane irreversible change	Several weeks
Benefit	Retentate stream products	Lignin concentration	Start: 38 g/L; End: 185 g/L
		volume reduction	80%
	Permeate stream products	Lignin concentration	Start: 9 g/L; End: 40 g/L

If we compare these key experimental results to the results from literature estimates and focusing on the literature with specific cost estimates and positive comments of the cost-effectiveness of membranes, we can observe the differences relative to Table 8-2.

Table 8-2: Comparison between experimental results in this research and reference results used in literature for general cost estimates of membrane treatment systems.

Experimental variables	Experimental value	Reference value	Reference Source
Average flux	7-21 LMH	15-40 LMH	(Wallberg and Jönsson 2006); (Jönsson and Wallberg 2009)
Pumping pressure	207 kPa	103 – 414 kPa	(Jönsson and Wallberg 2009)
Cross-flow velocity	1.06 m/s	3 – 5 m/s	(Jönsson and Wallberg 2009)
Membrane cleaning frequency	4-6 hours	1 day	(Jönsson and Wallberg 2009)
Irreversible membrane change time	Several weeks	1 – 1.5 year	(Jönsson and Wallberg 2009)
Volume reduction	0.8	0.6 – 0.9	(Jönsson and Wallberg 2009)
Retentate stream lignin concentration	Start: 38 g/L End: 185 g/L	Start: 50-60 g/L End: 150-250 g/L	(Wallberg and Jönsson 2006); (Jönsson and Wallberg 2009); (Wallberg, Holmqvist, and Jönsson 2005)
Permeate stream lignin concentration	Start: 9 g/L End: 40 g/L	Not clearly addressed in cost calculations	(Jönsson and Wallberg 2009)

As we can see, the average flux, pumping pressure, achieved volume reduction and retentate lignin concentrations are generally within the expected range and comparable to the results in literature. A few other experimental results stand out. First of all, due to the limitations of the experimental setup, the cross-flow velocity is generally low, which is likely to have allowed higher fouling. This is potentially related to the other two variables that also deviate from the previously reported results: the need for a higher frequency of membrane cleaning and the short time span before irreversible membrane change. Both could be partially associated with a low cross-flow velocity, but also possibly factors such as membranes that are not sufficiently fouling-resistant (e.g., narrow channels of the hollow fibers), less pre-treatment of the black liquor before membrane filtration, and so on. These deviations of experimental results may not be unique to our case because in general, the 1-day cleaning frequency and the 1-year membrane lifetime used in cost calculations in the literature are not derived from experiment results (Jönsson and Wallberg 2009). They are simply rough estimates for the generic ultrafiltration process, not taking into consideration the strongly fouling nature of black liquor. It is likely that the variables governing fouling have been broadly optimistic in literature in general, and the costs may have been consistently underestimated. Another parameter that stands out is the permeate lignin concentration, which was not sufficiently addressed in literature. The profitable product through the black liquor treatment is generally considered to be the lignin in the retentate stream, which is usually much better characterized to calculate the potential profits from the lignin. The fate of permeate streams, on the other hand, are not well described. Based on our results, the permeate stream is likely required to be recirculated for re-filtration due to the high concentration towards the end stages of volume reduction. This process is not described in detailed and the additional costs for reprocessing the permeate were not clearly addressed in the cost calculation process. Wallberg et al. mentioned the concern with the large energy cost associated with recirculation, but the exact extra costs for reprocessing the permeate stream was not specifically mentioned (Wallberg and Jönsson 2003).

In conclusion, our experimental results generally align well with experimental results in literature. However, a few of our results do not support the relatively optimistic estimates made in the cost calculation process, namely:

- The assumption of daily cleaning lasting 1 hour. Our experimental results suggest that more frequent cleaning up to 3-4 times a day may be required due to the declining black liquor flux.
- The assumption of 1 – 1.5 year of membrane lifetime. Our analysis indicates that membrane lifetime up to a few weeks is possible, but the 1-year life span is highly unlikely due to the obvious changes of the membrane characteristics just days after continuous processing of black liquor.
- The neglect of the re-filtration required for the permeate stream. Lignin concentration of the permeate stream towards the end of a concentrating cycle can go above 40 g/L, even higher than the initial concentration of lignin in the black liquor. A large portion of the permeate

stream would require refiltration and more membrane area is likely needed for this process, and this substantial cost item was not clarified in the cost calculations in the literature.

With these more realistic results for membrane cleaning frequency, membrane lifetime and permeate lignin concentration, the corresponding maintenance cost, membrane replacement cost, capital cost and operational cost, as listed in Table 8-1, would be substantially higher. The benefit of reusing the permeate cycle may also be reduced due to the high lignin levels and frequent need for re-filtration. These parameters can be improved upon. For example, membranes with more fouling resistant coating surfaces or ceramic membranes may offer a much better membrane lifetime. Increasing cross-flow velocity may also give more optimistic predictions of membrane cleaning frequency. More experiments are needed to explore these specific variables. However, with the results from the current research, membrane filtration treatment is unlikely to be cost-effective.

8.2 Uncertainties

There are a number of uncertainties in the experimental results.

To begin with, there is uncertainty associated with the composition of black liquor. Fresh black liquor coming straight out of the paper production process varies depending on the operational conditions. The different batches of black liquor obtained from the same paper mills all had different pH levels and different total dissolved solid levels upon initial testing. Experimental results from the different batches of fresh black liquor may also vary from time to time, so it may be difficult to obtain consistent and repeatable results with a solution that is as variable as black liquor. The synthesized black liquor is an attempt at creating more consistent experimental results, but for simplicity, a lot of other components have been neglected even though they may have important effects on the experimental results. The flux results, for example, suggest that the synthesized black liquor does not incur nearly as much fouling as the fresh Indian black liquor. Many inferences of fresh black liquor results have been made with the results from synthesized black liquor, and there is likely a lot of uncertainty associated with these estimated results for the case of fresh black liquor.

In addition, the black liquor quality during the course of the constant-composition experimentation is not exactly constant. The need to output the permeate stream onto a scale for measuring the permeate flux affects the composition of the feed, and although the permeate stream is returned frequently enough to ensure that the composition of the feed does not change more than 5%, fluctuations of the permeate flux can still be very clearly observed over the course of the experiment. Because of the fouling nature of black liquor, any change in composition may be easily reflected in the flux, so a more frequent remixing process may help reduce to level of fluctuation in the flux data, and give better estimates of flux decline rate. If it is possible to measure

flux through a mass flow meter (which uses sensor to detect flow rate) or other methods that does not require the separation of the permeate stream, then the permeate stream can be directly returned to the feed immediately, which would greatly improve the accuracy of the flux data.

The constant remixing process and sampling of the permeate solution also frequently disturbs the system. The pressure fluctuates during the sampling process because as the permeate tube is moved, it may have disturbed the flow in the system which would impact the pressure levels. The permeate sampling also cause gaps in the permeate data because the scale can no longer record the permeate change. Even without the disturbance of the sampling process, the system operation can sometimes be also unstable, and there would be fluctuations of the pressure once in a while, and sometimes a fluctuation of more than 15% can be observed. This may also be due to the fact that the tubes and fittings in the system are relatively thin, and while air tightness and leak-proofing of the system has been verified, it may not be perfect. All of these have resulted in variability in the data. Fluxes that deviate due to deviated pressure or sample collection are omitted from the figures and analysis, which result in some slight disconnects in the data, also increasing the uncertainty of the flux pattern.

The measurement of lignin concentration is also associated with slightly high uncertainties, especially for the results with fresh Indian black liquor. To measure lignin, dilution up to 300 times had to be conducted, which greatly increases the potential errors in the process. Also, sometimes the samples need to be stored for a while before the measurement of lignin, due to the availability of the analytical equipment, and lignin concentration may be affected as time goes on.

Lastly, there may have been uncertainties associated with the membrane quality. The membranes are usually continuously compacted with water before the experimental runs. However, in several cases, the water compaction caused continued decline of water quality even after a few days of compaction. This may be due to not thoroughly rinsing out the glycerin from the washing solution, but it may also be an indication of the instability of the membrane, which is also likely to affect the results of the filtration runs. The membranes used are generally lab-scale disposable membranes that may not be extremely chemical resistant, and some changes in flux of lignin rejection due to the membrane quality cannot be separately identified from changes due to fouling, which also increases the uncertainty in the data interpretation.

8.3 Future Work

Due to the limit of time and capacity, many aspects of the research still require expansion, and would benefit substantially from future work in the following areas.

First of all, as suggested in Section 9.1, the cleaning frequency, membrane lifetime and permeate lignin concentration are the major limiting factors of the cost-effectiveness potentials of a membrane treatment system for black liquor. Future work on the improvements of these variables is essential. More fouling resistant membranes, higher cross-flow velocities, a certain level of

sedimentation and pretreatment of black liquor before filtration are all potential solutions that need to be further evaluated in the future work.

Also, most of the results are still predicted by lab results on synthesized black liquor. Repeating all of the experiments with fresh Indian black liquor would yield much more accurate predictions than simply extrapolating fresh black liquor results from experiments with synthesized black liquor. This is particularly important considering that the synthesized black liquor has neglected a number of chemicals that may have been important to the experimental results. In the future, other chemicals identified in the fresh Indian black liquor, especially organic chemicals such as hemicellulose that may have an impact on the fouling characteristics of black liquor, should also be added to the synthesized black liquor to the extent possible to synthesize a new black liquor with much more resemblance to fresh black liquor. If experiments with newly synthesized black liquor are able to reproduce some of the field results of fresh Indian black liquor, then lab results with synthesized black liquor can predict fresh black liquor behavior much better.

A more automated setup for frequent returning of the permeate stream into the feed stream would also produce much better and consistent results. In particular, it would reduce human errors, such as forgetting to remix within the allotted time (which caused the feed concentration change to rise above 5%), which has happened during the course of the continuous-composition experiments. Similarly, more automated sampling of the permeate stream is possible through an inline flow-through cuvette that can be placed in a UV spectrophotometer, allowing continuous measurements of the lignin concentration. Of course, easier dilution methods would also have to be implemented before the automated lignin concentration measurements can become possible. In the end, it would allow much longer experiments to be carried out, which gives more accurate predictions of membrane cleaning frequencies and membrane lifetimes, in comparison to our current estimates through the general flux decline trend.

There are also other limits of the experimental setting that are preventing the treatment process to be carried out in the most optimized setup. If we can improve the experimental equipment so that cross-flow velocities up to 4 m/s and pressures up to 414 kPa can be utilized in the filtration process, it would give the results over a much wider range of variables, and offer better comparisons between our experimental results and similar observations in literature.

Longer membrane modules could also be explored to generate more realistic experimental results. The current membrane used generally 10-cm membranes, much shorter than the industrial scale membranes. As black liquor flow along the membrane, the flux and fouling would vary along the channel, so the filtration results from a 20-cm long membrane cannot be readily predicted by results from 10-cm membranes. More experiments on longer membranes can help find the best length for processing black liquor, and realistically demonstrate the effects of filtration by industrial-sized membranes.

Most importantly, it would be crucial to conduct an actual cost and profit calculation based on the improved experimental results. Currently, most of our analyses are based on comparison with literature results. However, the calculation of cost and benefit in different geographical locations

(literature generally focused on Europe) based on different types of black liquor cannot be directly applied to India. For example, the cost of membranes, electricity, and manual labor and so on would all be drastically different. The exact costs need to be further explored through more interviews with the local industry and local membrane facilities. With more comprehensive cost assumptions, and improved experimental data, it would be possible to create a reasonable cost estimate of a membrane treatment system and compare it with the existing multiple effect evaporator's capability in concentration black liquor and recovering caustics. With this comparison, we can then finally accurately assess the profitability of such a system, and give more solid recommendations to the local paper mills in terms of adopting the membrane filtration technology and what to explore as the next step in a pilot-scale study.

Appendix

1 Stakeholder Analysis and Value Articulation

1.1 Background

Black liquor, a toxic byproduct from Kraft pulping process in pulp and paper mills, are traditionally treated by being passed through multiple effect evaporators and burned in a recovery boiler to produce energy and recover chemicals. However, traditional treatment of black liquor are not viable for small-scale Kraft paper mills in Muzaffarnagar, India, due to the low alkali and total solids concentration of their black liquor. Alternative treatment methods including low temperature incineration and membrane filtration are explored to determine their effectiveness for industrial scale black liquor treatment as well as their economic viability. For low temperature incineration, field surveys will be carried out to determine the total expense and how it varies with the operating condition. Membrane filtration will be studied on a lab scale to determine its effectiveness of treatment and the associated cost. Eventually, a strategy for selecting different treatment methods including traditional recovery boilers, low temperature incinerator and membrane filtration based on the different pulping and mill operation conditions is developed, and recommendations for the optimal treatment method will be made accordingly for the small-scale Kraft paper mills in Muzaffarnagar.

The current short-term focus for the project is on evaluating the effectiveness of membrane treatment. Although advocated by many scholars as a possible alternative treatment method for pulp and paper factories, it has not been adapted in the paper mills in India due to concerns with the cost of membrane manufacture, membrane fouling, flux decline, energy input and so on. However, there hasn't been rigorous studies suggesting that these factors are valid reasons for rejecting the membrane filtration method for black liquor. Thus, it would be interesting to connect the industrial perspective and academia perspective by carrying out lab experiments to discover for what operating conditions, type of membranes and quality of black liquor, membrane treatment would become economically viable for small-scale paper mills.

There are two different stages of deliverables for this project. The first is just an evaluation of the feasibility of membrane treatment methods for these small factories, while the end-goal is to develop a general treatment selection guidance for pulp and paper mills.

The focus for this value proposition is more specifically on membrane method evaluation as a deliverable, although most of the important components could be applied to the general treatment selection guidance deliverable as well.

1.2 Key Stakeholders

Generally speaking, the stakeholders - our customers and partners, can be divided into three large segments, and for each category there would be a different value proposition. The segments include the public sector – mainly environmental regulation agencies, the private sector – mainly pulp and paper mills that we are directly or indirectly connected with as well as potential membrane providers, and last but not least, research institutes that are conducting similar researches on waste liquor treatments, especially membrane treatments. The details are stated below.

1.2.1 Private Sectors – Industries

a. **Major Players**: Bindlas Duplex, pulp and paper mills in or around Muzaffarnagar

- **Paper mill owners**

The pulp and paper mills are directly our customer because the research we are producing are targeting directly at their request for solutions on black liquor treatment. In addition to just being a customer, they can also be considered partners and provide valuable resources. They could provide useful data to analyze the effectiveness of the Low Temperature Incineration plant, and if lab scale membrane treatment experiments proved the method to be effective, they may also be able to construct pilot plants for membrane treatment to evaluate this method at the field scale – all of which helps us greatly advance the process of drafting a treatment method selection guidance in the long run.

More specifically, in Bindlas Duplux, the paper mill that our research activities were mostly based in, Mr. Aggarwal and other owners are the ultimate decision makers on whether or not to adopt new black liquor treatment technologies. Considering their decision-making position and their standpoint as businessman, the economic feasibility and business potential of the project is crucial. When we met with Mr. Aggarwal, he was excited at the idea of reusing or selling the sodium hydroxide and lignin retrieved from the black liquor, and even calculated the monthly profits with 500 tons of lignin/month sold at $2/kg. He did not focus on the common treatment method using boilers with condensed black liquor as fuel, since it was shown not to be economically viable for him in the past. The solution is of high-medium importance to the stakeholder since he wants to comply with regulations without economic sacrifice. While we have not yet talked to the other owners, it is highly likely that with Mr. Aggarwal's leadership position in the cluster, they would hold similar opinions. Many of them also belonged to Mr. Aggarwal's family as he suggested, so there is an additional reason that Mr. Aggarwal may more or less represent the collective opinion (MSME 2012).

He has the resources in the factory that may help realize the technology adoption, and he would offer capitals to install the system as long as he can be convinced that there is business potential.

He also has many influential connections that could help us most efficiently combine local and off-site research to carry out our research, and if a solution is eventually presented, he will also have sufficient connections and power to help lead us to other paper mills in UP or beyond so that they may eventually also adopt similar treatment methods.

- **Paper mill associations**

Additionally, Paper mill associations such as The UP Paper Mill Association will most likely be a good connector once the technology has been successfully adopted at one pilot location. Due to the general risk-averse nature of the mill owners, the initial adoption of technology would likely only depend on one or two mills, so the collective board of mill owners would be less important in affecting the initial stages. However, it would be a great marketing platform, providing valuable connection to spread the technology once it has proven to be relatively effective. The additional influence from the association may be that it can promote competitiveness between mills and actually promote the adaptation of the new technology. Since this stakeholder is simply a larger collection of stakeholder A&B, the tradeoffs for confronting is similar to that of the owners where business viability is crucial.

- **Paper mill workers**

While the owners decide on the adaptation of technology, the engineers and workers have to actually be able to become accustomed to new trials and new routines in their work. They will be the ones building up new facilities to support the new technology. Thus, it will be important to connect to them to determine the level of implementation that is practical. While they would not be the ultimate decision makers, they influence the type and level of new technology we can introduce, giving medium influence to the solution. The workers are more averse to change, particularly the less skilled workers, which may be the majority, so it would be unlikely that they can help us promote the adaptation of the solution to the owner. They may even advise against it. However, if there are high experienced and adventurous engineers, they can help showcase to the owner the feasibility of the technology, helping with our progress. On the other hand, it is necessary to make sure that we involve them in our discussions and listen to their ideas and suggestions enough to make them feel valued in the process and to gain their eventual trust and support. Although the workers may not recognize it, the solutions is of importance to them since it may entail a better working environment providing less health risks for the workers.

- **Byproduct customers**

Apart from directly burning the lignin for fuel and reusing the inorganic pulping chemicals if successfully retrieved, there are also wider markets for byproducts of black liquor treatment such as concentrated lignin solution, extracted lignin and lignin derivatives (depending on the exact method of treatment). While these are not the direct customers of a membrane treatment solution, their interest level may be important to the major player of pulp and paper industries and may largely influence the value proposition of potential black liquor treatment solutions. In fact, through our conversation with Mr. Aggarwal (as he calculated the potential gains from selling

lignin), the byproduct market is moderately to strongly influential to his decisions. On the other hand, since few customers have been recorded to push for lignin production in the paper industries, there is no strong evidence that these stakeholders have a very strong attitude for production of lignin, especially if they have sufficient supply or substitutes now.

b. **Potential Players:** Membrane Providers and Technology Developers

Membrane providers may be potential partners for the project due to their interest in providing membranes at a large scale to pulp and paper mills in the future, if membrane methods can be proven as viable. They may be able to provide discounted membranes for experimentation in India to help us with the evaluation process. In addition, since large-scale installations of membrane plants would also benefit membrane providers, they may also like to collaborate on distribution and marketing of membrane treatment methods for black liquor.

More specifically, we have spoken with Aastropure, a related membrane company, who is highly interested in solutions for pulp and paper industries. Companies like Aastropure may be a great alliance for us because they are more connected locally and can test samples and give trial runs immediately after new prototype technologies have developed. They may be well aware of local constraints and conditions that can determine crucial sections of the solutions, and they may be better at communicating the exact designs to the engineers and gaining their support. They may even help persuade the ultimate decision makers through a more culturally connected understanding of their needs.

It's important to know that while it's easier to motivate these stakeholders since the solution is also of high interest and value to them, a connection with them entails a sharing of technological details – more specifically, the final attributions of originality may have additional complications. An appropriate agreement may need to be formed with this stakeholder.

1.2.2 Public Sectors - Environmental Regulation Agencies

a. Major Players: Central Pollution Control Board (CPCB)

b. Potential Players: Uttar Pradesh Pollution Control Board (and other regional Pollution Control Boards)

The CPCB, UPPCB and the community are stakeholders that provide pressure to push for the implementation of the solution. The CPCB directs UPPCB to carry out monitoring and regulating the mills, so CPCB's influence is indirect and placed on the low side of the spectrum. UPPCB and local communities, on the other hand, would provide direct pressure. According to orders from the charter for Ganga River Basin, UPPCB is required to "carry out monitoring and surveillance activities" of Pulp & Paper units in Muzaffarnagars and implement "technological up-gradation action plan" (CPCB 2008). The solution is of interest to the political agencies and in reality,

UPPCB did push for black liquor and wastewater treatment, which induced the installation of a boiler system for black liquor and wastewater treatment plants. However, when we visited in August, neither system was actually functioning. It's clear that while they have urged the industries to work towards better solutions, there are still strong limitations to the role of UPPCB. Similarly, while pressure from the community may be a concern, it seems not to be on the priority list for the citizens since we did not hear of any public outcry in the region. When asked, Mr. Aggarwal also mentioned that the locals didn't have issues with the water. It seems that although the solution is of high importance to the stakeholders and they would hold supportive intentions and political power and even pushed the progress of the solution, they are still only medium-low influence. For these stakeholders, we only have to show enough evidence suggesting a possible decrease to pollution to gain their support due to the importance of the solution to them, but this alliance may be highly controversial due to its political nature.

They could be considered partner as well as potential customers for the membrane treatment method. The treatment guidance might be useful for these regulatory agencies to help industries that are in the process of developing treatment methods, and help them comply with regulations cost-effectively. In addition, they also have great knowledge of the current landscape of treatment, and can give us details on the current treatment methods in India. They can also potentially be a very important distribution channel. Once the membrane technology is approved by these agencies, it will become much easier to persuade more industries to adopt this practice. We have connected with CPCB but not yet communicated with local PCBs.

1.2.3 Research Institutes

Major Players: Central Pulp and Paper Research Institute, IIT labs (especially IIT-Roorkee and Kanpur)

These research institutes have research projects that are specifically focused on membrane treatment, and would be able to provide useful insights and support in the development of our research. Some of the labs have also looked specifically at membranes and can offer useful suggestions on developing membrane-related solutions for black liquor. IIT-Roorkee and CPPRI are also relatively close to Muzaffarnagar and have a lot of lab equipment that would be useful resource when we are carrying out local experiments and analysis in India. We have visited CPPRI and worked with them to characterize black liquor composition. We have also communicated with students and professors working on black liquor in ITT-Roorkee and IIT-Kanpur, and although they are not currently working on similarly treatment researches, they are willing to provide help with equipment and other support.

A summary of the connections is shown in Table 1 below.

Table 1-1-1: Summary of Key Connections

	Connection (Existing or Potential)	Category	Key Resources
Private Sectors	Pulp and Paper Mills	Customer	Demand Gauging Implementation
	Membrane providers and Technology Developers	Partner	Expertise; Marketing
Public Sectors	Central Pollution Control Board	Customer/Partner	Policy; Distribution
	Regional (Uttar Pradesh) Pollution Control Boards	Customer/Partner	Policy; Distribution
Research Institutes	Central Pulp and Paper Research Institute	Partner	Expertise; Experiment
	IIT labs (e.g. Roorkee, Kanpur)	Partner	Expertise; Experiment

1.3 Customer Segments

Currently the customers, as stated in the previous section, are mainly the pulp and paper industries from the private sector, and environmental regulatory agencies from the public sector. Details are stated below and summarized in Table 2.

The pulp and paper mills could be further categorized by the different sizes of paper mills, because generally larger paper mills can more effectively afford the traditional method and may not have such a high demand for alternative choices. On the other hand, the problem with larger mills is that traditional chemical recovery methods may produce an overabundance of energy that is not needed by the mill, and therefore it makes more sense to retrieve lignin out of black liquor and make other uses of it if the energy produced is otherwise just wasted. In that case, membrane methods may still be valuable to larger paper mills, but a different cost-benefit analysis would be needed.

The mills can also be categorized by white paper mills and brown paper mills. The black liquor from brown paper mills have a lower solids concentration, which makes less economically favorable for chemical recovery boilers due to a higher amount of evaporation required. Instead, the low solids concentration would suggest less fouling for membrane methods. White paper mills, on the other hand, have more concentrated black liquor and alternative solutions may not be as favorable.

Brown paper mills would potentially have the largest interest in the membrane treatment method, and is our main target. Mills of other categories may not be as interested in membrane alterative treatment methods, but may benefit from the treatment selection guidance that we are intending to develop in the long run. Detailed analysis can be made based on a range of different black liquor concentrations and the preferable method for the different qualities.

The regulatory agencies can be divided into the central agency of the Central Pollution Control

Board as well as regional agencies. The Central Pollution Control Board may be able to develop the overall plan and decide on adopting the method selection guidance. They can also distribute the plan to regional agencies to implement and engage more customers who are interested in alternative treatment methods. The regional agencies are implementers of this plan, so they may have more connections directly with local mills that can become potential customers through engagement with the agencies.

Table 1-2: Customer Segmentation

	Customer	Interest level
Pulp & Paper Mills	Small-scale Brown Paper mills	High
	White Paper mills	Low-Medium*
Regulatory Agencies	Central Pollution Control Board	Medium*
	Regional Pollution Control Board	Medium*

* It's likely that their interest level would increase for a treatment selection guidance in comparison for just the development of membrane treatment method

Based on Section 1.2 and 1.3, we can also map the stakeholder's influence and interest distribution as shown in Figure 1-1.

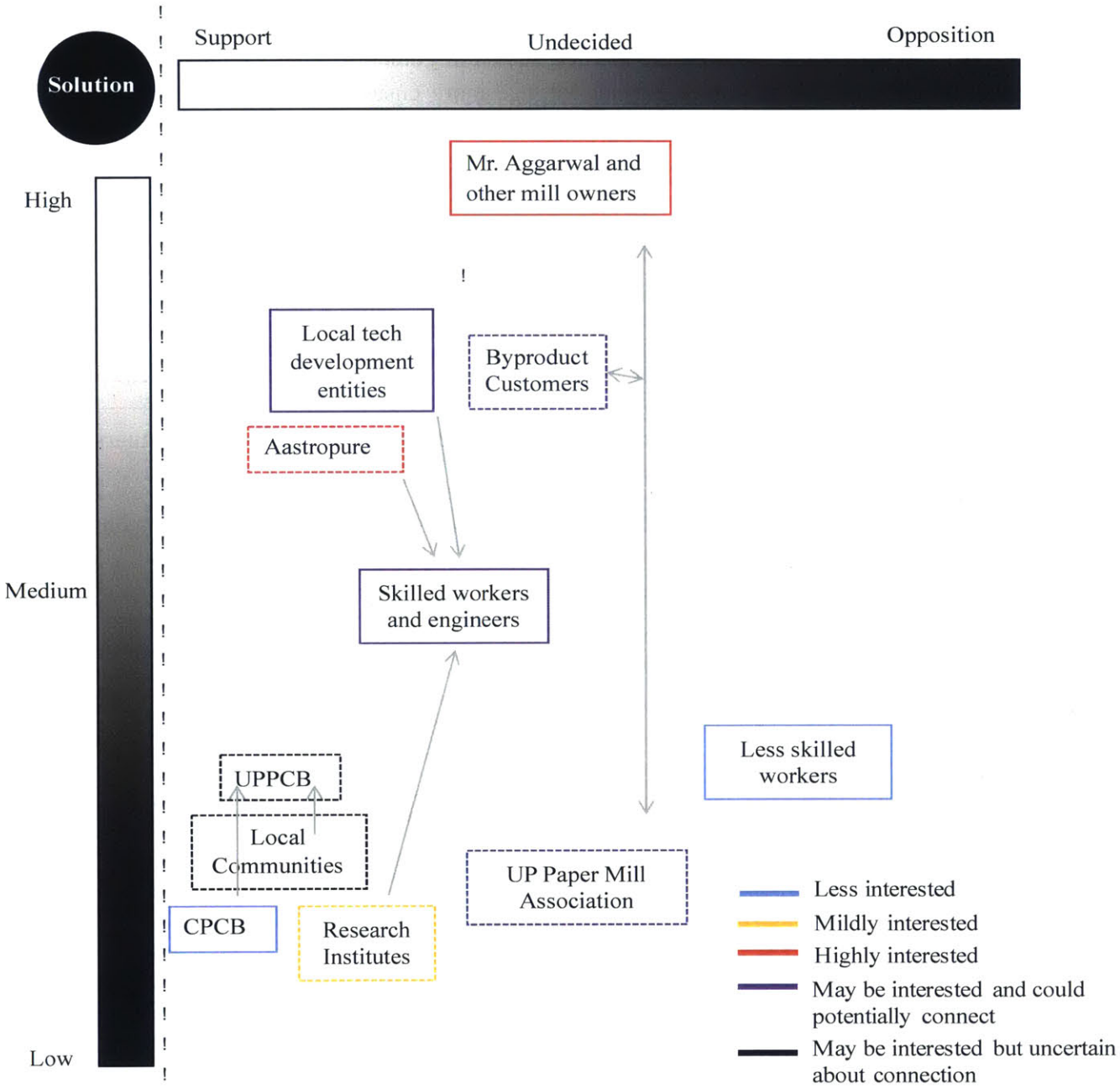

Figure 1-1: Stakeholder distribution group with the vertical axis is "level of influence" and horizontal axis is "position of the stakeholder towards the solution". The differently colored boxes indicate the level of importance and interest of this solution to the stakeholders and are shown as labeled. The dashed boxes indicate uncertainties in this figure due to lack of in-depth communication with the specific stakeholder, and constitute the most limitations of this analysis.

1.4 Value Preposition

A few key values of the membrane method evaluation and treatment method selection guidance

include the followings, categorized by short-term values that helps to immediately attract customers and partners, and long-term values that would eventually emerge as the treatment methods and selection guidance are being more widely utilized in the market.

1.4.1 Short-term Values

a. Potential profit for the mill from lignin extraction

This is the major value proposition for our private sector customer, currently considered our main customer. By extracting lignin through membrane filtration and utilizing lignin in alternative ways rather than just burning it through the chemical recovery boilers or low temperature incinerators as a low-efficiency fuel, there can potentially be more value gained. Lignin can be a relatively marketable product with a wide variety of potential uses (Table 1-3). These alternative applications of lignin is of great benefit, especially for small factories where the construction of boilers and running them day-to-day are a large cost that makes their business difficult. This is particular true for the mills that are not even running their recovery boilers and not recovering lignin in any form at present.

Table 1-3: Summary of uses of lignin and its derivative (reproduced from CPCB 2008)

Potential Areas	Application
In Ceramics	As binders to prevent cracking of clay during firing due to loss of moisture.
In Insecticide	Helps in decreasing the settling rate of insoluble insecticide powder suspension
In Rubber	The presence of lingo-sulphonates help in uniform carbon black dispersion in rubber It can also be used as an extender, modifier and reinforcing pigment in rubber and resin
As Emulsifier	Quite competitive with other commercially available emulsifier for stabilizing oil in water emulsion
Binders & Adhesives	Combination of lingo-sulfonates with urea, phenol and formaldehyde can be used as an adhesive for ply board /particle board
In Plasters	Addition of lingo-sulfonate to plaster allows the use of less water in the mix and gives improved set properties
As Sequestering agents	Ca, Ni,Zn,Al etc can be sequestered by lingo sulphonates
As protein precipitant	Lignin has the ability to react with amines and proteinaceous materials and thus can remove these compounds from sugar solutions, beer etc. Since lignin is relatively non toxic to cattle and poultry the protein – lignin complex can be used along with proteinaceous feed supplements
As Tanning Agent	Lignin sulphonates are widely used as tanning agent in leather industry

b. Decreasing environmental regulation violation

Currently, many smaller mills are only sporadically using traditional methods to treat black liquor because of the cost concern, and other times they are still directly discharging heavily polluted effluent into nearby water bodies. If membrane methods are proved to be economically more viable and more mills decide to adopt the method, there will be a decreasing amount of pollution discharge from pulp and paper mills in general. This helps mill to make better decisions on their treatment method and increases their chance of meeting regulations and maybe eventually creating zero-discharge, which is a trend in regulations now.

This value proposition is both attractive for paper mills and regulatory agencies. For paper mills, decreasing violation decreases the amount of fine and other potential risks and trouble, increasing the overall benefit. For regulatory agencies, an increase in environmental compliance would be highly valuable.

1.4.2 Long-term Values

a. Overall environmental benefit

In adopting membrane methods and learning to select the most effective methods for paper mills, there is more pollution and an increase possibility for environmental benefit. Additionally, in retrieving lignin from black liquor, the BOD, COD, TDS in the black liquor stream would significantly lower, creating a much better discharge even if the mills are not running chemical recovery boiler processes.

b. Scientific Research Value

Research progress in this project could potentially be more widely applied to the commercialization of membrane processes in industrial wastewater treatment in general. The eventual finding could be of interest to other research institutes that are working on membrane solutions for filtering complex organic molecules like lignin, and cost-benefit analysis for the filtering process

1.5 Cost and Benefit

The evaluation of cost and benefit factors are essential to determining whether our product would be accepted and widely distributed. In this evaluation, we are mainly focusing on the cost and benefit for our main customer if they decide to implement the membrane treatment system that the project puts forward. The general outline of the cost and benefit analysis for installation of membrane treatment system is shown in Figure 1, where the green "+" indicates potential profit and the red "-" indicated potential cost structures.

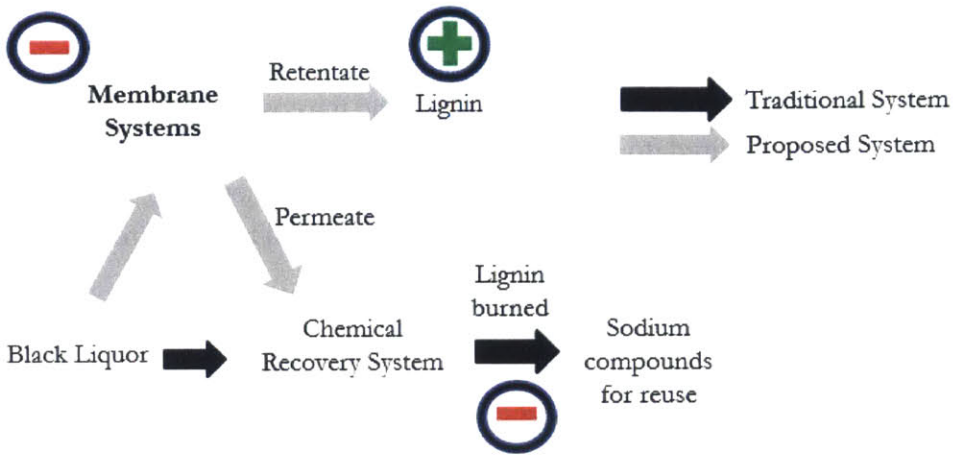

Figure 1-2: Cost and Benefit Diagram for installation of new membrane systems

1.5.1 Cost Structures for Paper mills

Cost for the mills to install this plant would first of all include cost of equipment installation and membrane purchase (indicated by the red "-" on membrane systems), as well as cost of operations including pressure pumps and cleaning process and so on. There would also be cost in extracting lignin from the boiler process, which means that less energy will be generated in the boiler due to the extraction (indicated by the red "-" below the lignin burned because with the new process, lignin is no longer burned as fuel). However, for mills that are not even operating the boiler or only operating it very infrequently to avoid the high operating cost, this cost of lignin extracting is negligible. This is unfortunately quite common in many small-scale brown paper mills in India. In addition, in the retentate stream, recovered lignin from the membrane may still be further refined to become usable or marketable, and that would also require extra costs.

1.5.2 Revenue Streams

Revenue for mills installing the membrane methods mainly include utilization of the lignin produced in the process (indicated by the green "+"). With lignin concentrated, it could be further used in recovery boilers or sent to the recovery boilers of other factors to use as a fuel. There has also been mentions of potentially using concentrated lignin solution as road construction materials (Mr. Aggrawal & CPPRI, personal communication). If lignin could be further separated and purified, it could also be directly used or sold on the market. In addition, a few costs will disappear (which could also be considered a relative revenue). For example, the caustics is recovered in the permeate steam, depending on the concentration of caustics and lignin, could potentially be reused in the cooking process. This reduces the cost of raw materials in the papermaking process. In

addition, the cost of environmental violations would slowly diminish. With previous practices, there have been environmental consequences with either fines from regulatory agencies or even having to shut down the factory for weeks due to pollution accumulation. With adoption of new treatment methods, these situations might appear less and less, and the cost would slowly diminish, creating a relatively revenue compared to cases before. Moreover, with the addition of the membrane operation, it's likely that the operational strength and frequency of the traditional chemical recovery system would decrease, and the cost of operation would also decrease, resulting in another relatively revenue.

1.5.3 Cost and Revenue for Developing Treatment Guidance

In addition to considering cost and benefit for the factory, it's also useful to think about the cost and benefit for the undertaking of this research & development process. This may be useful guidance for future groups who are interested in undertaking similar types of technology development. Current cost for developing treatment guidance includes cost of experimental design and equipment purchase. When research moves on to the next level, there will also be cost in setting up a pilot plant in the factory. If there is an existing customer with a strong interest, these costs are likely to be partially or fully sponsored by the customer.

For the treatment selection guidance, the revenue could potentially come from entities in need of using or purchasing this guidance to either improve their wastewater treatment systems as industries, or to improve regulatory schemes for public sector regulation agencies. In the long run, there could be a charge to using the guidance developed by our research, but currently there is no plan for commercializing the guidance. We intend to provide it as general scientific information that would be public to all, mainly because our costs are covered by the Tata Trust that intends to serve the general public. For future projects that not more self-contained and self-sustained, a stronger revenue stream is more likely to exist. There may also potentially be revenue streams from collaborative work with membrane manufactures, because our guidance would potentially increase the demand for membranes from paper mills across India. A collaboration could be formed and there may be shared profits with these manufactures. This conversation is yet to be carried out.

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