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BLACK LIQUOR IN PULP MILL AND ITS TREATMENT

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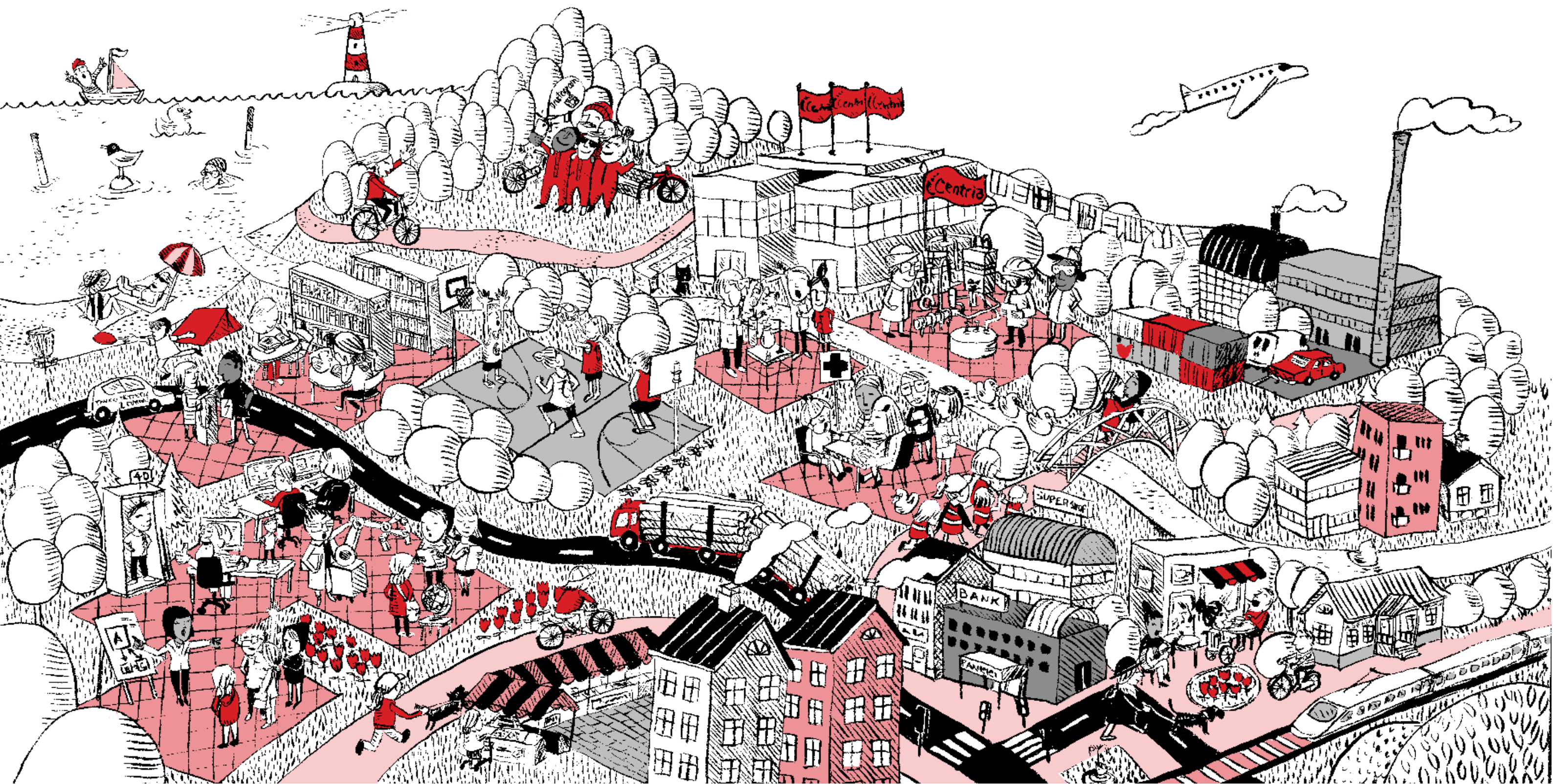

ABSTRACT

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Pulping process is an important part of papermaking. At present, the main steps of pulping production include wood handling, cooking, washing, screening, bleaching, drying and finishing. During the pulping process, black liquor is a kind of main spent chemicals, which is full of lignin, resin, starch, low molecular compounds, sodium hydroxide, sodium carbonate, sodium sulfide, sodium sulfate and other sodium salts combined with organic matter. Currently, the ways to treat black are combustion or acidification.

However, with the development of membrane separation, this technology has been studied by scholars and there are rich research results. Meanwhile, some research challenges and difficulties still exists, such as membrane manufacture and fouling; thus, it is supposed to be regarded as important research direction to actively explore various reliable and better treatment methods regarding black liquor.

This thesis work describes the pulping process, characteristics of white liquor and black liquor; then it depicts two current treatment technologies of black liquor in detail. It introduces new technologies of membrane separation in terms of different principles regarding black liquor, which are membrane filtration and electrodialysis, and some of the research results are listed. Moreover, the comparison of both two membrane treatments and the problems about membrane separation are also mentioned.

Key words
Black liquor, membrane separation

CONCEPT DEFINITIONS

List of chemical formulas

CO_3^{2-}

Carbonate ion

H_2SO_4

Sulfuric acid

Na^+

Sodium ion

Na_2CO_3

Sodium carbonate

$NaHCO_3$

Sodium bicarbonate

NaOH

Sodium hydroxide

Na_2S

Sodium sulphide

Na_2SO_4

Sodium Sulfate

OH^-

Hydroxyl ion

S^{2-}

Sulphur ion

TiO_2

Titanium dioxide

List of abbreviations

BOD

Biochemical oxygen demand

BL

Black liquor

BPM

Bipolar membrane

CBL

Carbonated black liquor

CEM

Cation exchange membrane

COD

Chemical oxygen demand

CSM

Cation selective membrane

ED

Electrodialysis

EDBM

Electrodialysis with bipolar membrane

Kappa number

Determination of lignin residues after pulp cooking

MC

Model compound

MF

Microfiltration

MWCO

Molecular weight cut-offs

NF

Nanofiltration

N_m

Membrane speed

N_s

Stirrer speed

pH

Hydrogen ion concentration

TMP

The transmembrane pressure

UF

Ultrafiltration

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1 INTRODUCTION

With the extensive development of the Internet, electronic media, and paperless communications, the demand for paper, like newsprint, high-value printing paper, and writing paper, has reduced since 2000 (FAO 2016). However, the global pulp and paper market is still growing stably at a rate of more than 1% per year (Bajpai 2018, 668).

Pulp mills convert wood chips into fibrous material called pulp, which is the raw material for different paper products (KnowPulp 2021). The production of pulp is completed through a mechanical or chemical pulping process or a combination of the two methods. As for chemical pulping, wood pulp is produced through chemical reactions. Sulfate pulping and sulfite pulping are two common chemical pulping processes. More than two-thirds of the world's pulp production comes from those two pulp mills (Domínguez 2016, 576).

Generally speaking, the pulp process includes wood treatment steps, such as debarking, chipping and storage; cooking process; screening and washing of pulp; bleaching and drying pulp; then pressing, drying and finishing. To gain white liquor again, spent chemicals called black liquor will be processed evaporation - incineration (occurred in recovery boiler) - causticization - lime burning operations, and then converted into white liquor in a causticizing plant (KnowPulp 2021). Moreover, acidification is also a mature method to gain lignin through neutralization, sediment, centrifugal dewatering and air drying, so that the finished product of lignin is extracted (Yang, Mu & Huang 2003, 698).

As a practical process for the concentration and purification of macromolecular substances in aqueous solutions, membrane technology has received extensive attention. Although the application conditions in the pulp industry are often harsh, many researchers are studying its feasibility (Liu, Liu, Ni, Shi & Qian 2004, 132). Up till now, numerous membrane technology has been investigated, such as microfiltration, ultrafiltration, nanofiltration and electrodialysis (Arkell, Olsson & Wallberg 2014; Bhattacharjee & Bhattacharya 2006; Haddad, Labrecque, Bazinet, Savadogo & Paris 2016; Kumar & Alén 2014; Liu et al. 2004; Mänttäri, Lahti, Hatakka, Louhi-Kultanen & Kallioinen 2015).

Owing to the limitation of space and time, it is hard to give an integrated introduction to all papermaking black liquor treatment technologies (Irfan, Butt, Imtiaz, Abbas, Khan & Shafique 2017; Buftia, Rosales, Pazos, Lazar & Sanromán 2018). The purpose of this paper is to describe the status of black liquor

treatment in the pulp industry and introduce membrane separation method of black liquor treatment. This paper is divided into three parts. The first part introduces the pulping process and characteristics of white liquor as well as black liquor. The second part describes the current treatment technology with respect to black liquor. The third part introduces new technologies of membrane separation about how the black liquor is treated, which are electrodialysis method and filtration technologies in terms of different principles, respectively.

2 BACKGROUND KNOWLEDGE OF BLACK LIQUOR

Pulp is an indispensable part of paper industry. At present, the commonly used pulping technology is Kraft pulping process (Haddad et al. 2016, 977; Mänttäri et al. 2015, 84). The pulping is a process of purely using physical or chemical methods or combining physical and chemical effectively to decompose and isolate plant fibres into primary colour pulp, and finally make the pulp into finished paper. The pulp mill will use white liquor to dissolve lignin, then the white liquor will be converted to black liquor (Rahman, Avelin & Kyprianidis 2020, 1231).

2.1 Pulp process

FIGURE 1. shows the overview of Kraft pulping process. There are main steps regarding production of pulp process and the two 'circles' describing the recycling of black liquor in papermaking (Rahman, Avelin & Kyprianidis 2020, 1231). To begin with, logs are cut in forest and then transported to pulp mill. The following step is debarking, which often happens in debarking drums aiming to eliminate bark. Through this process, logs will be chipped into chips by chipper, and those chips will be put in the chip yard (KnowPulp 2021).

The next step is cooking process. The aim of cooking in chemical pulp production is to utilize chemicals and heat to eliminate fragile fibrous lignin. Fibers including cellulose should be kept as long as possible, unbroken and strong as possible. In addition, attempts have been made to remove wood extracts that may cause blistering and precipitation during the process. Currently, sulfate cooking is the most common pulp production method. The chemicals used in the pulping process dissolve as much lignin as possible and as little cellulose as possible. Sulfate process uses a mixture of a transparent liquid, which is called white liquor and contains sodium hydroxide (NaOH) and sodium sulfide (Na_2S). NaOH reacts with lignin, while Na_2S inhibits cooking reaction and reduces cellulose degradation caused by sodium hydroxide, where the temperature is usually 150 ~ 170 ℃ (KnowPulp 2021).

After cooking process, the rest of main production process includes screening, washing, bleaching, drying and finishing. The object of screening is to remove hazardous substance such as knots, fiber bundles, shives, extractives, stones, sand and soot. As for washing, it aims to make the dissolved substances divide from pulp and recover the rest of liquor. Washing is able to minimize consumption of

bleaching chemicals. Bleaching is to increase the pulp's brightness and cleanliness, which is taken place in a bleach plant. In addition, the purpose of bleached pulp is to continue delignification and use bleaching chemicals to get rid of more residual lignin. Drying occurs after the wire and press sections, and here are two kinds of means: web drying and flash drying. During this process, the evaporated water combines with the dry air to complete the process. Finishing contains cutting and baling: cutting means that the continuous webs are cut into sheets in a cutting machine, and then stacked into bundles in a layboy section; in order to keep pulp in a good condition during the long transit, it is a necessary process to bale it (KnowPulp 2021).

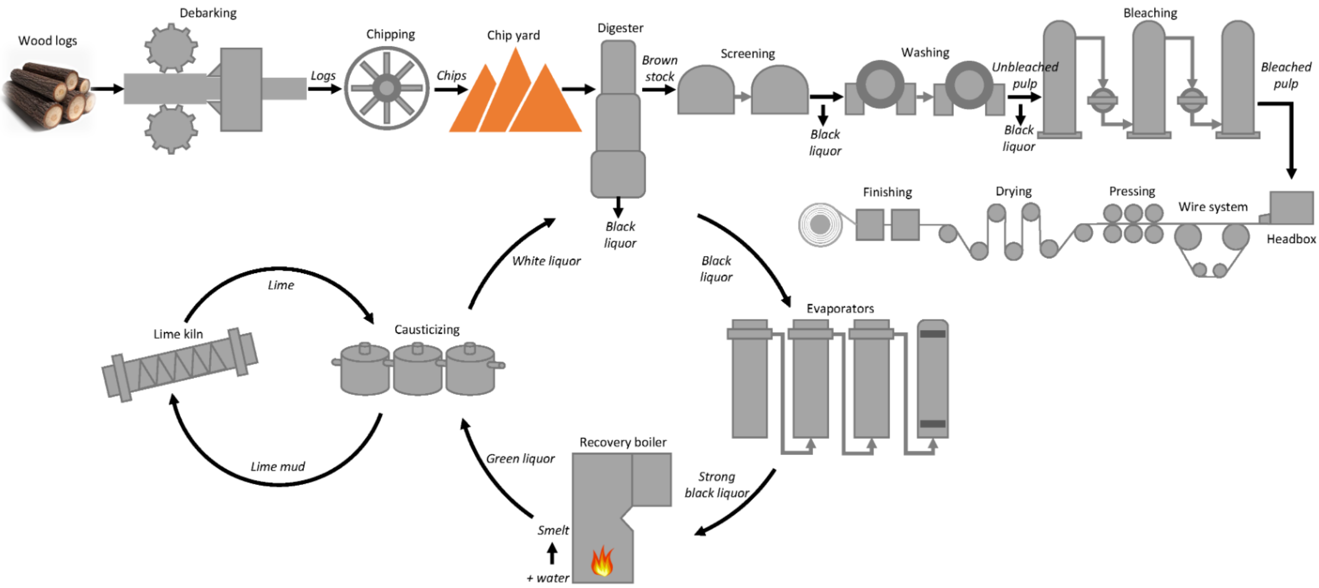

FIGURE 1. An overview of Kraft pulping process (from Rahman, Avelin & Kyprianidis 2020, 1231).

2.2 White liquor

Sulfate process uses a mixture of a transparent liquid, which is called white liquor and consists of an aqueous solution of sodium hydroxide (NaOH) and sodium sulfide (Na_2S) (KnowPulp 2021). The concentration of sodium hydroxide is 1.0 mol/L, the concentration of sodium sulfide is 0.2 mol/L, and the value of pH is 13.5 to 14.0. Besides, the active ingredients of the liquid are sodium hydroxide ion (OH^-) and sodium sulfide ion (CNBM International PULP & PAPER 2020). Sodium hydroxide (NaOH) reacts with lignin, while sodium sulfide (Na_2S) inhibits cooking reaction and reduces cellulose degradation caused by sodium hydroxide, where the temperature is usually 150 ~ 170 ℃ (KnowPulp 2021).

During the cooking process, non-fibrous materials such as lignin in the fibrous material react with the chemical solution to form a compound that is dissolved in the cooking liquor and then removed from the fiber to dissociate the fiber. When liquor is used for cooking, there are 3 stages of removal of lignin: the initial delignification stage, the main delignification stage and the residual delignification stage (CNBM International PULP & PAPER 2020).

In the initial stage, the temperature increases by 150 ℃, the delignification rate is 20 ~ 25%, and the α-aryl ether bond and the phenolic β-aryl ether bond in the lignin structure were destroyed. Heating the main delignification stage to 150 ~ 170 ℃ for heat preservation can remove 60% of the lignin and destroy the non-phenol β-ether bonds in the lignin structure. In the residual delignification stage, the de-lignin rate is 10 ~ 15% in the later stage of heat preservation at 170 ℃. At this stage, the carbon-carbon bonds are broken, lignin is condensed, and the pulp yield decreases (CNBM International PULP & PAPER 2020).

The main purpose of cooking process control is to improve the selectivity of delignification. It can be determined by factors like cooking time, cooking temperature, amount of alkali, and degree of vulcanization. The alkali concentration has a great influence on the speed of delignification, and also affects the yield and strength of pulp (CNBM International PULP & PAPER 2020).

2.3 Black liquor

The cooking liquor has dark colour after pulp cooking process so it is called black liquor. Black liquor is derived from the white liquor, which remains after cooking with sulfate and about 50% of the fiber material is dissolved in the cooking liquor; then it is divided from the pulp in the washing stage. In addition, the usual way to handle black liquor is by evaporation, and burn it in the recovery boiler to regenerate cooking chemicals and generate energy (CNBM International PULP & PAPER 2020; KnowPulp 2021).

The black liquor contains the inorganic matter and lignin, hemicellulose and cellulose degradation products, as well as the organic acids dissolved in the plant fiber raw materials. Inorganic substances are made up of free sodium hydroxide, sodium sulfate, sodium sulfide, sodium carbonate and sodium, silicon dioxide and other substances combined with organic substances. The black liquor contains about

30% ~ 35% of inorganic salts, and the main components are sodium hydroxide, sodium carbonate, sodium sulfide, sodium sulfate and other sodium salts combined with organic matter. Among them, the organic content takes up 65% ~ 70%, and the main components are lignin, resin, starch and low molecular compounds (CNBM International PULP & PAPER 2020).

3 CURRENT TREATMENT TECHNOLOGY

The cooking process in Kraft pulping produces black liquor; therefore, there are numerous proven approaches to treating and recycling the black liquor, such as combustion and acidification method. This chapter mainly states those two methods of handling black liquor (KnowPulp 2021; Macek 1999; Yang, Mu & Huang 2003).

3.1 Alkali recovery technology by combustion

The traditional combustion method for papermaking black liquor alkali recovery technology is a mature technology with a history of nearly one hundred years, which is also quite standardized (Macek 1999, 277). This technology is to evaporate and burn the black liquor to convert the sodium salt of organic matter in the black liquor into Na_2CO_3, dissolve it and then causticize it with lime to make the white liquor, and send it back to the boiling process for recycling as shown in FIGURE 1. This technology not only eliminates the hazardous substances of black liquor, utilizes the heat of organic matter in the black liquor, but also can recover alkali and white liquor at the same time. This alkali recovery technology is perfect in theory and mature in production practice. Therefore, this method is currently widely used all over the world, but it is only used in large paper mills at present (KnowPulp 2021).

There are 4 main steps of combustion: evaporation, recovery boiler, causticizing and lime burning. To start with, black liquor is transported to evaporators, and the main purpose of the evaporator is to remove the water in the black liquor and divide other streams which are mixed into black liquor. The main raw material entering the evaporator is weak black liquor with a dry solid content of 15 ~ 16%. Besides, the evaporator must also be able to recover the by-products during the cooking process, such as methanol, turpentine and soap. Then the following step is recovery boiler, which is used to get back some chemical such as sodium and sulphur of cook process; moreover, there are more power generated during the process of recovery, which can be changed into steam energy, therefore, the recovery boiler can also be regarded as a steam boiler (KnowPulp 2021).

The subsequent step is called causticizing, which is to convert the sodium carbonate in the green liquor into sodium hydroxide, with the help of slaked lime. The reaction of causticizing takes place in the causticizing tank, and the main reactants are slaked lime and sodium carbonate, which are the main

components of green liquor. And the reaction products are NaOH as well as lime mud. The last process is lime burning: after the causticizing reactions, lime reburning converts the lime mud to calcium oxide, which can be reused in the causticizing process. Lime reburning is part of the chemical cycle, which is named the “lime cycle”. The process is completed in the causticizing process, and the causticizing equipment and the lime reburning equipment together form a lime circle. After the causticizing reaction, the lime is burned again to convert lime mud into calcium oxide, which can be reutilized in the causticizing process (KnowPulp 2021).

3.2 Acidification method

The traditional acidification method is to precipitate the alkaline black liquor with acid. On the one hand, it adjusts the pH of the black liquor. On the other hand, it can make lignin insoluble substance, which can help separate lignin and change the colour of original black liquor from black to brown. Using this method to produce lignin from black liquor can effectively remove organic matters. It is suitable for the treatment and utilization of black liquor in small and medium-sized paper mills as well (Yang, Mu & Huang 2003).

Below is a flow diagram (FIGURE 2.) to describe how the black liquor treated using acidification method: to begin with, add H_2SO_4 to neutralize black liquor; secondly, filter the mixed solution to get the sediment, and the rest of mixed solution will be recycled; thirdly, the sediment, lignin, then is put into centrifugal machine for dehydration; next step is to dry the lignin. In this way, the finished product of lignin is produced (Yang, Mu & Huang 2003, 698). Yang, Mu & Huang (2003, 700) did some experiments regarding 2 kinds of black liquor which are derived from pine chips and bamboo chips, through acidification, they have found when the black liquor is acidified to pH 3.5 ~ 4.0 and under the optimum flocculation conditions (temperature 70 ℃, time 3 h), the lignin removals of pine and bamboo black liquor reach 92.3 % and 93.7 %, respectively, which can be regarded that the lignin will be almost eliminated.

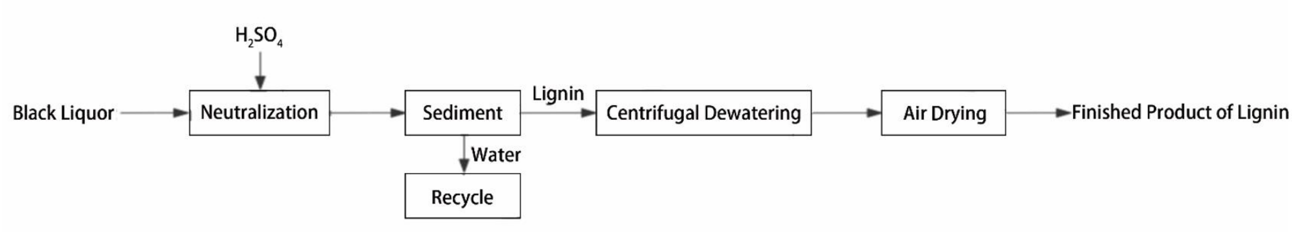

FIGURE 2. Extraction of lignin from black liquor by using acidification method (adapted from Yang, Mu & Huang 2003, 698).

4 MEMBRANE SEPARATION METHOD OF TREATING BLACK LIQUOR

Nowadays, membrane separation technology has been widely used in many fields of water treatment. Generally, membrane technology can be used to produce drinking water from surface water, groundwater, brackish water or seawater, or to treat industrial wastewater, which is then discharged or reused. At the same time, membrane technology has entered the field of treating secondary or tertiary municipal wastewater. In most cases, it can be implemented at room temperature, with little loss of active ingredients, such as antibiotics and protein production. Moreover, the membrane system is compact and modular, and takes a small area compared with traditional processing systems. In countries where land is scarce, such as Japan and Singapore, the application of membrane technology can greatly save land occupation (Chen, Mou, Wang, Matsuura & Wei 2011, 272).

With the development of the times and the progress of science and technology, the application of membrane separation method in the treatment of black liquor from the pulping industry has made considerable progress in recent years. Membrane separation method refers to the general term for methods that use special membranes to selectively separate certain components in liquids. According to the principle of the membrane separation, the used solid membrane separation method can be divided into membrane filtration like microfiltration (MF) and electrodialysis (ED) (Chen et al. 2011, 272-273 & 281).

As for this chapter, it takes some examples of membrane filtration method as well as electrodialysis technology to treat black liquor, lists some problems about this technique, and gives the comparison of different membrane separation approaches.

4.1 Method of membrane filtration

Today, microfiltration, ultrafiltration and nanofiltration technology are being used worldwide for treating various waters, including river, reservoir and lake waters. This technology has been used in municipal drinking water application for more than 10 years as well, which are most commonly used to separate a solution that has a mixture of some desirable components and some that are not desirable (Chen et al. 2011, 277). FIGURE 3 includes a simple schematic of membrane process in which the feed stream is divided into a retentate and a permeate stream. (Mulder 1991, 5).

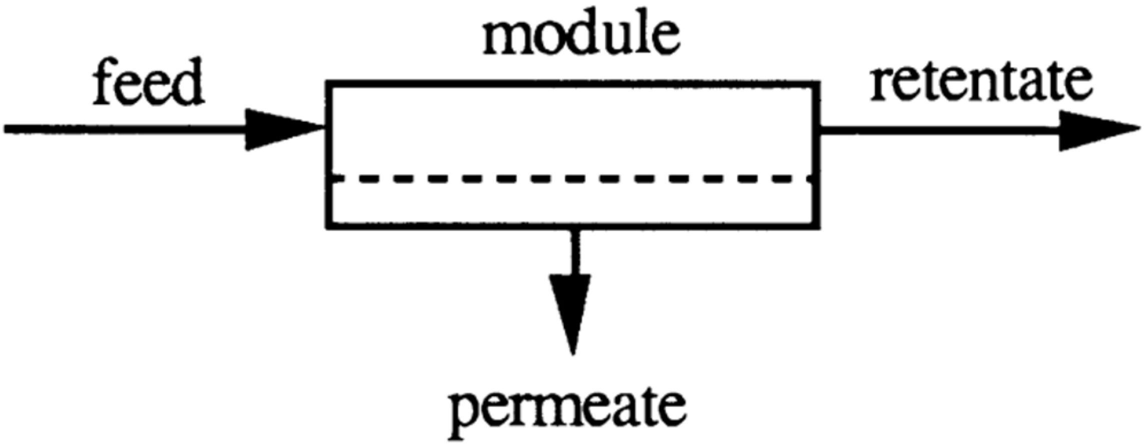

FIGURE 3. Schematic of a membrane process (from Mulder 1991, 5).

Membrane is the core of every membrane process and can be regarded as a selective barrier for the penetration between two phases. FIGURE 4 is a schematic diagram of membrane separation (Mulder 1991, 6). According to different driving force such as pressure difference, the different kinds of substance in mixture can be separated, and MF, UF as well as NF are a kind of the application by using that principle (Chen et al. 2011, 274-279; Mulder 1991, 6).

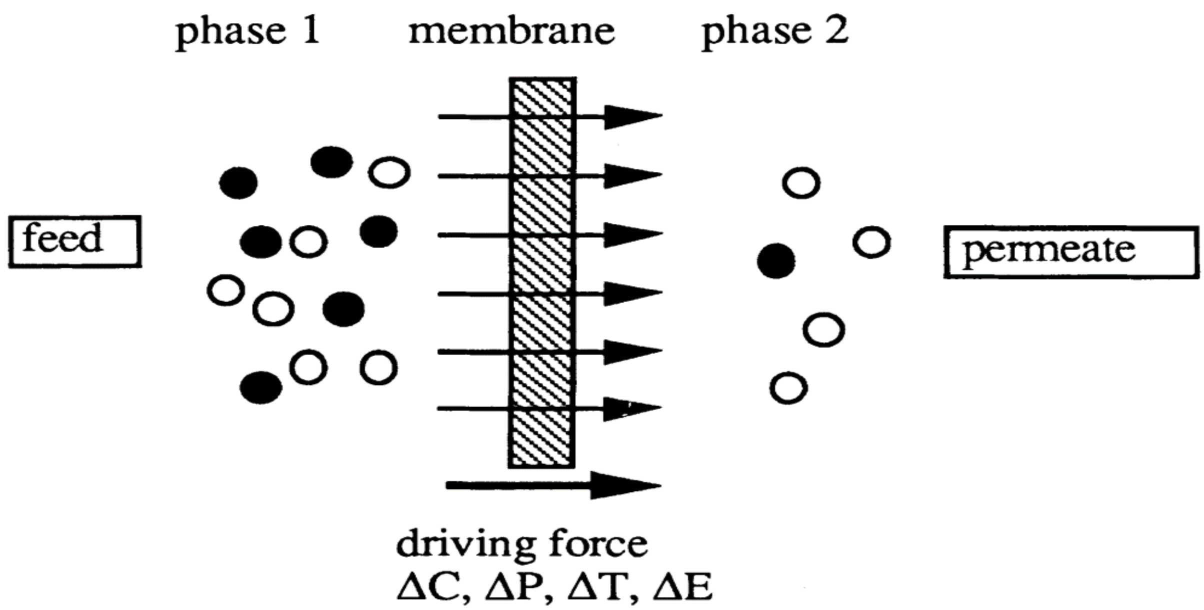

FIGURE 4. Schematic representation of a two-phase system separated by a membrane (from Mulder 1991, 6).

Microfiltration is a membrane filtration process that removes micron-sized particles from fluids. The pore size of MF membrane pore sizes ranging from 0.1 to 10.0 mm, through which microorganisms cannot pass. Therefore, microfilters can be applied to disinfect water solutions. For instance, the smallest bacterium pseudomonas diminuta with a diameter of 0.3 mm can be disinfected by the MF membrane with a smaller pore size. Besides, both organics and inorganics can be through the MF membranes (Chen et al. 2011, 274-275).

Adsorption and entrapment are the main mechanism for traditional depth filtration, while the MF membrane mainly adopts a sieving mechanism with distinct pore sizes to keep particles larger than the pore diameter. Hence, this the technology provides membranes with absolute rating, which is highly desirable for critical operations like sterile filtration of parental fluids, sterile filtration of air, and preparation of particulate, and ultra-pure water for the electronics industry. Generally, the MF membranes are usually manufactured from natural or synthetic polymers such as cellulose acetate, polyvinylidene difluoride, polyamides, polysulfone, polycarbonate, polypropylene and polytetrafluoroethylene. Additionally, some newer MF membranes are ceramic membranes based on alumina, which is formed during the anodization of aluminium, and some are carbon membranes. Glass is being used as a membrane material. Zirconium oxide can also be piled onto a porous carbon tube. Sintered metal membranes are made from stainless steel, silver, gold, platinum and nickel, in the form of discs and tubes. The properties of membrane materials are directly reflected in their end applications. Their criteria for their selection include mechanical strength, temperature resistance, chemical compatibility, hydrophobic property, hydrophilicity, permeability, perm-selectivity and the cost of membrane material as well as manufacturing process (Chen et al. 2011, 275-276).

The principle of ultrafiltration is also a principle of membrane separation process. Using a pressure-active membrane, ultrafiltration traps colloids, particles, and substances with relatively high molecular mass in the water under the external driving force, while water and small solute particles pass through the membrane. Its separation mechanism mainly relies on physical sieving. In ultrafiltration separation, after a certain pressure is applied to the material liquid, the ultrafiltration membrane can retain high molecular substances and colloidal substance, while water and low molecular substances pass through the membrane. That is, when the water passes through the ultrafiltration membrane, most of the colloids contained in the water can be removed, and a large amount of organic matter can be removed at the same time. In general, ultrafiltration membrane is able to retain species in the range of 300 ~ 500,000 Da of molecular weight. They are typically rated by molecular weight cut-off (MWCO), which is a

fictive value used to perform the retention property of membrane (Chen et al. 2011, 277). As for treatment of black liquor, ultrafiltration membrane can permeate water and solute with low relative molecular mass in the black liquor. The use of membrane separation method can not only greatly decrease the organic loading of black liquor, but also can recover and comprehensively utilize lignin, while concentrating the black liquor (Arkell, Olsson & Wallberg 2014).

The transmembrane pressure (TMP) is defined by the equation (1), where P_{in}, P_{out} and P_p are the pressure at the inlet, outlet and permeate side of the membrane, respectively (Arkell, Olsson & Wallberg 2014, 1793).

$$TMP = (P_{in} + P_{out})/2 - P_p \qquad (1)$$

Nanofiltration is a form of filtration that uses membranes to separate different fluids or ions. As it can operate at much lower pressures, normally 7 ~ 14 bars, and passes some of the inorganic salts, NF is used in applications where high organic removal and moderate inorganic removals are desired. NF is capable of concentrating sugars, divalent salts, bacteria, proteins, particles, dyes and other constituents that have a molecular weight greater than 1,000. Membranes used for NF are made of cellulose acetate and aromatic polyamide with characteristics such as salt rejections from 95% for divalent salts to 40% for monovalent salts and an approximate MWCO of 300 for organics (Chen et al. 2011, 278-279).

4.1.1 Treatability of Kraft black liquor by microfiltration and ultrafiltration

Liu et al (2004) has studied the feasibility of black liquor treatment by various organic UF and inorganic MF membranes. The MF membrane is based on batch experiments under a transmembrane pressure of 200 kPa and temperature of 30 ℃. The results show that although the diameter of the lignin molecule is one-hundredth to one-tenth of the membrane, the MF membrane can retain about 80% of lignin, while UF membrane can retain about 90% of lignin, and both MF and UF membranes can reject silica. According to the results of batch experiments, the flux of the inorganic membrane are closely related to concentration polarization, while the flux of organic ultrafiltration membrane depends on the material and the pore sizes. In addition, the inorganic membranes could be regenerated by washing of NaOH solution and hydrochloric acid solution and other steps.

A continuous experiment under a crossflow velocity of 2.3 m/s and transmembrane pressure of 200 kPa, the flux of the 0.2 μ inorganic MF membrane was 200 L/(m^2·h) at 32 °C after operation for 374 h, and 400 L/(m^2·h) at 63 °C for 625 h. The membrane was not cleaned during the operation, and the experiment ran smoothly for over 40 days (Liu et al. 2004).

In this early study, it only uses fewer chemicals in the process, which helps reduce the negative impact of these chemicals on the entire process (Chen et al. 2011, 272), and most of the lignin in the black liquor was recovered through the use of microfiltration membranes and ultrafiltration membranes. At the same time, factors affecting the flux of inorganic membranes and organic membranes, and cleaning methods of repairing inorganic membranes were also discovered. Moreover, this team also conducted an experiment: after more than 40 days, the inorganic microfiltration membrane can still maintain good operating condition (Liu et al. 2004).

4.1.2 Ultrafiltration of black liquor using rotating disk membrane module

Bhattacharjee and Bhattacharya (2006) used a laboratory fabricated stirred and rotating disk batch UF cell in an attempt to improve flux for the treatment of black liquor obtained from sulfite pulping industries. Asymmetric cellulose triacetate membrane of 5000-molecular weight cut-off was applied in the experiments.

After experiment, using pore-plugging model and a combination of osmotic pressure model with Speigler–Kedem model from irreversible thermodynamics to confirm the relationship of different operating variables, like transmembrane pressure (TMP), stirrer speed and membrane rotation speed. For example, when constant stirrer speed (N_s) is 1000 rpm, a 32% enhancement of initial flux as compared to fixed disc was obtained with membrane rotating at 600 rpm speed, whereas, a 22% increase in initial flux as compared to fixed disc was observed with membrane rotating at 300 rpm according to FIGURE 5. But higher values of flux means that the cost of power will also increase (Bhattacharjee & Bhattacharya 2006, 289-290).

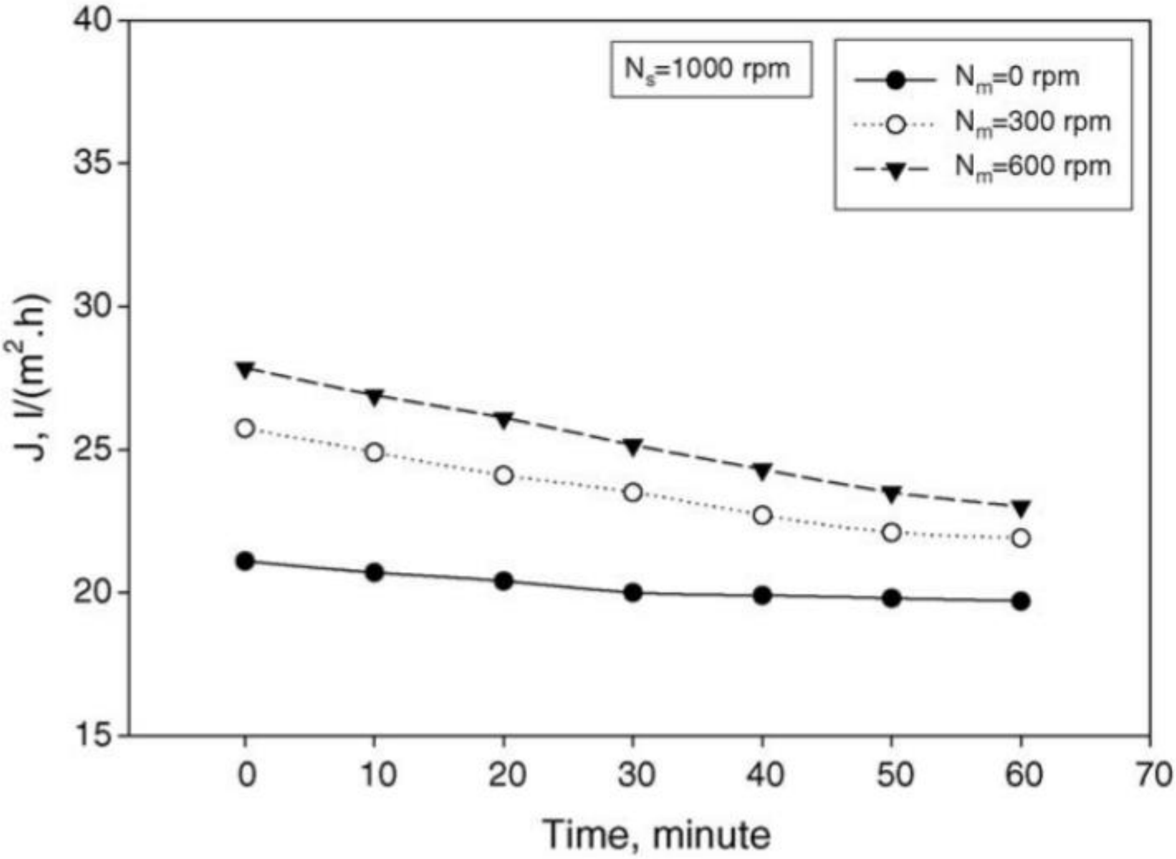

FIGURE 5. Effect of membrane rotation speed on flux (TMP = 5 kg/cm^2, N_s = 1000 rpm) (from Bhattacharjee & Bhattacharya 2006, 288).

Another result showed that flux enhancement of the order of 60% was observed after a period of 1 h of UF experimentation using rotating disc module as compared to the fixed disc one at a TMP of 7 kg/cm^2. Furthermore, membrane rotating was proved to be more efficient in reducing concentration polarization compared to stirring action (Bhattacharjee & Bhattacharya 2006, 290).

After measurement, when TMP is 8 kg/cm^2, the retention rate of lignin is about 75%. And lower retention was discovered at lower pressures. As the pressure rises, more liquid passes through the membrane, leaving more solute retention, therefore, reducing pore openings and then increasing rejection. In the original black liquor, the lignin purity is 36 ~ 38% (based on lignin concentration/total solid concentration) at first; the purity of lignin can become 48% after the ultrafiltration operation with the stirring speed of 500 rpm using the turntable membrane module at TMP of 7 kg/cm^2. Both BOD and COD are reduced by increasing TMP. The results showed that when ultrafiltration was performed in a rotating disk membrane with a TMP of 7 kg/cm^2 and a stirrer speed of 500 rpm, the BOD of the

permeable membrane was reduced by 70%, while the COD was reduced by 67% (Bhattacharjee & Bhattacharya 2006, 289).

This is a novel and interesting way to solve the problems of membrane separation by redesigning the arrangement of UF membranes, and this design solution to a certain extent solves the problems of flux decline and associated fouling. Through a series of analysis, this method has achieved beneficial results such as reduction of both BOD and COD, but the control of energy consumption and cost are also worth paying attention to (Bhattacharjee & Bhattacharya 2006).

4.1.3 Lignin separation from softwood black liquor

Arkell, Olsson and Wallberg (2014) used one ceramic and three polymeric nanofiltration membranes, whose molecular weight cut-offs (MWCO) in the range of 200 Da to 1 kDa, separated lignin from black liquor. The results showed that Tami membrane (made of TiO_2) and MPF-36 membrane (polymeric nanofiltration membrane), which both have the MWCO of 1 kDa, have a good performance of treating black liquor. And the operating conditions of the concentration study are: cross-flow velocity of Tami membrane is 4 m/s, TMP is 20 bar; cross-flow velocity of MPF-36 membrane is 4 m/s, TMP is 35 bar. TABLE 1. shows the characteristics of the membrane.

TABLE 1. Characteristics of the membranes used (adapted from Arkell, Olsson & Wallberg 2014, 1794).

Name	Type	MWCO (Da)	Material	Length (mm)	Inner diameter (mm)	Area (m^2)	NO. of channels
Atech	UF	20,000	Al_2O_3-TiO_2	1000	6	0.13	7
Tami	NF	1000	TiO_2	1178	6	0.20	8
MPF-36	NF	1000	Composite	1000	12.7	0.040	1
MPF-31	NF	600	Composite	1000	12.7	0.040	1
MPF-34	NF	200	Composite	1000	12.7	0.040	1

Ultrafiltration was regarded as a form of pretreatment before nanofiltration, which was able to increase the flux significantly in the nanofiltration step. Besides, the ceramic membrane (Tami) showed a higher flux and lower lignin retention than the polymeric membranes. The two membranes with a molecular

weight cut-off value of 1 kDa proved to have the best performance in the parameter study, so they were used in the concentration study. After the concentration study, with Tami membrane, the concentration of total lignin in the retention went up to 230 g/L, and with MPF-36 membrane to 284 g/L. The hemicellulose concentration of the two membranes increased to 9 g/L (Arkell, Olsson & Wallberg 2014, 1797-1798).

In the permeation process of ultrafiltration, the flux of nanofiltration is significantly higher than that of untreated black liquor. The flux of Tami membrane in the two conditions, with or without UF, is higher than that of MPF-36 membrane. In untreated black liquor and pretreated black liquor, the retention rate of lignin and hemicellulose by MPF-36 membrane is higher than that of Tami membrane in NF, which is consistent with the results of the parameter study. Regardless of if the black liquor is subjected to ultrafiltration treatment, the lignin retention of MPF-36 membrane is basically the same. After ultrafiltration pretreatment, the lignin retention rate of Tami membrane declined a little compared with that of Tami membrane without UF (Arkell, Olsson & Wallberg 2014, 1797-1798).

The nanofiltration technology can effectively separate the lignin and hemicellulose in the black liquor with or without pre-trement of UF. The introduction of UF before NF can increase the flux of NF, but it will reduce the retention rate of lignin. The preliminary economic analysis shows that MPF-36 membrane without UF pretreatment is recognized as the most cost-effective choice.(Arkell, Olsson & Wallberg 2014, 1799).

4.1.4 Recovery of organic acids from Kraft black liquor

Mänttäri et al (2015) have studied separation phenomena in the ultrafiltration and nanofiltration stages of the recovery and purification of organic acids from black liquor. To evaluate if the nanofiltration performance is affected by ultrafiltration. The experiments were designed and compared as shown in FIGURE 6. The difference between the two process schemes tested was that in the first the lignin removal was started at the ultrafiltration stage and continued during the precipitation with acid. In the second test option, only the acid precipitation stage was applied for lignin removal.

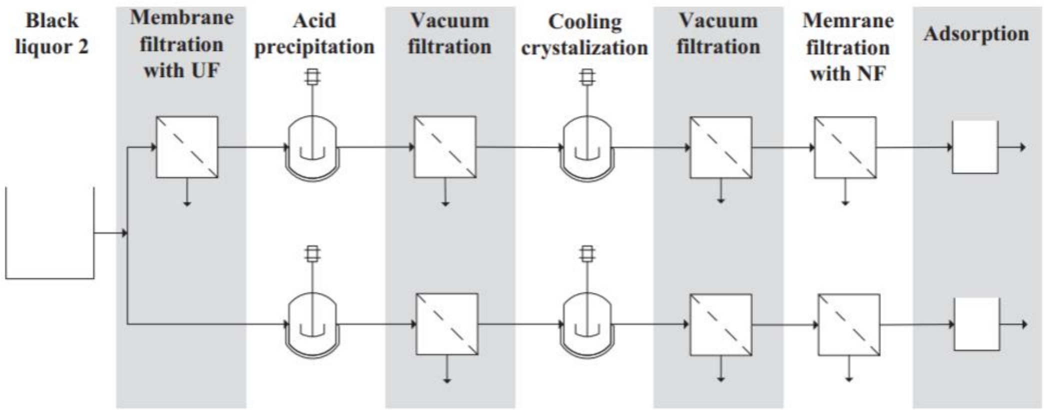

FIGURE 6. Process scheme under examination in this study (from Mänttäri et al. 2015, 85).

The experimental comparison results showed that a 1 kDa UF membrane is used for pre-filtration before acid precipitation to produce a concentrated lignin fraction by removing 75% of lignin. The permeation rate of organic acids in the UF membrane is 1.4 times that of water, which makes the yield of acid in the UF permeate very high. The acid purity on total dissolved solids also increased to 33% (Mänttäri et al. 2015, 89-90).

The results proved that the acidification of black liquor, and the separation of sodium salt by cooling crystallization and nanofiltration, can increase the purity of analytical organic acids from 21% in the original black liquor to more than 80% penetration in NF. However, the ultrafiltration before the precipitation and cooling crystallization process has an adverse effect on the acid purity and flux of the downstream nanofiltration, and will not increase the acid purity after the nanofiltration (Mänttäri et al. 2015, 90).

The results also showed that the retention of small molar mass compounds (acids and phenolic compounds) is very sensitive to changes in filtration conditions and feed composition. Nanofiltration removes a large amount of sulfate ions and residual phenolic compounds, but penetrates most of the acidic molecules under acidic pH conditions, and the final organic acid purity of the total dissolved solids after nanofiltration is up to about 80% (Mänttäri et al. 2015, 90).

According to this experiment, the membrane separation system is easy to operate and has a good selectivity, which can separate substances at the molecular level; in addition, it also has an excellent performance (Chen et al. 2011, 273-274). This is another attempt at membrane separation. It focuses on

the organic acids in the black liquor, rather than other ingredients such as lignin. Throughout the experiment, although the ultrafiltration membrane can remove a lot of lignin, it cannot increase the purity of the acid after nanofiltration. In addition, this method is quite groundbreaking, and it is also relatively rare to extract organic acids by using membrane separation methods. Therefore, this method has the value of in-depth research and good development prospects (Mänttäri et al. 2015).

4.2 Electrodialysis technology

There have been many reports on the alkali recovery of papermaking black liquor by electrodialysis method. The basic principle of the alkali recovery of Kraft pulping black liquor by electrodialysis method can be shown in FIGURE 7. (Haddad et al. 2016; Jin et al. 2013).

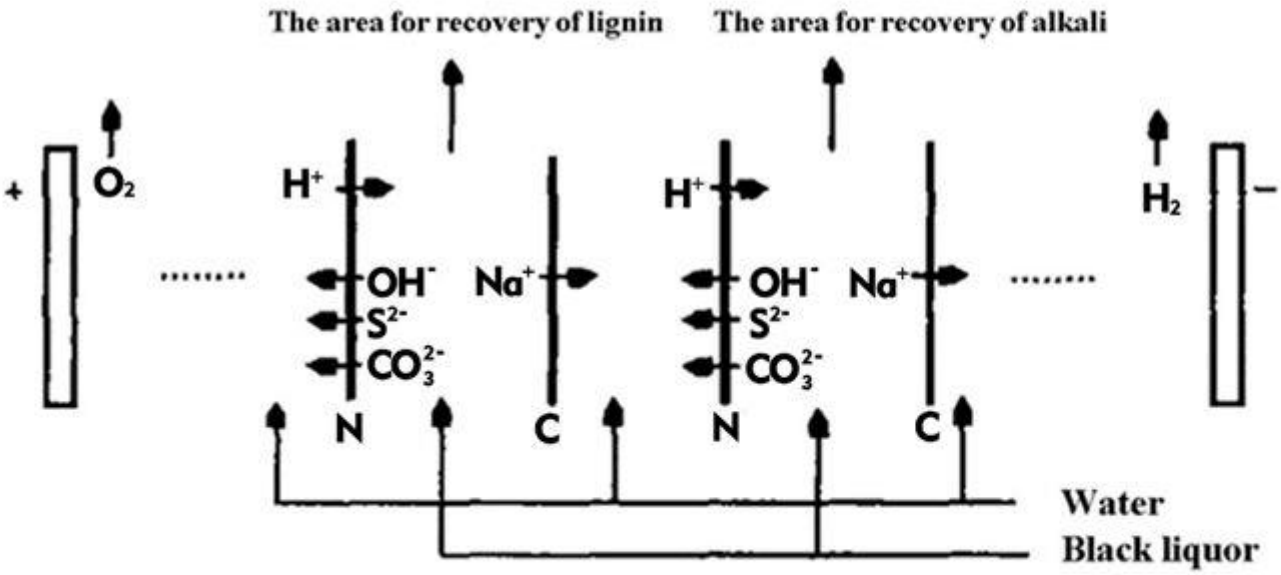

FIGURE 7. The principle diagram of electrodialysis method (adapted from Haddad et al. 2016, 979).

Between the positive electrode and the negative electrode of this electrodialyzer, several groups of positive and neutral membranes are alternately placed in parallel. Among them, the cation membrane only allows cations to pass, while the selected neutral membrane does not have selectivity for charge, but it has selective to particle size; in other words, it allows both anions and cations to pass through. However, large molecules like lignin are not allowed to pass (Jin et al. 2013, 978-979).

The black liquor is introduced into each compartment, and water is introduced into the adjacent chamber of the black liquor. When a voltage is applied at both ends, the Na^+ in the black liquor enters the right adjacent chamber through the cationic membrane under the action of an electric field, while the OH^-, S^{2-} and CO_3^{2-} enters the left adjacent chamber through the neutral membrane. The lignin flows out with the mixed liquid after removing those ions and then it will be recovered (Jin et al. 2013, 978-979).

In the adjacent chamber, Na^+ passing through the positive membrane form NaOH, Na_2S and Na_2CO_3 by combining with OH^-, S^{2-} and CO_3^{2-} passing through the neutral membrane, thereby achieving the purpose of recovering alkali. Meanwhile, an electrode reaction occurs in the anode chamber to release oxygen, while hydrogen will be released in the cathode chamber (Jin et al. 2013, 978-979). As a result, black liquor will be converted into white liquor again.

4.2.1 Electrodialysis method of recovery of sodium

Electrodialysis is used to partially recover sodium hydroxide and sodium-free fatty acids (formic acid, acetic acid and various hydroxycarboxylic acids) from alkaline hardwood black liquor with a pH of about 14. The whole experiment is divided into 2 stages. In the first stage, part of the lignin is carbonized (pH = 8.5) black liquor precipitation. In the second stage, the carbonized black liquor is quite acidified with H_2SO_4 (pH about 2.5) to precipitate more lignin and release fatty acids. The generated Na_2SO_4 was divided from the acidified liquid by methanol precipitation, and NaOH and H_2SO_4 were obtained by electrodialysis (ED) treatment (Kumar & Alén 2014).

TABLE 2. presents the concentration of lignin in different black liquors, where the cooking yield is 52% and kappa number is 19 for black liquor (BL). To start with, carbon dioxide is used to lower the pH of the solution to precipitate lignin. In the initial stage of acidification (pH approximately 9), approximately 59% of the initial lignin was eliminated. Directly acidify carbonated black liquor with H_2SO_4 or dilute carbonated black liquor (1:5) to decrease its pH value (about 2), which is able to make the removal rate of lignin reach 76% and 66%, respectively (Kumar & Alén 2014, 9468).

TABLE 2. Concentration of lignin in various black liquor samples (g/L) (adapted from Kumar & Alén 2014, 9468).

Liquor sample	pH	Lignin (g/L)
BL	13.5	82.1
CBL	8.5	34.0
CBL (1:5)	8.2	6.2
Acidified CBL	2.0	8.3
Electrodialyzed CBL (1:5)	2.3	2.1

After 5 hours of treatment of 1 L carbonated black liquor (1:5), the data shows that sodium recovery rate is about 90%, the average recovery rate of sodium is 0.044 mol sodium per hour, and the power costs are 1.76 kWh/mol sodium. In the last step of the experiment, these values increased significantly (Kumar & Alén 2014, 9468).

Using 5 L carbonated black liquor (1:5) as the diluent for the ED experiment, the energy consumption and the recovery rate of sodium are enhanced. The data of sodium shows that the speed of recovery is pretty high (0.138 mol sodium per hour); besides, the energy consumption of 0.2 kWh/mol sodium gains the maximum recovery rate about 70% after 10 hours. It was also found that energy consumption appeared to be constant and began to rise when the sodium concentration of the diluent reduced (Kumar & Alén 2014, 9468).

As for MC Na_2SO_4 and precipitated Na_2SO_4, during the ED experiment, the behavior of MC Na_2SO_4 and precipitated Na_2SO_4 (containing some black liquor impurity) was nearly similar (FIGURE 8.). This corresponds to a final sodium concentration of 13.2 g/L and 12.6 g/L, respectively, with a sodium recovery rate of about 90% (Kumar & Alén 2014, 9468).

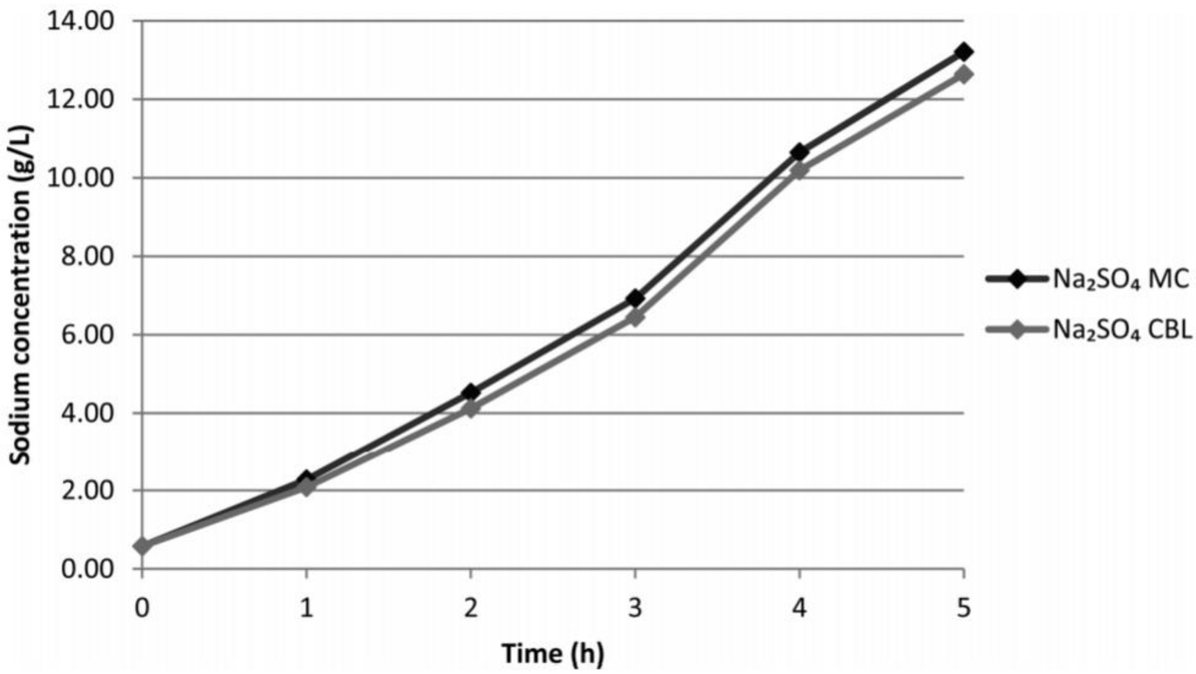

FIGURE 8. Behavior of MC and precipitated Na_2SO_4 during the electrodialysis experiments (from Kumar & Alén 2014, 9468).

In the treatment time of 5 h, the recovery rates of sodium in carbonized black liquor, model Na_2SO_4 and precipitated Na_2SO_4 were 0.044, 0.110, and 0.104 mol sodium per hour, respectively, and the corresponding energy consumption was 1.76, 0.38, and 0.43 kWh/mol sodium, respectively. In each case, the total sodium recovery is approximately 90% (Kumar & Alén 2014, 9468).

As for the black liquor produced during the Kraft pulping, there are a large amount of degraded organic matter from carbohydrates (i.e. aliphatic carboxylic acids) and lignin. Integrating part of their recycling into the Kraft plant is an interesting alternative fuel. In this way, a basic problem is to recover the sodium chemically combined with these fractions. Research results show that lignin can be separated from black liquor by carbonation and H_2SO_4 acidification. The results also show that ED is an attractive technology to recover NaOH from Na_2CO_3/$NaHCO_3$ and Na_2SO_4, which also leads to the recovery of H_2SO_4. In addition, ED can release sodium in a high efficiency from organic substances and can produce fatty acid-rich fractions for further utilization (Kumar & Alén 2014, 9468).

4.2.2 Effect of electrodialysis with bipolar membrane

Using electrodialysis with bipolar membrane (EDBM) is a promising and green way to acidify the black liquor and extract the lignin. Therefore, Haddad et al. (2016) took the study to evaluate the performance of the EDBM acidification process according to current efficiency and energy consumption. Studies have shown that improving the hydrodynamic characteristics of the system can delay and slow down the self-aggregation and precipitation of lignin in the EDBM pile as well (Haddad et al. 2016).

The BPMs and CEMs were placed in an alternating pattern and the EDBM stack was surrounded on one end by the anode compartment and on the other end by the cathode compartment according to FIGURE 9. The stack was connected to three holding reservoirs by three pumps. There was 2 liters of black liquor, NaOH and electrode rinse solution, which is Na_2SO_4, in each of the reservoirs, respectively (Haddad et al. 2016, 978).

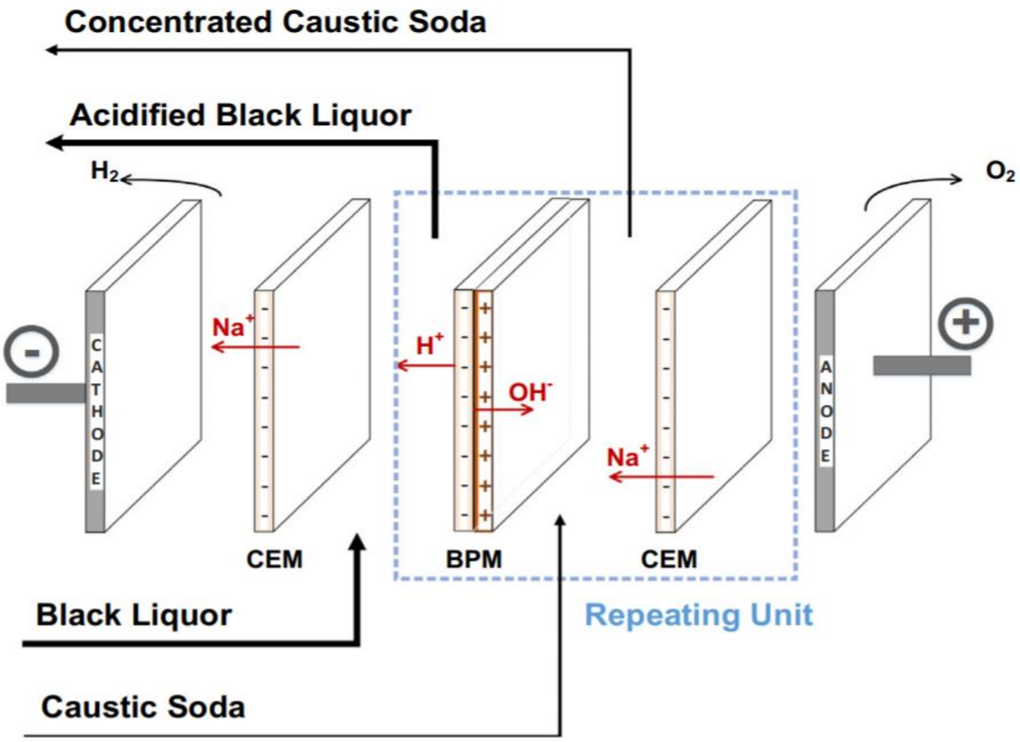

FIGURE 9. A schematic illustration of EDBM stack (from Haddad et al. 2016, 979).

In order to reduce the membrane fouling, all the experiments were conducted at the maximum flowrate corresponding to the pumps and stack configuration. A jacket coil heat exchanger was installed in each reservoir to maintain a constant temperature. Direct current power is the driving force of the system.

When the EDBM process temperature is 55 ℃ and the total dissolved solid content in the black liquor solution is 20 wt.%, the current efficiency is the highest and the energy consumption is the lowest (Haddad et al. 2016, 983-984).

In addition, in order to promote the filtration of lignin and improve the extraction rate of lignin, the final pH value of acidified black liquor is supposed to be between 8 and 10. The lowest pH of acidified black liquor was 10.45 during the experiment. Therefore, it is best to terminate the EDBM step before the overall system resistance rises rapidly and to continue the acidification process through chemical acidification to prevent the consumption of large amounts of energy (Haddad et al. 2016, 982).

It is a kind of application of bipolar membranes, which is also a new design scheme. Compared with the traditional design scheme of electrodialysis, the internal components have been optimized. However, the way to reduce membrane fouling still needs chemical cleaning (Haddad et al. 2016).

4.2.3 A novel membrane-assisted electrochemical approach

Jin, Tolba, Wen, Li & Chen (2013) studied a novel membrane-assisted electrochemical approach for the precipitation of lignin from black liquor has been developed. Without the addition of acid or carbon dioxide, the pH in the black liquor solution was lowered to 4.7 due to water electrolysis, leading to pH-dependent lignin precipitation. Meanwhile, sodium ions traversed the membrane to the cathode compartment to balance the OH^- that was generated in the cathodic reaction, facilitating caustic recovery. In addition, it has been demonstrated that the pH change was significantly influenced by the electrolyte condition in the system. With decreasing cation concentration in the cathode compartment, Na^+ transport through the membrane was facilitated, which inhibited competitive hydrogen ion transport and improved the performance of the electrochemical cell. A U-shaped electrochemical cell as shown in FIGURE 10. was segmented into the anode and cathode compartments.

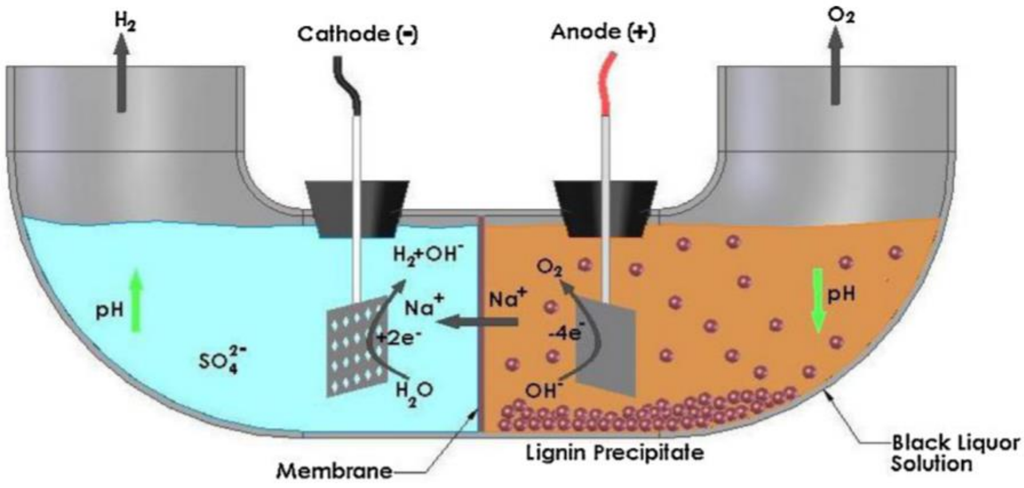

FIGURE 10. Schematic diagram of the experimental setup designed for the membrane-assisted electrochemical treatment of black liquor (from Jin et al. 2013, 612).

Jin et al (2013, 616) have studied the methods of acidification and membrane-assisted electrochemical treatment to precipitate lignin from black liquor, and found that its final pH value is basically the same, as shown in TABLE 3. The removal of lignin is very important for the treatment of black liquor, which can be estimated by measuring COD value. Under different treatment methods, the final COD value is different. The removal of COD by electrochemical treatment is better than that by acidification treatment. In acidification treatment, longer electrochemical treatment time can improve the removal of COD, because the oxidation and precipitation of lignin leads to a significant decrease of COD value.

TABLE 3. Comparison of the performance for 10% black liquor solution treatment using different operation methods and conditions (adapted from Jin et al. 2013, 616).

Treatment	Current density (mA/cm^2)	Cathodic solution	t (min)	COD (mg/L)	Precipitated lignin (g)	Na^+ recovery	Final pH
EC	100	0.05 M NaOH + 0.20 M Na_2SO_4	220	4781	1.01	51%	4.72
EC	150	0.05 M NaOH + 0.04 M Na_2SO_4	80	5310	1.06	43%	4.70
EC	150	0.05 M NaOH	75	5520	1.09	49%	4.69
Acid	-	-	-	5975	1.45	-	4.70

Compared with traditional acidification methods, another improvement of electrodialysis treatment is the recovery of NaOH in the same time. Due to the electrolysis of water, the OH^- produced in the cathode compartment increases, which promotes the transportation of Na^+ from the black liquor solution through the cation exchange membrane. About 50% of the Na^+ in the black liquor solution can be recovered in the electrochemical system developed in this research. This novel approach may be regarded as a promising alternative for the extraction of lignin and recovery of NaOH from the black liquor (Jin et al. 2013, 616-617).

This new membrane-assisted electrochemical technology provides a new method, the aim of pH reduction can be achieved via the electrolysis of water. When comparing with the conventional acidification method, the results are similar. In terms of reducing COD, the effect of membrane-assisted electrochemical technology is better than that of conventional acidification; besides, sodium hydroxide is recovered at the same time, which can bring some economic benefits. Therefore, this method also has good development prospects (Jin et al. 2013).

4.3 Comparison of membrane treatments and traditional ways

The fundamental principle of both ways is to utilize the selective permeability of membrane; however, the principle of how to let mixed liquid pass through the membrane is different. Microfiltration, ultrafiltration and nanofiltration use the pressure difference on both sides as the driving force to make inorganic ions and small molecules in the mixed liquid pass through, while some particles and macromolecules is trapped by membrane (Chen et al. 2011, 274-279).

As for the electrodialysis method, it uses the selective permeability of an ion exchange membrane in the solution to select and permeate the ions under the action of an external direct current electric field, so that the anions and cations in the solution undergo ion migration, and they are able to be respectively transited through the anion and cation exchange membrane to achieve the purpose of recovering chemicals (Strathmann 2010).

The recovery products targeted by the two methods are different. Using membrane filtration can effectively recover lignin and organic acids, while electrodialysis has a good recovery effect on alkali when contrasting with acidification method, such as sodium hydroxide (Jin et al. 2013; Kumar & Alén

2014; Mänttäri et al. 2015; Yang, Mu & Huang 2003). Compared with combustion method, membrane method has an advantage of recovery organic acids while combustion can only burn those and change them into energy, which may not generate more profits (KnowPulp 2021; Mänttäri et al. 2015). Because of that, if possible, those two membrane technologies can be combined and gradually replace the combustion technology so that more useful substances will be recycled from black liquor instead of being burned, which can be regarded as a positive attempt.

4.4 Problems in the popularization and application of membrane

Although the effect of treating papermaking with membrane is considerable, most of the membrane technologies are still in the stage of laboratory research, and there are not many researches, mainly due to its application still has some problems.

The manufacturing process of membrane is not very mature. For example, the ceramic nanofiltration (NF) membrane made of TiO_2 is a high-efficiency inorganic separation membrane, and the research and development of its carrier directly affect the industrial application and development of related inorganic membrane. Some of the currently applied technologies are also quite complicated, and the performance of the produced membrane is not very satisfactory. Technical incompleteness is bound to lead to high prices, which makes it difficult to promote in production (Arkell, Olsson & Wallberg 2014).

Besides, an inevitable problem when using membrane to treat black liquor is membrane fouling and degradation. Membrane fouling means the change of membrane performance caused by external factors such as the formation of an adhesive layer on the membrane surface or the blockage of membrane pores. Membrane degradation means the change of membrane performance caused by internal factors such as irreversible changes in the membrane itself (Liu et al. 2004).

Generally, the substances causing membrane fouling can be divided into three categories: the first is inorganic salt with low solubility; the second is colloid and dissolved organic matter; and the third is microorganisms. The main method to prevent membrane fouling is to improve the pretreatment process and strictly abide by the operating procedures. In addition, membrane fouling cannot be completely avoided, so the membrane components must be cleaned regularly. The cleaning methods of membrane components are mainly divided into physical cleaning and chemical cleaning (Rowe & Abdel-Magid, 1995, 212).

In order to be more suitable for the separation of black liquor components, the following problems of membrane need to be solved urgently in the future as well: developing new materials, improving the membrane-making process, and increasing the permeation rate as well as separation selectivity (from microfiltration to nanofiltration). At present, it is also of great practical significance to develop low-cost membrane-making processes and materials to reduce costs; and solving the technical problems of high-temperature and high-pressure connection, sealing and thermal expansion in the separation equipment (Chen et al. 2011; Jin et al. 2013; Kumar & Alén 2014; Liu et al. 2004; Mänttäri et al. 2015). Those problems are challenges for each scholar and membrane technology still has a broad development prospect.

5 CONCLUSION

Black liquor is from white liquor in pulp mill after cooking process, and it is not a single substance, but a mixture of multiple substances, in which the main components are lignin, sodium hydroxide and sodium salts. Since 1930s, combustion and acidification as traditional technologies are gradually utilized to treat black liquor. In general, it can be converted to white liquor again after treatment.

There are two kinds of common approaches to treating black liquor by utilizing membrane separation: method of filtration and electrodialysis technology. Some examples are cited for each method, such as the separation of organic acids and lignin in black liquor through microfiltration, ultrafiltration, and nanofiltration; the redesign of the membrane arrangement to reduce membrane fouling and increase economic efficiency; compared with conventional acidification methods, the advantage of electrodialysis is the recovery of sodium hydroxide and other sodium salts.

In addition, the principles of these two membrane separation methods are not exactly the same: the principle of micofiltration, ultrafiltration and nanofiltration is due to pressure difference while electrodialysis membrane utilizes the selective permeability under the action of an external direct current electric field to select different ions to achieve the goal of separation of different substances. And the main recycled products of membrane filtration and electrodialysis are different as well. A single treatment technology cannot completely and effectively purify the black liquor, which often requires a combination of multiple methods. Therefore, if these two membrane separation methods can be combined, the black liquor may be better treated. Although the current development of membrane separation level is limited and there are some problems, which mainly are difficulty of membrane manufacture and membrane fouling, this method still provides new ideas for black liquor treatment.

Furthermore, there is a more realistic question: how to extend the membrane separation method to various pulp mills? If the achievements in scientific research cannot be put into practical applications, even perfect methods will be buried. Therefore, scientific researchers are obliged to participate in the actual investigation. They not only need to communicate with the management personnel of the pulp mill, but also understand more difficulties in the black liquor treatment, as well as combine their own scientific research results to solve those problems afterwards. In this way, the scientific payoffs will not be limited to the laboratory. After obtaining the support and assistance of the pulp mills, follow-up research can be carried out, which can form a virtuous circle, thereby promoting the continuous

improvement of black liquor treatment methods. Although the current development technology is still limited, this technology has broad prospects.

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