

Chapter 2

Extraction of Technical Lignins from Pulping Spent Liquors, Challenges and Opportunities

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2.1 Introduction

Forest biorefinery is an alternative approach for the pulping industry [1–3] and aims to produce value-added products from lignocelluloses [2]. One biorefinery scenario is to produce value-added products from lignin that is generated, but partially utilized, in pulping processes. To be industrially attractive, processes for producing lignin based chemicals should be able to be integrated into the pulping industry.

Lignin is the second largest renewable source after cellulose and the largest source of aromatic compounds on Earth. However, due to its amorphous and robust structure, the valorisation of lignin is challenging. Lignin can be converted to many products. Kraft lignin is currently used as a fuel in the Kraft pulping process, but it may be used in the production of carbon and composite fibers [4, 5]. Lignosulfonates have been proposed to be used as adhesives [6], plasticisers in concrete [7] and dye dispersants [8]. Moreover, lignin has been used in polymeric applications as stabilizers [9], surfactants [10], epoxy resins [11] and superabsorbent hydrogels [4]. Finally, lignin of prehydrolysis liquor was proposed to be used as a filler modifier [12] and a fuel source in the past [1, 2].

However, lignin needs to be isolated from pulping spent liquors to allow the production of value-added products. Pulping spent liquors have many different

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characteristics [13], and contain organic compounds (mainly lignin derived compounds, hemicelluloses and acids) and inorganic materials (mainly residual chemicals of pulping processes) [2]. The chemistry of spent liquors significantly impacts the processes by which lignin can be selectively and effectively isolated [14, 15]. To have an economically feasible lignin production process, lignin needs to be extracted from pulping spent liquors effectively and selectively. In this chapter, various methods that have been proposed in the literature, experimentally evaluated at laboratory scales or are commercially practiced for producing lignin are comprehensively reviewed. The challenges and perspectives of each method will be critically discussed. The main objective of this chapter is to familiarize readers to the alternatives for isolating lignin compounds from four industrially produced spent liquors, which are black liquor and prehydrolysis liquor of Kraft pulping process and spent liquors of sulfite pulping and neutral sulfite semichemical (NSSC) pulping processes. This chapter includes the evaluation of only wood based pulping spent liquors. Methods to deal with less commonly practiced pulping methods, e.g. organosolv, are excluded from this chapter.

2.2 Kraft Pulping Process

2.2.1 Properties of Black Liquor

The black liquor of Kraft pulping process contains a significant amount of lignin and residual pulping salts. Table 2.1 shows the properties of black liquor obtained from softwood and hardwood black liquors. It is observable that the solid, lignin and ash contents of black liquors could vary significantly, and this variation is due to the amount of water used in pulping, and the evaporation stage, from which black liquor samples were collected in commercial processes.

In these samples, the amount of sugars in the black liquor samples was not reported, and the pH was higher than 13. Research study has focused on the isolation of Kraft lignin from black liquor, as described in the following sections.

Table 2.1 Properties of black liquors from commercial Kraft pulping processes

Black liquor source	Solid content, wt. %	Lignin content, wt. %	Ash content, wt. %	Sugars, wt. %	pH	Ref.
Softwood	40	30.2	52.5	N/R	13.6	[16]
Softwood	41	29.6	47	N/R	13.3	[16]
Hardwood	49.7	27.9	48.4	N/R	13.5	[16]
Softwood	18.3	6.38	8.43	0.35	13.4	[17]
Softwood	12.7	4	N/R	N/R	N/R	[18]
Softwood/hardwood	21	7.1	N/R	N/R	N/R	[18]

N/R not reported

2.2.2 Acidification

Acidification has been regarded as an efficient and economical process for isolating lignin from black liquor. In this process, the pH of black liquor is reduced to 9, thus forming lignin particles that can be separated from black liquor via filtration [19, 20]. Table 2.2 shows the properties of precipitated lignin from softwood (weak) black liquor from a Swedish mill [21]. The results in Table 2.2 show the properties of lignin after washing and purification as acidification of black liquor that generally produces lignin with an ash content of more than 1 wt.% prior to purification.

As shown in Table 2.2, the precipitates consist mainly of Klason lignin and marginal amounts of carbohydrates and ash. As expected, the main element of the precipitates is carbon with a trace of sulfur [21]. It was claimed that increasing temperature during acidification can generate large flocs that might cause filtration problems [21]. The lignin precipitated at pH 9 had between 3000 and 13,000 g/mol molecular weight [21]. Reducing the pH of black liquor is reported to decrease the average molecular weight of both softwood and hardwood lignin, but this also increases the sulfur content of lignin [21, 22]. Kraft pulping degrades lignin into low molecular weight components with a high degree of sulfur substitution. Some elementary sulfur may also be released as a by-product and may contribute to sulfur content of Kraft lignin when the pH of acidification is very low [22].

However, black liquor filtration at pH 9 is generally challenging because the ionic strength gradients are formed in the lignin precipitates during the washing process [23]. LignoBoost technology was developed and is now commercially used by Domtar Inc. in North Carolina, USA. Figure 2.1 shows the block process

Table 2.2 Properties of lignin precipitated at pH 9 via acidification of a softwood (weak) black liquor [21]

Carbohydrate, wt.%	Klason lignin, wt.%	Acid soluble lignin, wt.%	Precipitated materials, wt.%	Ash, wt.%	S, wt.%	C, wt.%	H, wt.%
2.7	93.7	2	3.3	0.1	1.69	64.88	6.3

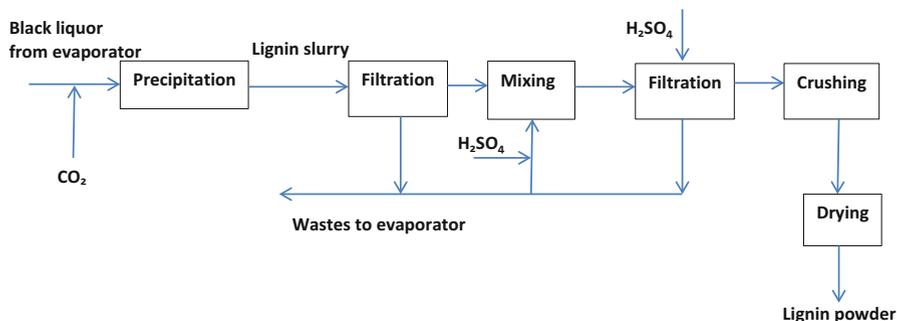


Fig. 2.1 Block diagram of LignoBoost Technology [23]

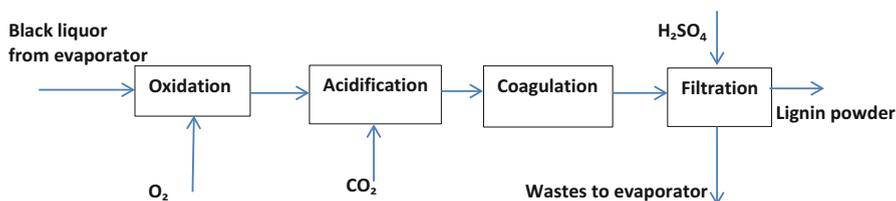


Fig. 2.2 Block diagram of LignoForce technology [24]

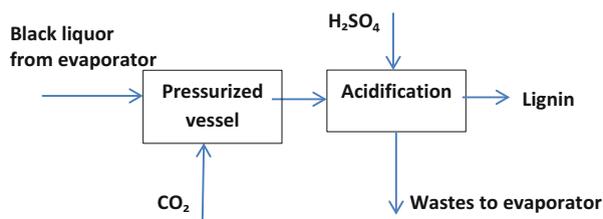
diagram of the LignoBoost technology [23]. In this process, black liquor is taken from evaporators of the recovery section of Kraft process, and is acidified with the help of CO₂ to pH 9. Lignin is precipitated at this pH (in a precipitation tank), and filtered. The reduction in pH of black liquor may result in generation of H₂S gas in the process. The precipitated lignin (slurry) is re-dispersed in a subsequent mixing tank with acidic filtrate that is generated in a subsequent filtration stage. In this stage, the pH and temperature of precipitation and mixing tanks are the same, but the concentration gradients of acids in the washing stage (second filtration) are low [23]. It has been reported that the acidification of black liquor in the absence of mixing tank generates large crosslinked lignin macromolecules, but LignoBoost generates small uncrosslinked lignin precipitates [23]. In the LignoBoost process, the change in the pH level, ionic strength and in lignin solubility will take place in the slurry, and not in the precipitates, which helps the properties of precipitated lignin [23]. After the second stage of filtration, precipitated lignin is crushed and dried to form lignin in powder form (Fig. 2.1).

Another process, LignoForce, was developed for isolating Kraft lignin from black liquor by FPInnovations [24]. LignoForce technology was commercialized by West Fraser Inc. in Alberta, Canada in 2016. In this process, black liquor is first oxidized with O₂ and then acidified to pH 9 by CO₂. After the coagulation step, it is washed with acid in a filter press, where lignin precipitates are formed and separated from the system (Fig. 2.2). In this process, the filtrate of coagulation stage is sent to the evaporator of the Kraft process [24].

Both LignoBoost and LignoForce technologies have been commercialized in North America; however, there is no true comparison for the quality of lignin products generated in LignoBoost and LignoForce. Table 2.3 shows the properties of precipitated lignin with and without the oxidation stage conducted in the LignoForce technology. It can be observed that the filtration rate, lignin content and the particle size of the precipitates were increased significantly, but the ash content of the precipitates was reduced. The solid content of the precipitates was similar in both cases. As is well known, the oxidation and acid/base neutralization reactions are exothermic. Therefore, the temperature of black liquor is increased after oxidation and acidification. The charged groups of lignin are more associated at a higher temperature leading to more and larger colloidal lignin particles that are more easily filtered/separated from the suspension [24].

Table 2.3 Properties of lignin precipitated with or without oxidation with LignoForce technology [24]

Property	Without oxidation	With oxidation
Filtration rate, kg/h.m ²	0–80	100–200
Total solids, wt.%	30–58	60–62
Ash content, wt.%	0.2–15	0.1–0.7
UV lignin, wt.%	50–98	97–98
Lignin particle size, μm	0.2–1	5–10

**Fig. 2.3** Block diagram of sequential lignin liquid recovery and purification process [16, 25]

However, both LignoForce and LignoBoost are typically operated in batch or semi-batch modes, and they both have a low operating temperature of 70–75 °C. To have a continuous process, sequential liquid lignin recovery and purification (SLRP) was introduced [16, 25, 26]. In this process, black liquor is acidified with CO₂ to pH 9, and heated to 100–150 °C and kept at 4–8 bar (Fig. 2.3). This pretreatment generates a concentrated lignin phase at the bottom of the pressurized vessel that can be pumped in a continuous mode. In the subsequent acidification stage, lignin is separated from black liquor via reducing pH to 2. It has been reported that the temperature changes from 100 to 150 °C increases the molecular weight of precipitated softwood Kraft lignin 4 times [25]. In this process, black liquor with a high ionic strength generates lignin product with a higher molecular weight [16].

2.2.3 Membrane

Membrane filtration has been used to extract lignin from black liquor [17]. In the past, the application of ultrafiltration [27–30] and nanofiltration [31] for isolating lignin from black liquor has been investigated. These studies reported promising results in isolating lignin. Ultrafiltration results in low retention of lignin and a high retention of high molecular weight hemicelluloses, which is larger than that of lignin. In one study, lignin and hemicelluloses were separated from softwood

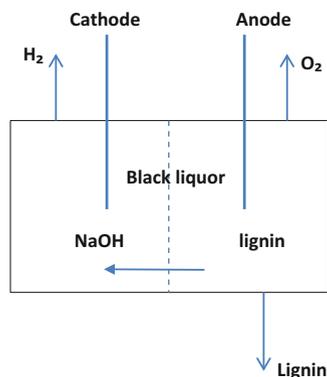
black liquor by nanofiltration [17]. The introduction of ultrafiltration prior to nanofiltration provided a high flux in the nanofiltration, but the retention of lignin on the nanofilter was reduced [17]. Various membrane types, e.g. polymeric or ceramic, have been used for isolating lignin, and polymeric membranes are found to be more cost effective than ceramic ones [17]. The cost of lignin production for generating 230 g/L lignin solution with nanofiltration was 46 €/t in 2013, while the production of lignin solution with the same concentration using ceramic nanofiltration cost 68 €/t in 2013. The introduction of ultrafiltration increases the cost to 120 €/t (2013) when the same concentration of lignin solution is achieved [17]. Although the application of ultrafilter increases the production cost, it generated lignin with fewer purities (i.e. less of hemicelluloses and other components in the lignin solution). However, the main problem of ultrafiltration/nanofiltration is the adhesion of lignin to the filter surface. As membranes separate lignin components based on their size, they also tend to isolate other components having a similar size (hemicelluloses). Although membranes increase the concentration of lignin in the solutions, they may not necessarily improve the purity of lignin. As lignin possesses functional groups, e.g. phenolic, carboxylic, they may be charged. Therefore, a membrane with a similar charge introduces repulsion force for lignin segments. To increase the purity of lignin and improve the filtration performance of membranes, membrane filters can be designed to repel lignin and other compounds in the solution. In this case, membranes with advanced surfaces that repel the black liquor components may improve the separation of lignin from black liquor [18].

2.2.4 *Electrolysis*

Electrolysis has also been introduced as an alternative to acidification of black liquor. Electrolysis has the advantages of coagulating *in situ* of lignin and generating sodium hydroxide [32, 33]. In the past, electrolysis treatment was carried out on black liquor at different electrode potentials. Figure 2.4 shows a process for separating lignin from black liquor *via* electrolysis technique in a continuous mode. In this process, a membrane separates anode and cathode compartments. In the anode section, oxygen is generated, pH drops and lignin precipitates via oxidation, while sodium hydroxide and hydrogen gas are generated on the cathode section. The production of hydrogen and oxygen gases as well as sodium hydroxide reduce the overall cost of this process, as they are value-added by products of this process.

This process was only conducted at lab scales [34] and feasibility studies were executed to investigate if it is a viable process to be implemented commercially [34, 35]. The main challenges of this process are the electricity requirement, membrane foaling/cleaning and separation of lignin from this system. A study in 1998 reported that, compared to CO₂/acidification process (\$ 9.7 M), electrolysis process needed for 6–10% production increase was \$ 12.5 M capital investment for a pulp mill that produced 700 t/day pulp [35].

Fig. 2.4 Process for separating lignin from black liquor via electrolysis [32]



2.2.5 Solvent

Solvents have been applied to extract lignin from black liquor. Water-insoluble organic solvents, e.g. chloroform or dichloromethane, were added to black liquor to precipitate lignin [36], which had an acceptable filtration performance. It was proposed that the creation of hydrogen bonds between lignin and solvent molecules caused the precipitation and improved filtration of black liquor, as lignin was proposed to be surrounded by solvent molecules that made the lignin heavier and hydrophobic, which resulted in lignin agglomeration and precipitation [36].

The precipitation of lignin from black liquor with water-soluble solvents has also been studied. Alcohols were reported to be effective in extracting lignin. For example, the treatment of eucalyptus Kraft black liquor with ethanol at different ratios (0.2–12 L ethanol/L of black liquor) resulted in approximately 40% of the pentosanes and 22% of lignin removal [36]. In another study on the use of ethanol, methanol and isopropanol in black liquor, a large amount of alcohol to black liquor (10–1) could be extracted yielding 60% of the available lignin [37]. Furthermore, lignin recovery of more than 90% was achieved via having cation-alcohol mixture in black liquor, e.g. calcium (II) or aluminum (III) salt (1.7 g/L of black liquor) and ethanol (0.5 v/v ethanol/black liquor). However, these studies were all conducted at a laboratory scale, and the industrial application of solvent based process requires solvent recovery, which presently is expensive and impractical in Kraft pulping processes.

2.3 Prehydrolysis Based Kraft Process

2.3.1 Properties of PHL

Dissolved pulp is produced via sulfite or Kraft process. Presently, 60% of dissolving pulp is produced via sulfite process, while 40% is produced via Kraft process [38]. In the Kraft based dissolving pulp process, prehydrolysis is conducted prior to

Table 2.4 Chemical composition of industrially produced prehydrolysis liquor (PHL)

PHL ID	pH	Dry Solids, wt. %	Ash, wt. %	Acetic acid, wt. %	Furfural, wt. %	lignin, wt. %	Hemicelluloses, wt. %	References
1	3.68	5.39	1.11	1.31	0.18	1.01	1.50	[38]
2	3.80	7.60	1.21	1.41	0.31	1.51	3.16	[14]

Kraft process and is performed *via* treating wood chips with saturated steam (at 443 K for 30 min) or hot water [38]. The prehydrolysis process isolates a part of lignin and hemicelluloses from wood chips. The chemical composition of prehydrolysis liquor (PHL) is shown in Table 2.4.

PHL contains less than 10 wt.% solids, in which approximately 1 wt.% is inorganic material [38, 39]. It contains approximately 1.5–3% hemicelluloses, 1–1.5% lignin, 1.4% acetic acid and less than 0.5 wt.% furfural. Acetic acid is formed *via* liberation of acetyl groups of woody biomass during hydrolysis that reduces the pH of the mixture to 3.6–3.8 (Table 2.4). Although the lignin content of PHL is small, the large production of PHL may provide an incentive for the producing lignin-based value-added products. The low lignin concentration and the presence of other components in PHL make the direct use of PHL impractical [40]. Various methods have been proposed for isolating lignin from PHL [41–43]. These processes have different efficiencies and selectivities for isolating lignocelluloses.

2.3.2 Acidification of PHL

Similar to the acidification of black liquor, the acidification of PHL may be a viable method to isolate lignin from PHL (i.e. similar to black liquor) [39]. Table 2.5 lists the lignin and hemicelluloses removed from PHL at pH 2. It can be observed that approximately 50% of lignin can be separated from PHL [40], but it was marginally removed from the PHL in another study [41, 42]. These variations can be related to the properties of lignin in PHL [41]. Lignin removal/precipitation via acidification is significantly affected by the structure/functional groups and molecular weight of the dissolved lignin in the PHL [43]. The variation in the efficiency of acidification can be attributed to the difference in the structures of lignin polymers in PHL. However, the removal of hemicellulose via acidification may contaminate the isolated lignin in PHL. These results imply that acidification process is case dependent, and may be an effective process for lignin removal.

The addition of poly (ethylene oxide) or PEO (0.02 g/g of lignin of PHL) to acidified PHL causes 43% of lignin to be removed (pH 2) [41]. In another study, 0.03 g/g addition of dodecyltrimethyl ammonium chloride (DTAC) to PHL facilitated lignin removal by 17% [44]. In these studies, hemicellulose removal was marginal. The separated lignin contained lignin/PEO or lignin/DTAC complexes, which can be used in composites [45, 46]. As the lignin or lignin flocs usually contain

Table 2.5 Performance of acidification of industrially produced prehydrolysis liquor (PHL)

PHL	Lignin removed, %	Hemicelluloses removed, %	Reference
1	47	41	[39]
2	4	NR ^a	[40]
3	5	11.8	[41]

^aNot Reported

more than 50 % dry solids, their incineration is cost-effective. Alternatively, these flocs can be used in the production of phenolic compounds such as adhesives and carbon fibers [47, 48], as the impurity content of these separated lignin or lignin flocs is not significant [41, 42, 49].

2.3.3 Adsorption

Adsorption can be an alternative to separate lignin from PHL. In this regard, an adsorbent is mixed with PHL in a continuous stirred tank reactor (CSTR) to adsorb lignin. Then, the adsorbent encapsulated with lignin can be used as a value-added filler for composite production or transferred to another stage, in which the desorption of lignin from the adsorbent will take place under desired conditions [14]. The absence of chemical reaction between the adsorbent and lignin promotes the desorption and the recyclability of the adsorbent. In one report, activated carbon was used for adsorbing lignin from industrially produced PHL [50]. It was observed that the maximum adsorption of 400–700 mg/g for lignin was achieved. Furthermore, 200–300 mg/g of hemicelluloses and 100 mg/g of furfural were adsorbed on activated carbon implying that adsorption was not selective. As this process is not selective in lignin isolation, the subsequent desorption and purification of lignin may be complicated and expensive.

2.3.4 Flocculation

Flocculation has been practiced in industry for many years, and recent studies show that it could be used in separating lignin from PHL. In the past, poly diallyldimethylammonium chloride (PDADMAC) and chitosan were added as flocculants to PHL [2, 51]. It has been reported that the separation of lignin is affected by the amount of flocculant applied to the PHL, and the removal of lignin and other PHL components seems to be able to happen simultaneously. However, the concentration of flocculant can control the removal of lignin and other components. A maximum removal of lignin (40 %) was achieved by adding 1.4 mg/g of PDADMAC or 1.6 mg/g of chitosan to the PHL [51]. In this case, the maximum hemicelluloses removal was obtained via 0.5 mg/g of PDADMAC or chitosan addition. As hemicelluloses

can also precipitate in the flocculation, the lignin-based materials with different compositions can be made via controlling the dosage of flocculants in the PHL, and the product can be used in corrugated container (CC) boards or medium density fiber board (MDF) production [51].

2.3.5 *In Situ Adsorption/Flocculation System*

To increase the adsorption of lignin, flocculation and adsorption has been simultaneously applied to PHL [49, 52]. By adding flocculants, larger flocs are formed in adsorbent/PHL systems, which can be more easily removed from the PHL system [49, 52]. In one report, the addition of 0.5 mg/g PDADMAC to activated carbon/PHL system (1/40) at room temperature increased the adsorption of lignocelluloses from 200 to 250 mg/g [49], while the application of 0.8 mg/g cationic poly (acryl amide) or CPAM to precipitated calcium carbonate/PHL system (at 40 °C and 120 rpm) enabled the adsorption of 110 mg/g lignin. In addition, 250 mg/g of hemicelluloses and 65 mg/g of furfural were adsorbed on precipitated calcium carbonate (PCC) in the system [53]. When CPAM was replaced with PDADMAC, 203 mg/g of lignin, 530 mg/g of hemicelluloses and 58 mg/g of furfural were adsorbed on PCC under the same experimental conditions [53]. Similar to the adsorption or flocculation processes stated above, the precipitates of in situ systems are impure and thus can only be directly used in composites as stated above.

2.4 Spent Liquor of Sulfite Process

2.4.1 *Properties of Spent Liquor*

The spent liquor of the sulfite pulping process is generally acidic and contains liginosulfonate, sugars and residual pulping chemicals. In the sulfite pulping process, lignin is sulfonated under acidic conditions to form liginosulfonate. Table 2.6 lists the properties of two spent liquor samples produced from magnesium based sulfite pulping of *Eucalyptus globulus*.

It can be seen that the pH of the spent liquors is approximately 3–4, and they contain 7–8 wt.% liginosulfonate and 4 wt.% sugars. The overall dry solid content of

Table 2.6 Properties of spent liquors of the sulfite pulping process [54]

pH	Conductivity, mS/cm	Liginosulfonate, %	Sugars, %	Total solids, %	Suspended solids, %
3	14	7.9	4	16.9	–
3.7	14	8.3	4.1	16.1	0.21
3.7	15	8.5	5.7	17.1	0.3

the spent liquors is 16–17 wt.%. Presently, the spent liquors are mainly treated in the wastewater system of the sulfite pulping process. In contrast to Kraft lignin, lignosulfonate cannot be precipitated by acidification, which introduces challenges in its separation [55–57]. Membrane, ion exchange, amine extraction and electro dialysis have been used on a laboratory scale for separating lignosulfonate [58].

2.4.2 Membrane

Membrane technology has been studied for separating lignosulfonates from spent liquors for more than 30 years. The possibility for relatively easy scaling up makes ultrafiltration attractive [59]. This process is not very sensitive to pH or temperature, and the molecular weight of the products can be controlled *via* selecting a desired membrane size. Generally, reverse osmosis can separate a solute/solvent of a similar molecular size. The application of reverse osmosis for concentrating sulfite liquors have been studied in the past [60–63]. In one study, the total solid of spent liquors was increased from 6 to 12 % with a flux of about 40 L/m²h by reverse osmosis that had lifetime of more than a year with efficient membrane cleaning two to six times a week [64]. However, reverse osmosis needs a highly selective membrane, and salt rejection may hamper the separation [65]. The most promising ultrafiltration system consists of a Microdyn-Nadir UP010 membrane that can separate high molecular weight lignosulfonates from the low molecular weight ones in the spent liquor [59].

Lignin recovery and fractionation by ultrafiltration have been studied by several researchers [64, 66, 67]. Different membranes from polysulphone, cellulose acetate, fluoropolymer with altered molecular weights cut-off (1 K, 5 K, 10 K, 20 K, 25 K, 50 K and 100 K) have been used for ultrafiltration of spent liquors [68]. In one study, the ultrafiltration of softwood calcium based spent sulfite liquors with cellulose acetate membrane resulted in 40–66 % sugar concentration from 20 to 27 % [68]. The membrane was operated at the pressures of 300–600 psi (20–40 bar) and temperatures of 50–60 °C for 500–1100 h. A lignosulfonate solution of 50–80 wt.% was achieved that contained 80–96 % lignosulfonate on a solid basis [68].

A full-scale ultrafiltration with a membrane area of 1120 m² was installed at Borregaard Industries (Sarpsbog, Norway) in a calcium bisulphate pulp mill in 1981 [64]. A membrane with molecular weight cut-off of 20 k allowed concentrating the spent liquor from 12 to 22 wt.% with a flow rate of 16 m³/h [64]. The lignosulfonate production from the spent liquor of an ammonium based sulfite pulping process was also commercialized in Canada in the 1990s [69]. Figure 2.5 shows the process for producing lignosulfonate from spent liquor of this pulping process. The spent liquor is concentrated from 12 to 22 wt.% prior to the fermentation of sugar present in the spent liquor to ethanol with *S. cerevisiae* [69]. After fermentation, the residual liquor is concentrated to produce liquid lignosulfonate (50 wt.%), which can also be spray-dried and sold as lignosulfonate [69]. However, most membranes are unable to fractionate lignosulfonates or selectively purify them (i.e. they contain sugar contaminants) due to the overlap in the molecular weights of lignosulfonate and sugars.

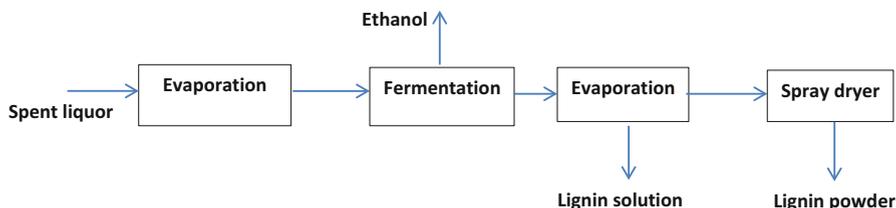


Fig. 2.5 Commercial process for producing liginosulfonate from spent liquor of an ammonium based sulfite pulping process [59]

The membrane technology also requires a special selection of membranes for each spent liquor to reach an optimum yield and degree of purification. In addition, dialysis is a time-consuming process [59].

2.4.3 Amine Extraction

Amine extraction has been proposed for separating liginosulfonate from spent liquors [70]. In this process, liginosulfonate is converted to liginosulfonic acid-amine adducts which are water insoluble [70]. The adducts can be isolated from liginosulfonate via liquid-liquid extraction [70]. In the past, long chain aliphatic amine, tri-n-hexyl-amine, and poly ethyleneimine have been used for extracting liginosulfonates from spent liquors [55, 71–74]. The main challenges of this process are the complete removal of the amine, the formation of salt, foam and emulsion, and the relatively slowness of the process [71]. Moreover, the high consumption of organic solvents limits the application of the process in the industrial scale.

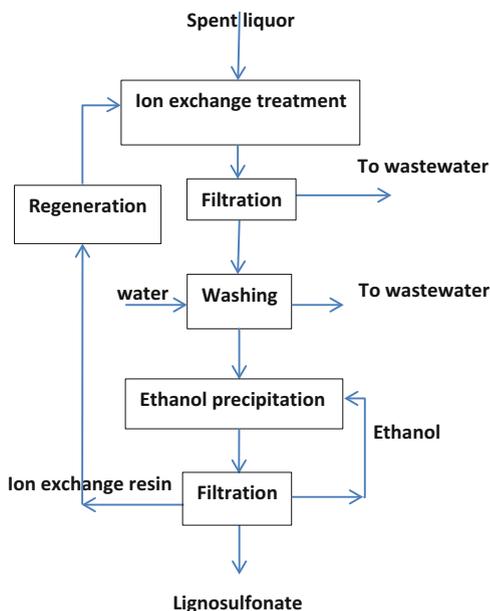
2.4.4 Electrolysis

Similar to Kraft pulping, electrolysis can be applied to isolate liginosulfonate from spent liquor of sulfite pulping process. In the past, spent liquor derived from magnesium bisulfite pulping of beech was electrolyzed in an electrolysis cell [71]. During the electrochemical treatment (125 mA/cm²; 60 °C; 180 min), anolyte was desalinated and the magnesium concentration was reduced to 60%, which also reduced the pH of the solution from 5 to 1. The results showed that the electrolysis time increased the molar mass of the liginosulfonates from 5700 g/mol at pH 5 to 7400 g/mol at pH 1 and that the phenolic hydroxyl and sulfonic acid groups of separated liginosulfonate were similar. However, liginosulfonates obtained after electrolysis had 1.92 meq/g charge density at pH 1, whereas it was 1.59 meq/g at pH 5 prior to electrolysis [75]. The main challenge of this process is the high cost of electricity and the fouling of the electrodes, which adversely impacts its industrial application.

2.4.5 Ion Exchange Resin

Adsorption processes have been regarded as alternative approaches to separate lignosulfonates from spent liquors, as they are simple and have relatively low operational costs. In the past, the adsorption and desorption of lignosulfonate on minerals such as sandstone, limestone and dolomite have been studied [75, 76]. Polyacryl or polyaromatic based resins, such as Amberlite XAD-4, XAD-7, and XAD-16, have high adsorption capacities that can be used for this purpose [59]. Generally, the adsorption process of phenolic compounds follows either the Freundlich or Langmuir model, and is spontaneous and exothermic. Therefore, conducting the process at ambient temperatures results in a more favourable adsorption and a maximum adsorption of 100–300 mg/g can be achieved [59]. Figure 2.6 shows a process that includes the application of ion exchange resin, filtration and solvent treatment to isolate lignosulfonate from a spent liquor. It is seen that, lignosulfonate is first adsorbed on the resin, then the resin is washed with water to remove the adsorbed sugars from the resin. Then, the resin is treated with ethanol, and this process desorbs and precipitates lignosulfonate in the system, which can be separated from the system with a filter. A series of filtration steps after this treatment can isolate lignosulfonate and ion exchange resin from ethanol. The ion exchange resin is regenerated and recycled, and lignosulfonate is the main product while ethanol is recycled to a previous stage. In the past, the adsorption of lignosulfonate from sulfite pulping spent liquor (250 mg/L lignosulfonate concentration) was studied on resin Amberlite XAD-7 adsorbent. The results showed that mixing the resin with

Fig. 2.6 Process for producing lignosulfonate from spent liquor using ion exchange resin [59]



the spent liquor at the weight ratio of 900 mg/g of lignosulfonate/resin (in solution but on a dry basis) led to 300 mg/g of adsorption and thus extraction of lignosulfonate after 10 h at pH 2. The process resulted in lignosulfonates with the molecular weight ranging between 4600 and 398,000 g/mol [59].

2.5 Isolation of Lignosulfonate from Spent Liquor of NSSC Process

2.5.1 Properties of Spent Liquor in NSSC Process

Neutral Sulfitte Semi Chemical (NSSC) is a semichemical pulping process that produces pulp with a yield of 60–80%. In this process, wood chips are first chemically treated with sodium sulfite and sodium bicarbonate, and the treated wood chips are mechanically ground to produce pulp [15]. The chemical treatment of wood chips generates spent liquor that contains organics and inorganics. As an example, the spent liquor, which was produced in a Canadian NSSC process that used mixed hardwood, had a pH of 5.7 and contained 60.22 g/L of lignosulfonate, 22.13 g/L of hemicelluloses, 26.5 g/L acetic acid and a trace of furfural (0.52 g/L) [77]. It also contained about 63.8 g/L of ash, which probably originated from the pulping chemicals used in the pretreatment stage. In another study, the spent liquor of an NSSC process using hybrid poplar contained 59–69% lignosulfonate, 2–24% hemicelluloses, 12–29% acetic acid and 1.6–2.4% formic acid on ash free basis [78, 79]. The hemicelluloses had two different molecular weights of 8000–19,600 g/mol and 1000 g/mol. The lignosulfonate had average molecular weights of 1030 and 235 g/mol [78, 79]. Based on the molecular weight differences, lignosulfonate and hemicelluloses were separated using an ultrafilter in the same study.

2.5.2 Adsorption/Flocculation/Coagulation

Lignosulfonate has a phenolic structure that is hydrophobic in nature. If a surfactant is added to a spent liquor that contains lignosulfonate, it can interact with lignosulfonate and coagulate it. This may lead to the precipitation of lignosulfonate from the spent liquor. In one report, a pH reduction to 1.8 caused 6% lignosulfonate and 53% hemicelluloses removal from a spent liquor [80]. Interestingly, acidification followed by dodecyltrimethylammonium chloride (DTAC) treatment of the spent liquor under the conditions of 22 °C, 1.8 pH and 10 mg/g of DTAC/SL resulted in 40% lignosulfonate extraction from the spent liquor [81]. In this process, hemicellulose extraction was 78%.

Adsorption using activated carbon has also been used for separating lignosulfonate from spent liquors [81]. The results showed that activated carbon adsorbed 0.1 g/g of lignosulfonate and 0.15 g/g of hemicelluloses at the original pH of spent liquor (5.7).

The maximum lignosulfonate adsorption of 0.33 g/g on activated carbon was obtained under the conditions of spent liquor to activated carbon of 30 g/g, 360 min treatment and 30 °C. The hemicellulose adsorption was 0.25 g/g under these conditions [81]. The maximum adsorption of 0.9 g/g lignosulfonate and 0.43 g/g of hemicelluloses on activated carbon was obtained for conditions of 30 °C, 3 h and pH 7 with SL/AC weight ratio of 90 [82]. In another report, the adsorption of lignosulfonate and hemicelluloses was 0.26 g/g and 0.27 g/g on bentonite, respectively, which was achieved under the conditions of 50 °C, 100 rpm and 40 g/g SL/bentonite after 3 h of treatment [13].

Flocculation concept has been also used for extracting lignosulfonate from spent liquors. For example, poly (ethylene imine) or PEI (15 mg/g) treatment of an spent liquor that was produced in an NSSC process of mixed hardwood under the conditions of pH 6, 30 °C resulted in 37% of lignosulfonate and 37% hemicelluloses removal from spent liquors. In addition, the simultaneous application of poly (diallyldimethyl ammonium chloride) or PDADMAC and PEI (7.5 mg/g) showed 47% lignosulfonate and 50% lignosulfonate removals in the same study [77].

Alternatively, the simultaneous application of adsorption and flocculation can be used for isolating lignosulfonate from spent liquors. In one study, the addition of poly (diallyldimethylammonium chloride) or PDADMAC to the spent liquor and activated carbon system led to 2.5 g/g adsorption of lignosulfonate to 2.5 g/g on AC [82]. In another work, the adsorption of lignosulfonate was increased to 1.8 g/g and that of hemicellulose to 0.45 g/g via adding 15 mg/g of poly (diallyldimethylammonium chloride) or PDADMAC to the system of SL/bentonite stated above (treated under the conditions of 40 g/g of SL/bentonite at 50 °C and 3 h) [13].

However, the precipitates made from the addition of flocculants, surfactants or adsorbents are not pure lignosulfonate, as they contain organic compounds, such as hemicelluloses, flocculants such as PDADMAC, or adsorbents such as bentonite. Therefore, a desorption stage is needed to isolate lignosulfonate from precipitates and to further purify lignosulfonate so that lignosulfonate can be used as a value-added product. However, it is possible to use in packaging paper production as fillers without purification. Although flocculation/adsorption/coagulation process seems to be simple and industrially attractive, they are mainly based on laboratory scale experiments. Large scale analyses should be conducted to promote their industrial development.

2.5.3 Solvent Extraction

The application of solvents in removing lignosulfonate from spent liquor of an NSSC process has been assessed by Tarasov et al. [83]. It was reported that lignosulfonate could be removed from the spent liquor via mixing it with ethanol, acetone or isopropyl alcohol. A maximum lignosulfonate removal of 59% was achieved via mixing isopropyl or acetone with the spent liquor at the weight ratio of 20/80 (solvent/spent liquor) and pH 5.7. A lower removal was obtained via mixing ethanol

with spent liquor under the same experimental conditions. About 30% of the hemicelluloses was also removed via mixing solvents with spent liquor, regardless of the solvent type. This study also reported a molecular weight and anionic charge density of 5000–70,000 g/mol and 0.2–1.8 meq/g for the precipitates, respectively [83]. As precipitates contain impurities (e.g. hemicelluloses), the product can be used as organic compounds in composites. The recovery of solvent complicates the application of solvents in lignin recovery and makes the practical application of solvent treatment less likely on an industrial scale.

2.6 Conclusions and Future Outlook

Different options have been reviewed and evaluated on the laboratory scale to extract lignin from pulping spent liquors. To extract Kraft lignin from black liquor, acidification is the most industrially reliable process, and LignoBoost and LignoForce technologies were designed based on the acidification concept. Pure lignin can be produced in these processes. To extract lignosulfonate from sulfite spent liquors, ultrafiltration seems to be the most industrially applicable method, but the extracted lignin will have impurities such as hemicelluloses. Laboratory experiments on adsorption and flocculation techniques for isolating lignin derivatives from prehydrolysis liquors (PHL) or spent liquor of the NSSC process show acceptable results. Flocculation seems to be more attractive than adsorption for extracting lignin based compounds from spent liquors as it is easier to be implemented in a large scale. However, the flocculation and adsorption processes cannot generate pure lignin and the product contains either organic impurities such as hemicelluloses or inorganic impurities such as clay (as an adsorbent). There is no clear means for producing pure lignin via the flocculation concept. A desorption process is required to separate lignin from an adsorbent to produce pure lignin via the adsorption concept. Electrolysis and solvent extraction showed promising results on a laboratory scale, but the main barrier for their implementation on the industrial scale is the high usage/cost of electricity and solvent recovery.

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