Research Article

Recovering Lignin in a Real-Case Industrial Kraft Pulp Mill: Pilot-Scale Experiment and Impact on the Mill Commodities

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ABSTRACT: Existing industrial Kraft mills can be the basis for the deployment of lignin valorization into added-value products. Lignin can be recovered by its precipitation from black liquors. However, it is of tremendous importance to better determine the impact of lignin extraction on the overall chemical and energy balances of the mill. Therefore, we have sampled the black liquors from an industrial Kraft mill (treating softwood), which is a typical European mill. Lignin has been precipitated by CO_2 at a pilot scale in order to quantify the consumption of chemical commodities. Black liquors and lignin cakes were comprehensively characterized in order to evaluate the mineral and organic balances. The experimental results were implemented in a global simulation of the industrial Kraft mill in order to assess the impact of lignin recovery from the black liquor on the chemical and energy balances. The additional consumptions of chemicals are 258−266 kg of H_2SO_4 and 163−195 kg of NaOH/t of produced lignin. The pulp mill capacity can be increased by 1.5 t of pulp/t of lignin to overcome the steam loss (i.e., 6.7−7.1 t of steam/t of lignin).

KEYWORDS: biorefinery, wood, pulping, black liquor, CO_2 acidification, precipitation
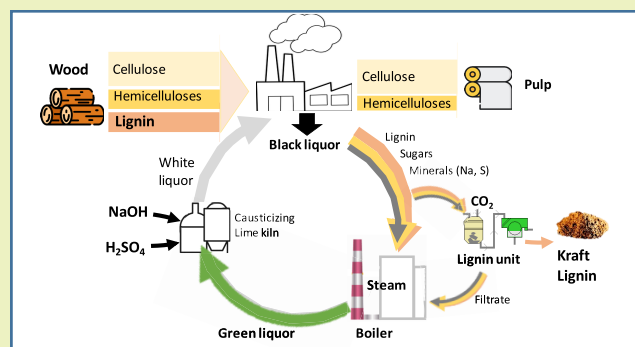
INTRODUCTION

Kraft pulping is still the dominant industrial biorefining process in the world with about 400 million tons of wood valorized to produce 107 million tons of pulps.[1] The Kraft pulping produces a large variety of bio-based materials, mainly cellulose fibers for papers and board, and co-products such as turpentine and tall oil.[2−4] The Kraft recovering loop presents an efficient balance of energy and minerals (Figure 1).

Only few amounts of sodium (10−20 kg eq. Na/ADTP, air-dried ton of pulp, i.e., 10 wt % moisture content based on the total wet mass) and even less in sulfur (2−3 kg eq. S/ADTP) are needed to cover the losses occurring during the process (i.e., in the final product, in effluent or air emissions).[6,7] Therefore, the Kraft process is an excellent basis toward sustainable and multi-product biorefineries.[2,5]

Historically, Na_2SO_4 was the only chemical added in the process, giving the other name of sulfate process to Kraft pulping. Nowadays, NaOH has turned to be the main sodium makeup, whereas H_2SO_4 addition regulated the sulfur balance and alkali charge in the black liquor circuit.[6]

The recovery boiler is among the most expensive and essential equipment of the Kraft process,[8−10] and most of the mills are designed according to the boiler capacity for a maximal and limited pulping production, with an average mill size of 400 k ADTP per year, with a new large mills of 1300−1500 k ADTP/year.[7]

One way to overcome this limitation is to derive a part of the residual lignin contained in the black liquor and entering in the boiler[9] and to recover lignin after acidification and drying (Figure 1 and Figure S1 in the Supporting Information).[5,11] Lignin becomes another revenue source for the mill especially when high added-value applications are envisioned.[12] Indeed, lignin presents an increasing interest to produce renewable molecules (hydrocarbon aromatics, phenols, fuels)[13,14] and materials (various polymers, carbon fibers, etc.).[15−18] The existing industrial Kraft mills are an excellent basis for the deployment of lignin valorization routes. Nevertheless, few Kraft lignin extraction units are already industrially implemented based on proprietary technology (e.g., Ingevity formerly MeadWestvaco) or based on advanced processes such as LignoBoost[11] and LignoForce System.[19−21] Such implementation is costly and impacts the overall energy and chemical equilibrium of the mills.[22,23] Uloth and Wearing[24] have shown based on an economical evaluation and lab-scale experiments that 15% of lignin removal would lead to 12−15% of pulp
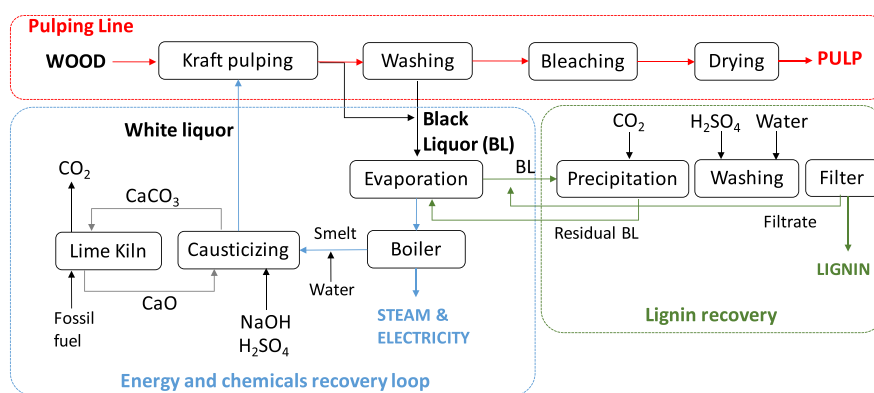
Figure 1. Simplified scheme of the Kraft process highlighting lignin recovery from the black liquor (adapted from ref 5) and chemical makeup.

production increase with a possible payback of the investment in less than 1 year. Loufti et al.[25] and Davy et al.[26] investigated lignin extraction in combination with increased pulp production using process models of a standard Kraft mill and based on laboratory experiments. They showed that the lignin recovery unit was closed to 5 years of payback.

According to Vakkilainen and Valimaki[27] and Hamaguchi et al.,[22] a maximal recovery of 20 to 30% of the total lignin present in the black liquor would have a limited effect on the recovery boiler in the case of a Scandinavian mill of 600 kADTP/year and a Brazilian mill of 1.5 M ADTP/year, respectively. Based on the LignoBoost demonstration plant, Tomani[11] demonstrated that the main operational cost was related to the chemicals, especially to CO_2 added for lignin precipitation and NaOH needed to keep the Na/S balance in the Kraft process. The profitability of a lignin extraction unit has been extensively studied by a model representing typical Scandinavian mills, with an emphasis on the energy system, especially because lignin removal will affect the steam production in the boiler and it will increase the need for additional evaporation because of washing in the lignin removal unit.[9,28] The profitability depends highly on energy prices and on CO_2 cost for the precipitation using the LignoBoost technology. Lindgren et al.[29] showed that the lignin price presents the largest impact on the economic feasibility of a LignoBoost unit, based on the modeling of a standard Kraft mill under WinGEMS 5.0. The same findings were also indicated for the LignoForce process applied to a standard Canadian bleached Kraft mill of 750 ADTP/day.[30]

All these interesting studies are on model standard Kraft units, but they do not rely on an industrial unit in operation. They do not integrate the whole Kraft mill, as presented in Figure 1. For instance, they focus only on the impact of the lignin extraction on the boiler or the recovery loop but there is still a lack of studies dealing with the impact of lignin extraction on an entire (existing) Kraft unit.

For this reason, this work presents the effect of a lignin extraction unit (similar as a LignoBoost type process) on an existing industrial unit. We combine unique industrial and experimental data and a global simulation approach. The experimental data were obtained from a pilot-scale production of Kraft lignin (5 kg of lignin) from an industrial black liquor. The black liquor was collected from a softwood unbleached Kraft pulp mill as well as all the operating data of the mill. The experimental data were integrated in a lignin recovery unit simulation and in the overall process line simulation. Then, different scenarios for the recovering of lignin were studied. As sodium hydroxide is the most expensive chemical of unbleached

Kraft pulping,[7] the simulation tool was especially developed to follow the Na/S equilibrium. Chemical and energetic costs for each scenario were also evaluated.

MATERIAL AND METHODS

Kraft Pulp Mill Description. The integration of a lignin extraction unit has been studied in the case of a French Kraft pulp mill producing 1300 ADTP/day, presented in Figure 2 and Table S1 (in the Supporting Information). This mill is an interesting and typical case because it presents a continuous digester (Kamyr type), an unbleached pulp (so without a bleaching unit), a European average scale, and a single wood feedstock (pine). Therefore, it is a well-controlled and stable biorefinery case. The black liquor boiler was running in its full capacity.

Lignin Extraction at the Pilot Scale and Characterizations. Kraft lignin extraction was carried out at the pilot scale (presented in the Supporting Information, Figure S2) using the industrial black liquor sampled in the cbl45% (concentrated black liquor 45%) tank of the evaporation line (see Evaporation Line in Figure S2).

50 kg of black liquor were neutralized in a thermo-regulated reactor at 70 °C under continuous stirring until pH 9 by bubbling $CO_2(g)$.[31] This acidification of the black liquor led to lignin particle formation, usually performed in warm diluted black liquor at 30−35% dry content and at pH 9, which are the best conditions for high yield, filtration ease, low chemical consumption, and low H_2S emission.[9,25,32−34] The lignin suspension was filtrated using a spin dryer equipped with a polypropylene filtration medium of 5 μm pore diameter. The obtained lignin cake has been purified by two successive washing steps using diluted acidic solution (30 L of H_2SO_4 2%, 20 °C), as usually practiced.[11,19,25] The final purified lignin cake was spread-dried at ambient air. The final purified lignin cake, washing filtrates, and residual black liquors were weighted, sampled, and characterized, according to the various analytical methods detailed in the Supporting Information. All these data were then embedded in the simulation tool.

Process Simulation Tool of the Entire Kraft Mill. Our institute has developed the PS2000 simulation platform devoted to pulp and paper processes, using the advanced computer-aided modeling environments Gensym G2. This simulation tool leads to a simplified schematic representation of the process as simple operations linked together for which models have been established (primarily volumetric and mass balance equations). The volumetric and mass balances are the results of industrial data derived from the process control panels of the mill and also from analytical data obtained on various streams (wood, pulp, liquor, effluents, etc.) sampled in the mill.

Compared to Aspen Plus or Prosim software, the PS2000 platform presents a visual interface similar as the industrial control system of the mill (operator control screens), which facilitates its industrial transfer. In addition, it allows user-friendly modifications of the operational units. Wood, pulp, and white liquors were collected and analyzed, as well as mill data (flows, makeup of several chemicals, pulp production, boiler production, etc., and annual, monthly, and daily industrial data).
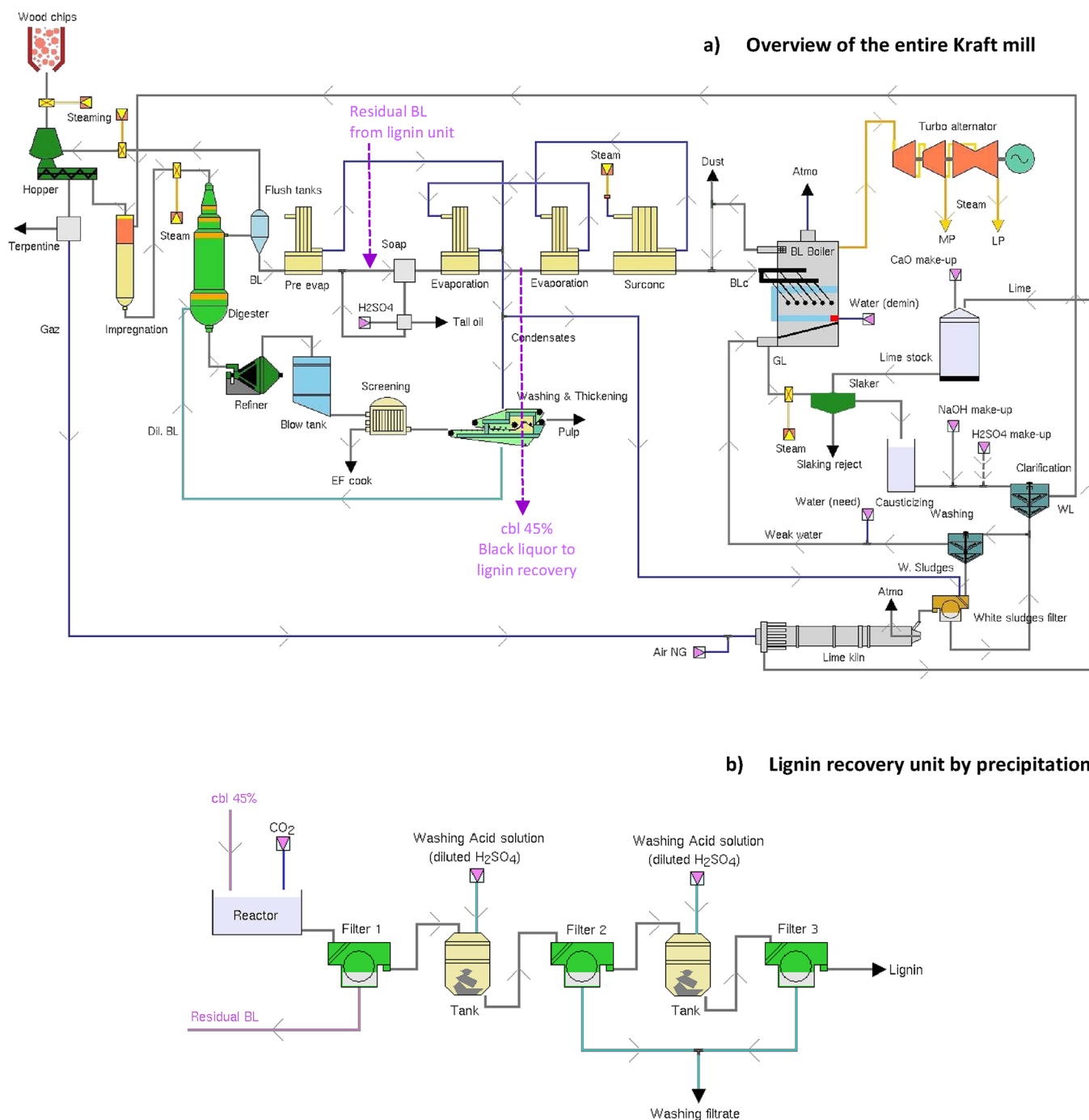
Figure 2. Simplified representation of (a) the entire Kraft pulp mill and (b) the lignin extraction unit.

The entire Kraft mill is constituted of five main units: (i) wood chip feeding and pulping, (ii) pulp washing, (iii) black liquor evaporation, (iv) boiler and recovering loop, and (v) lime kiln (Figure 2a, more details are provided in the Supporting Information, Figure S3 and Table S3).

The results on lignin recovery from the black liquors as obtained by the experiments at the pilot scale were also included in the simulation tool, which is presented in Figure 2b. The model of this unit is composed of (i) a black liquor neutralization reactor, (ii) filtration equipment (represented by a drum filter) to separate the crude lignin cake and the residual black liquor (three filters numbered from 1 to 3 in Figure 2b), and (iii) two washing lines in a series constituted of a washing tank connected to a filter, to collect a final purified wet lignin cake.

The total dry matter, lignin content, inorganics, and especially sodium and total sulfur contents in the different flows were taken into account (see the section presenting the experimental results). Mass balances of these elements were achieved by setting the filtration retention factors (based on pilot-scale data) of the separation equipment (see Results section) and chemical makeup (especially NaOH and H_2SO_4). Energy production was also considered by a direct relation vs the dry matter content of the black liquor entering in the boiler.

■ RESULTS

Experimental Data of Lignin Extraction at the Pilot Scale. Two campaigns of lignin production at the pilot scale were carried out, 1 year apart, in order to study the stability of

Table 1. Analytical Data of Lignin Extraction Unit at the Pilot Scale (Campaign No. 1)[a]

	black liquor	lignin cake	residual black liquor	first washing filtrate	2nd washing filtrate
volume/mass	50 kg (40 L)	8.1 kg	26 L	44 L	35.5 L
dry matter content	42.9% (w/w)	57% (w/w)	409 g/L	82 g/L	27 g/L
density at 20 °C	1.26 g/cm^3	nd	nd	nd	nd
pH$_{20°C}$	13.6	nd	10.2	8.6	1.5
lignin content	AIL: 25.4%	AIL: 93.1%	AIL: nd	AIL: nd	AIL: nd
	ASL: 7.3%	ASL: 3.0%	ASL: 23 g/L	ASL: 9.5 g/L	ASL: 1.4 g/L
	total: 32.7%	total: 96.1%			
carbohydrates	nd	2.3%	nd	nd	nd
elemental analysis (CHON)	C 34.5%. H 3.6%. O 35.8%. N < 0.1%. total: 73.9%	C 71%. H 5.6%. O 21.3%. N < 0.1%.total: 97.9%	nd	nd	nd
total sulfur (S)	4.0%	2.0%	16 g/L	8.1 g/L	9.5 g/L
sodium (Na)	19.6%	0.28%	116 g/L	22 g/L	4.5 g/L
potassium (K)	1.5%	0.15%	10.5 g/L	nd	nd
inorganic sulfur:	3.25%	0.3%	8.6 g/L	6.1 g/L	6.2 g/L
sulfide (in eq.S)	1.7%	nd	0.6 g/L	<0.5 g/L	<0.5 g/L
sulfate (in eq.S)	0.83%	0.30%	4.5 g/L	6.0 g/L	6.0 g/L
sulfite (in eq.S)	0.08%	<0.02%	0.46 g/L	<0.02 g/L	<0.02 g/L
thiosulfate (in eq.S)	0.64%	<0.02%	3.05 g/L	0.14 g/L	0.17 g/L
minerals (ashes 525 °C)	nd	2.0%	191 g/L	50.6 g/L	19 g/L

[a]wt %/100 of equivalent anhydrous sample. nd: not determined.

the Kraft mill (by two different black liquor samplings). The comprehensive analyses of the different pilot streams (campaigns 1 and 2) are presented in Table 1 and Table S2 (in the Supporting Information).

The two studied black liquors present a similar chemical composition during campaigns 1 and 2, with only slight variation in sodium content (Na: 19.6 and 17.6 wt % of eq. anhydrous black liquor, respectively, Table 1 and Table S2). The measured chemical contents were in agreement with the typical composition of European softwood black liquor, i.e., CHON in the range of 68−77 wt %, sodium in the range of 18−22%, potassium in the range of 1.5−2.5%, and sulfur in the range of 4−7%.[8] The total CHON analysis (i.e., 73−74 wt %) exhibit the organic matter contents in the black liquor. Lignin represents 33 wt % of the black liquor, and it accounts for 45−47% of the total organics (considering CHON analysis). Our results are in good agreement with previously reported data.[35] The aliphatic carboxylic acids represent the other half part of the organic matter.[35] Therefore, the 50 l of black liquor treated during campaigns 1 and 2 contained 7.1 kg (Table 1) and 7.4 kg (Table S2) of lignin, respectively. The lignin recoveries at the pilot scale were of 63 and 61 wt % (g of eq. dry recovered lignin per 100 g of initial lignin in the black liquor) and of 21.4 and 21.5 wt % (g of eq. anhydrous recovered cake per 100 g of initial dry matter in the black liquor) during campaigns 1 and 2, respectively, which are in the same range of the literature data for the same final pH.[20,35−38,30] Indeed, lignin in black liquor is in the weak base form of phenolates (pK_a ∼ 7.4−11.3). It turns into acid form by acidification with CO_2 which is less hydrophilic and thereby less soluble in aqueous solution and further forms a suspension (which precipitates).[24,35,37,39]

The black liquor presents a very high amount of sodium, which constitutes the main impurity of the lignin cake. Sodium removal is usually performed by acidic washings.[11,24] The low sodium content of the lignin cake (i.e., 0.3 and 0.4%) demonstrates the high efficiency of the acid washing performed, with 98−99% of the sodium reduction, in the same range as in the LignoBoost process.[11] The re-slurry washing procedure has

already been indicated to remove sodium, as well as the use of diluted acid, preferably H_2SO_4 than HCl.[24,25,40] The obtained lignin is of high purity (see the Supporting Information for more details) and contained 93% of acid-insoluble lignin (AIL, or Klason Lignin), 3% of acid-soluble lignin (ASL), and 2.3% of carbohydrates in excellent agreement with Helander et al.[41] for a similar process.

The retention factors of each chemical (i.e., "X") in the different filters ($R_X = X$ in the cake (g)/X in the feed (g)) are presented in Table 2. They were determined according to the experimental data of the extraction of the lignin as performed at the pilot scale during the first campaign (Table 1).

Table 2. Retention Factors (R) of the Main Chemicals and of Lignin Extraction Unit[a]

R_X (wt %)	filter no. 1 (cake dryness 90%)	filter no. 2 (cake dryness 90%)	filter no. 3 (cake dryness 60%)
lignin	95%	95%	99%
all minerals	67%	85%	1%
sodium	24%	18%	7%
sulfur	49%	39%	18%

[a]Data obtained by the experiments at the pilot scale and then implemented in the simulation tool.

The three filtration equipment retained 95−99% of the lignin flow constituting the initial black liquor (Table 2). These retention factors are in the same range than those mentioned by Uloth et al.[24] (i.e., 89−93%) and Öhman et al.[38] (i.e., 88%). The retentions of sodium and sulfur decrease along the process line with a first lignin cake (from filter no. 1) containing 24% of the sodium and 49% of sulfur, compared to 7 and 18%, respectively, in the washed lignin cake (from filter no. 3). The first washing (filter N°2) eliminates 15% of the total minerals (85% of minerals are keep in the cake), and during the second washing (filter no. 3), most of the minerals were removed (1% retention factor, Table 2).

D

Simulation of the Whole Kraft Mill with Lignin Recovery. All the Kraft mill data were recorded during the two campaigns (from the control panels of the mill) and included in the simulation tool (see the Supporting Information). The lignin extraction unit has been integrated in the simulation of the Kraft pulping process line based on the pilot-scale experimental results. Three scenarios of lignin uptake (1, 10, and 50 t/day) were assessed. The residual black liquor was still rich in minerals, constituting 47−50 wt % of the total solids, and especially sodium and sulfur compounds (Table 1 and Table S2), with 70−80 and 45−55% of sodium and sulfur, respectively, remaining in the black liquor after lignin extraction. Therefore, the re-introduction of the residual black liquor in the evaporation line was considered in all simulation schemes (see Figure 2).

The global mass balances along the Kraft mill are presented in the Supporting Information (Tables S4 and S5). To the best of our knowledge, such mass balances based on an industrial mill (and on pilot-scale lignin precipitation) are not common in the literature.

As previously mentioned, sodium and sulfur are among the main chemicals introduced in the Kraft pulping process, in order to ensure sufficient sodium hydroxide (NaOH) and sodium sulfide (Na_2S) entering in the digester for the cooking. Sodium and sulfur makeup are usually implemented along the Kraft pulp process, in the black liquor before the boiler (here in the cbl45% tank) and/or in the green/white liquor line (here in the pipeline of the white liquor after causticizing and before separation) (Figure 2a and Figure S3).

The annual and medium makeup of the Kraft pulp mill was in 2018−2019 of 18.05 kg NaOH/ADTP, 7.06 kg H_2SO_4/ADTP (H_2SO_4 mainly used for tall oil preparation), and 0.17 kg Na_2SO_4/ADTP. The sodium and sulfur amounts were in the range of usual data for an unbleached Kraft mills.[30,39,42]

During the extraction of lignin, additional sulfuric acid is needed for the washing stage. The lignin cake contains sodium (until 0.39%), and its extraction will affect the sodium balance of the mill. The simulation of the lignin extraction in this Kraft mill shows that 261−297 kg H_2SO_4/t of crude lignin produced and 163−195 kg NaOH/t of crude lignin would be needed to insure the same quality of the white liquor entering in the digester (Table 3 and Figure S4 presenting simplified Sankey mass flows). These sodium and sulfur amounts are in the same range as literature data.[9,29,30]

Concerning steam production, the extraction of lignin reduces the concentration in organic fuel (lignin) of the black liquor entering in the boiler. The simulation highlights a significant reduction of organic matter in the black liquor at the boiler entrance with 2 kg eq. dry/kg of produced crude lignin in a demo plant and an industrial unit. This reduction would lead to a decrease of 6.7−7.1 t of steam/t of produced lignin (Table 3). In the case of an industrial unit of 50 t/day of lignin extraction (representing 10 wt % of the total lignin available), the steam reduction would be of 6%. This value is in the same range as Kannangara et al.,[23] who showed that a 15% extraction lignin unit would lead to 13.5% steam loss using CADSIM Plus simulation (but for a different mill than in our case).

A simulation of an increase in pulp production has been performed to keep constant the lignin content in the black liquor entering in the boiler and, therefore, in order to maintain the steam production constant (Table 4). In that scenario, an additional 1.5 ADTP/t of crude lignin would be produced, representing an increase in 6.2% of pulp (when 50 t/day of lignin

Table 3. Simulation of a Lignin Extraction Unit Integrated in the Kraft Pulping Process of the Studied Mill: Impact of Lignin Extraction on Sodium and Sulfur Balance and on Steam Production

scenario	reference	pilot	demo plant	industrial unit
lignin production (eq. dry ton/day)	0	1	10	50
lignin production (kg crude lignin/ADTP)	0	0.85	8.37	41.84
sodium makeup (kg NaOH/ADTP)	18.05	18.21	19.36	24.87
additional sodium (kg eq. NaOH/t of crude lignin)		188	195	163
sulfur makeup (kg SO_4^{2-}/ADTP)	0.11	0.23	1.28	4.80
sulfuric acid addition (kg H_2SO_4/ADTP)	7.06	7.19	8.27	13.21
additional sulfur (kg eq. H_2SO_4/t of crude lignin)		297	265.8	261.5
black liquor entering in the boiler (t eq. dry/ADTP)	1.360	1.357	1.343	1.276
steam produced in the boiler (t/ADTP)	4.622	4.616	4.565	4.340
steam losses (ton of steam/t of crude lignin)		7.06	6.81	6.71

Table 4. Simulation of the Lignin Recovering Unit Integrated in the Kraft Pulping Processes: Cases with an Increase of Pulp Production to Keep Constant the Steam Production by the Boiler

scenario	reference	pilot plant	demo plant	industrial unit
lignin production (eq. dry ton/day)	0	1	10	50
steam loss (ton of steam/t of crude lignin)		7.06	6.81	6.71
steam produced in the boiler (t/ADTP)	4.622	4.616	4.565	4.340
pulp produced (ADTP/day)	1196	1197	1211	1271
additional pulp produced (ADTP/t of crude lignin)		1.5	1.5	1.5
sodium makeup (kg NaOH/ADTP)	18.05	18.24	19.69	26.17
additional sodium (kg eq. NaOH/t of crude lignin)		223	196	194
sulfur makeup (kg SO_4^{2-}/ADTP)	0.11	0.23	1.28	5.26
sulfur makeup (kg H_2SO_4/ADTP)	7.06	6.76	8.17	12.43
additional sulfur (kg eq., H_2SO_4/t of crude lignin)		220	275	254

is extracted). This result is in agreement with Lindgren et al.[29] on dissolving pulp mill (i.e., 8%) and in the same range than Kannangara et al.[23] (10−15% increase).

The simulation also highlights that this gain in the mill capacity would lead to a higher sodium need, with a supplement of 31−35 kg/day of NaOH. This increase in pulp production would not affect the sulfur makeup. If the mill would not increase its pulp capacity, the steam loss at the black liquor boiler can be compensated by an additional production of steam at the bark boiler devoted to green electricity on this specific studied mill. In that case, and considering that the production is of 3.73 t of steam/t of bark, the lignin extraction would need an additional bark feed in the bark boiler of 1.8−1.9 t of bark/t of crude lignin.

Costs Assessment of the Commodities. The lignin recovery unit requires CO_2 for the acidification of black liquor, as described in "Lignin Extraction at the Pilot Scale and

Characterizations" (Figure S2). It was not possible to quantify the CO_2 consumption during the pilot-scale trials. Therefore, the theoretical CO_2 consumption was evaluated by thermodynamic modeling as presented in details in the Supporting Information (Figure S5). We found an average CO_2 consumption of 200 kg/t of lignin. This value is in the same range than previous literature data.[11,20,25]

The sulfuric acid amount used for the lignin washing at the pilot scale was 0.6 kg ($=2 \times 30$ L of H_2SO_4 at 2% w/v), meaning 67 and 74 kg/t of lignin during campaign no. 1 and campaign no. 2, respectively. Together with the sulfuric acid need to keep the sulfur balance in the mill, the total sulfuric acid can be evaluated in the case of the steam loss compensation by an additional pulp production (Table 4). In this case, a total of 220−275 kg of H_2SO_4/t of crude lignin would be needed (Table 4), which is in the same range as previous results: from 100 kg of H_2SO_4/t eq. dry lignin[28,29] and until 340−400 kg of H_2SO_4/t eq. dry lignin.[30]

The NaOH makeup was evaluated to be 163−188 kg/t of crude lignin when steam is lost (Table 3) and 194−223 kg/t of crude lignin when additional pulp production is assumed (Table 4). This estimation was slightly higher than the 100−160 kg/t of lignin indicated in the literature.[19,30]

Therefore, upon these chemical consumptions and according to the usual market prices in 2021, the chemical costs for lignin recovery varied from 76 to 85 €/t without additional pulp production to 77−87 €/t with additional pulp production (Table S6), for the different scenarios (i.e., 1 t of lignin/day, 10 and 50 t/day). This assessment is in good agreement with Benali et al.[20] who compared the costs for chemicals of the LignoBoost process (i.e., 100−150 $/t of lignin) and of the LignoForce system (i.e., 129−227 $/t of lignin).

The second large part of expenses is the cost of the steam losses. As previously pointed out, our simulation shows a deficit of 6.7−7.1 t of steam/t of crude lignin (Table 3), which means a loss of 132−142 €/t of crude lignin (considering 20 €/t of steam). Together with the chemical cost, this scenario of integration led to a total production cost of 210−227 €/t of eq. dry of lignin (Table S6).

To compensate the steam loss, one potential way would be to valorize additional biomass in the second boiler ("bark" boiler). In the case of the studied mill, it would represent 1.8−1.9 t of barks/t of crude lignin. This is slightly higher than the estimation of Kannangara et al.[23] with 47 t/day of additional biomass in the case of 73 t/day of lignin produced. This cost was evaluated to be 122−129 €/t of crude lignin. That scenario impacts only weakly the total production cost, which becomes 198−214 €/t of eq. dry lignin.

The other way is to produce additional pulp to overcome the lignin deficit entering in the black liquor boiler. An additional pulp production of 1.5 ADTP/t of crude lignin would be possible. It would lead to an additional income of about 900 €/t of crude lignin (considering an additional 3 t of eq. dry wood raw materials entering in the mill and a Kraft pulp market prize of 900 €/ADTP[43]). In that case, no steam losses should be compensated and the production cost is only related to the chemical cost. It was evaluated to be 77−87 €/t of crude lignin. This chemical cost would only account for 10−15% of the total operating expenses, as it is the case for the LignoBoost process. It can be compared to the lignin market prize of 600−800 US$/t[44]. This last scenario is by far the most economically interesting one, as already pointed out by Benali et al.[44] and Vakkilainen and Valimaki.[27]

CONCLUSIONS

The recovery of Kraft lignin has been experimentally studied at the pilot scale with industrial black liquors. The lignin recovery unit has been integrated in a global simulation platform (PS2000) of the studied industrial pulp mill. Its integration in the whole Kraft process has been assessed for different production scale scenarios (1, 10, and 50 t/day of lignin produced). 163−195 kg of NaOH and 258−266 kg of sulfuric acid would be needed to cover the extraction of 1 t of crude lignin and to keep the Na/S balance in the Kraft process.

At the same time, the lignin extraction leads to a decrease in organics entering the boiler, which would cause a reduction of 6.7−7.1 t of steam produced per ton of crude lignin. The energy production of the mill can be maintained by increasing the pulp production (i.e., 1.5 ADTP/t of crude lignin), which is followed by an additional sodium makeup (but no additional sulfur) or by using additional biomass in the second boiler (i.e., 1.8−1.9 t of wet barks/t of crude lignin).

The chemicals and energetic costs have been calculated for the different scenarios. For this pulp mill case, the most profitable scenario is a recovery of lignin together with a pulp capacity increase.

ASSOCIATED CONTENT

ⓈI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.2c07678.

> Principle of lignin recovery by acid precipitation; Kraft mill parameters; lignin precipitation conditions, analytical methods, and results; pulp mill simulation tool and mass balances of the mill; CO_2 consumption; costs assessment of chemicals and energy (PDF)

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Notes

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