

A Quantitative Comparison of the Precipitation Behavior of Lignin from Sweetgum and Pine Kraft Black Liquors

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Lignin is a by-product of the pulp and paper industry that can be precipitated by acidification from black liquor as a potential feedstock for valuable green materials. Precipitation and quantification of lignin from softwood black liquors have been documented and commercialized with well-established methods; however, applying those methods to the precipitation of lignin from hardwood black liquors has produced low lignin yields. A need to understand the main differences between hardwood and softwood lignin precipitation prompted the current investigation. Multiple black liquor samples from sweetgum and pine pulping were obtained at different times of standard kraft cooks. Two lignin fractions were precipitated from each of these black liquors, one at pH 9.5 and one at pH 2.5. Detailed lignin and carbohydrate material balances were performed around each of the sample sets, starting with the wood and ending with precipitated lignin fractions. For all conditions tested, the amount and purity of pine lignin precipitated were superior to sweetgum lignin. The maximum recovery for sweetgum lignin was 69.7%, while for pine lignin, it was 90.9%.

Keywords: Lignin; Precipitation; Material balance; Purity; Hardwood; *Pinus taeda*; *Liquidambar styraciflua*

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INTRODUCTION

Kraft (or sulfate) pulp mills account for around two-thirds of the global pulping capacity (Magdeldin and Järvinen 2020). The kraft process is based on the application of sodium hydroxide (NaOH) and sodium sulfide (Na₂S) to wood chips, under pressure and relatively high temperatures (150 to 170 °C), which targets lignin fragmentation/hydrolysis, dissolution, and subsequent fiber liberation while retaining the majority of the carbohydrates in a fibrous form. The process generates a residual process stream (spent liquor/black liquor) that is rich in organic degradation products (lignin and carbohydrates) and spent inorganics (*e.g.*, sulfides, sulfates, carbonates, hydroxides). Typically, this black liquor is subjected to a recovery system in which it is evaporated to a high solids content of 65 to 72 wt% and then combusted to smelt in a recovery boiler to recover the original chemicals (NaOH and Na₂S) with the concomitant production of steam and power from the dissolved organics.

Many recovery boilers are limited by total solids loading or steam generation (circulation limit), and hence they represent the capacity-limiting step in several pulp mills. Lignin isolation from black liquor is considered a potential method for reducing these process limitations (Öhman *et al.* 2007). In fact, the creation of new economic downstream uses for the black liquor enables greater pulp production and an increase in total revenue (Zhu *et al.* 2014; Klett 2017) since the recovered lignin can serve as a feedstock for biomaterials and biochemicals.

Lignin is produced at large scale: approximately 78 million tons are generated globally each year by kraft pulp mills (Miller *et al.* 2016). Additionally, research efforts also use lignin precipitation as a method to obtain selected, purified samples for lignin component analysis.

Lignin is a complex biopolymer biosynthesized by repetitive dehydrogenation and cross-coupling of three major phenylpropanoid (C6–C3) units, namely, sinapyl alcohol, coniferyl alcohol, and *p*-coumaryl alcohol; forming syringylpropane (S), guaiacylpropane (G), and *p*-hydroxyphenylpropane (H) units in lignin (Lin and Dence 1992). These structural building blocks are zipped together by ether linkages and carbon-carbon bonds (Alén 2000).

Although the chemical structure of lignin has been extensively investigated by both wet chemical and spectroscopic methods, its structural complexity has never been fully elucidated (Ralph *et al.* 2004). However, it is well known that the structural characteristics of lignin from hardwoods and softwoods profoundly differ from each other. Guaiacyl lignin is typically found in softwoods and appears to vary little amongst species (Sarkanen *et al.* 1967; Akiyama *et al.* 2005). Guaiacyl-Syringyl lignin is typically found in hardwoods, and the S to G ratio tends to vary greatly between species (Santos *et al.* 2012).

Lignin properties depend on feedstock from which they are obtained, the extraction method employed, and downstream purification processes (dos Santos *et al.* 2014). LignoBoost and LignoForce processes are the two main commercial technologies for precipitating lignin from spent liquors (Dessbesell *et al.* 2020). LignoBoost is an industrial process that uses dissolved carbon dioxide (CO₂) to decrease the pH of the process stream from approximately 13 to 10. “LignoForce” is another commercialized technology that first oxidizes the black liquor with oxygen (O₂) and then acidifies to around pH 9 with CO₂ (Fatehi and Chen 2016). It is known that when the black liquor is acidified, the phenoxide groups of the dissolved lignin become protonated, and lignin solubility decreases, *i.e.*, the lignin precipitates. After precipitation, the solids are separated by filtration and subsequently resuspended in water and sulfuric acid (H₂SO₄) to obtain a lower pH of about 2.5 to remove impurities (Wallmo *et al.* 2016).

The bulk of the work on lignin precipitation from kraft black liquor has been performed on softwood, while very little has been published about hardwood black liquors (Zhu *et al.* 2014). It was initially thought that the lignin precipitation methods developed and proven to work for the majority of softwood species would be acceptable for hardwood species. However, investigations into various hardwood lignin compositions have used the softwood precipitation techniques and obtained unexpectedly low lignin yields (Santos *et al.* 2011, 2012; Kumar *et al.* 2016; Gomes *et al.* 2018; Giummarella *et al.* 2019). Lack of understanding of hardwood lignin precipitation is a significant hurdle toward fully characterizing and utilizing this raw material, which prompted this study.

The current work aimed at establishing a material balance over the kraft pulping process and lignin precipitation from hardwood and softwood black liquors obtained at different pulping extents. Quantification of lignin recovery was also intended. Thus, two fractions of sweetgum lignin were precipitated from black liquor at distinct pHs (pH 9.5 and 2.5), and a baseline comparison between these lignins and pine lignins was accomplished. The impact of H-factor on yield and purity of precipitated lignins was also investigated.

EXPERIMENTAL

Materials

Southern sweetgum (*Liquidambar styraciflua*), a hardwood, and Southern pine (*Pinus taeda*), a softwood, were the samples investigated. Wood logs were processed into chips and screened according to the standard method “Size distribution” (SCAN-CM 40:01, 2001).

Methods

Kraft pulping

Kraft pulping experiments were carried out in a 10 L laboratory pulping digester (Greenwood Instruments, LLC; Andover, MA, USA) equipped with a temperature controller, liquor recirculation piping, and an indirect heating system. The general cooking conditions are shown in Table 1. Batch cooks were performed using 1000 g oven-dried (O.D.) chips. Pulped chips were placed in a stainless-steel box equipped with a 150-mesh screen, washed thoroughly with water, and disintegrated. The washed pulp was then centrifuged to approximately 30% consistency and subsequently stored in polyethylene bags for follow-up characterization. Pulp yield was gravimetrically determined. The black liquor was collected and characterized according to the protocols “Solids Content of Black Liquor” (TAPPI/ANSI T650 om-15) and “Residual Alkali” (SCAN-N 33:94). The black liquor samples were stored in sealed Nalgene bottles for lignin precipitation.

Table 1. Kraft Pulping Conditions

| Parameter | Hardwood (Sweetgum) | Softwood (Pine) |
|---|------------------------|--------------------|
| Liquor/Wood ratio | 4/1 | 4/1 |
| Effective Alkali as Na ₂ O (%) | 16 | 19 |
| Sulfidity (%) | 25 | 25 |
| Temperature (°C) | 160 | 170 |

Pulping runs were done at 30, 60, 90, 120, and 150 min to obtain different H-factors covering an entire typical bleachable grade cook. All other pulping conditions remained constant (Table 1). H-factor and pulping temperature at the time of sampling are shown in Fig. 1 for both the sweetgum and pine cooks. Each raw material generated five pulp samples and five black liquor samples. A sample of pure wood chips was also collected.

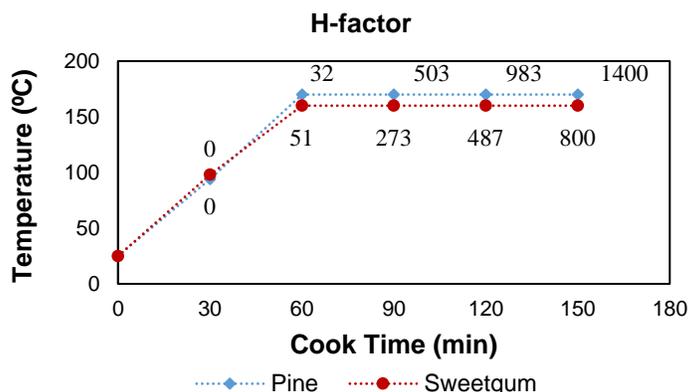


Fig. 1. H-factor of each sample for the sweetgum and pine cooks

Lignin precipitation

Collected black liquor samples were filtered over Whatman #3 filter paper to remove fines. Filtered black liquors were evaporated to a solids content of approximately 20% and used for precipitation experiments of two lignin fractions (pH 9.5 and 2.5). Concentrated black liquors were sparged with CO₂ at a low flow rate to attain a pH of 9.5. The concentrated mixtures were allowed to equilibrate over 30 min. The precipitated materials were isolated from the liquors through centrifugation, and the supernatants were stored for further precipitation. The solids were washed with hydrochloric acid (HCl) to remove ash at pH 2.5 and subsequently washed with acetic acid to remove residual HCl at pH 3.5. After washing steps, the solids were isolated by centrifugation, suspended in deionized water, and freeze-dried. Typically, precipitated lignin is washed with H₂SO₄; however, in this work, washing was performed with HCl because it is reported to improve ash removal compared to sulfuric acid (dos Santos *et al.* 2014). Washing with acetic acid was carried out to remove residual HCl because it is less harmful to the freeze-drier vacuum pump compared to HCl. These solids, called lignin fraction at pH 9.5, were obtained according to commercially known lignin isolation protocols (*e.g.*, LignoBoost).

The supernatants after carbonation were further acidified with 6 N HCl to pH 2.5 in order to precipitate a second lignin fraction, which was also washed with HCl, acetic acid, and freeze-dried. These solids were called lignin fraction at pH 2.5 and were obtained with the understanding that at pH 2.5, all remaining lignin or most of it would be precipitated.

Precipitation experiments were performed at room temperature, atmospheric pressure, and constant stirring. A schematic representation of the precipitation and purification processes is shown in Fig. 2.

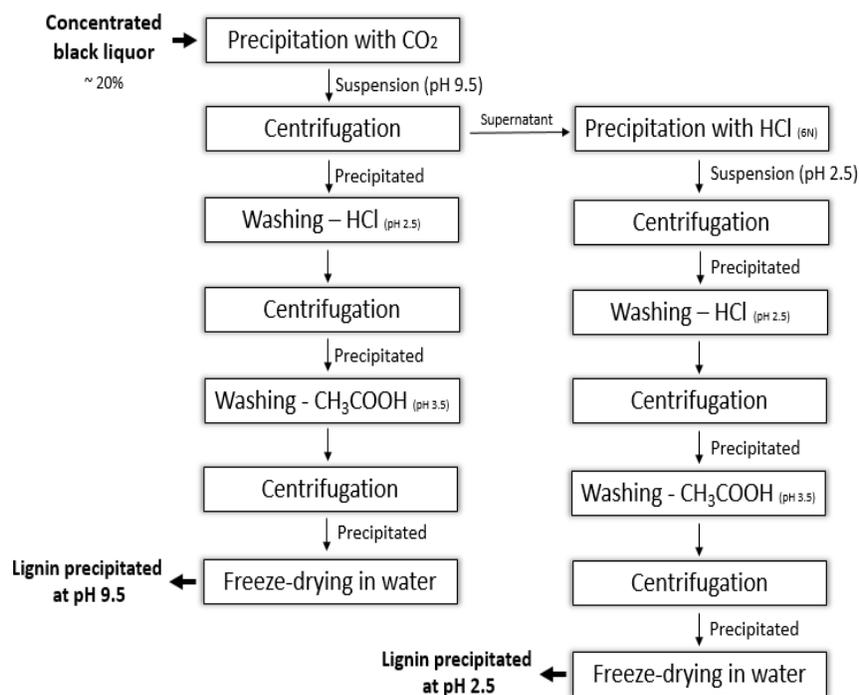


Fig. 2. Schematic representation of the protocol used for lignin precipitation from kraft black liquor of two lignin fractions: pH 9.5 and pH 2.5

The influence of pH, ionic strength, temperature, agitation speed, solids content, and atmosphere on precipitation have been well studied and reported before (Howell and Thring 2000; García *et al.* 2009; Wallmo *et al.* 2009; Theliander 2010; dos Santos *et al.* 2014; Zhu *et al.* 2014; Helander *et al.* 2016; Durruty *et al.* 2017; Sewring *et al.* 2019). The experimental conditions applied to sweetgum and pine black liquors in the present investigation were chosen to establish a fair comparison between the behavior of both lignins over precipitation.

Characterization of wood, pulp, and precipitated lignin

The wood chips were ground in a Wiley mill. The resulting milled wood was screened, and the fraction, which passed through a 40-mesh screen and was retained on a 60-mesh screen was kept for analyses. The milled wood was extracted in a Soxhlet apparatus for 6 h using a benzene-ethanol mixture (2:1 v/v ratio) (TAPPI Standard Test Method T 264 cm-07 “Preparation of wood for chemical analysis”). Carbohydrates and lignin contents were quantified according to the Technical Report NREL/TP-510-42618 “Determination of structural carbohydrates and lignin in biomass.” Ash content was measured according to “Ash in wood, pulp, paper and paperboard: combustion at 525 °C” (TAPPI Standard Test Method T 211 om-16). The same protocols were applied to the characterization methods for the lignin samples precipitated from the black liquors.

Material balance

Table 2 shows the template used for the material balance calculations.

Table 2. Material Balance of the Lignin Isolation from Sweetgum Black Liquor at 60 Min. Balance Assumes 100 O.D. g of Wood as the Starting Material

| Sample Location | Inputs (g) | | Intermediates (g) | | Outputs (g) | |
|--|------------|--------|-------------------|--------|-------------|-------------|
| | Carbs | Lignin | Carbs | Lignin | Carbs | Lignin |
| Wood Chips | 64.5 | 25.9 | --- | --- | --- | --- |
| Pulp | --- | --- | --- | --- | 47.7 | 10.8 |
| Black Liquor | --- | --- | --- | --- | 16.8 | 15.1 |
| Black Liquor | 16.8 | 15.1 | --- | --- | --- | --- |
| Supernatant from CO ₂ Precipitation | --- | --- | 15.1 | 12.0 | --- | --- |
| Supernatant from HCl Precipitation | --- | --- | 14.8 | 8.8 | --- | --- |
| Lignin @ pH 9.5 | --- | --- | --- | --- | 1.7 | 3.1 |
| Lignin @ pH 2.5 | --- | --- | --- | --- | 0.4 | 3.2 |
| % Recovery from Black Liquor | --- | --- | --- | --- | 12.2 | 41.8 |

The starting wood chips were used as the input materials for the pulping process, while pulp and black liquor were the outputs. For the precipitation experiments, black liquors were the input, whereas the solids isolated were the outputs of the system. Solid and liquid flows were accounted for in order to determine lignin recovery (yield) over precipitation experiments. The calculations were based on the compositional analysis of wood, pulp, and solids precipitated from black liquor. In addition, the volume of white liquor and solids from the chemicals added to the pulping process were taken into

consideration. The data in Table 2 were obtained for sweetgum pulp and liquor after 60 min of cooking time (51 H-factor).

The amounts of carbohydrates and lignin in the sweetgum wood chips were 64.5 g and 25.9 g, respectively. After 60 min of pulping (at H-factor 51), the residual carbohydrates mass was 47.7 g, whereas the residual lignin mass was 10.8 g. The determination of carbohydrate and lignin contents in the wood and in the produced pulp allowed calculation of the amount of carbohydrates and lignin dissolved in the black liquor. Therefore, at an H-factor of 51, the amount of carbohydrates in the black liquor was 16.8 g (64.5 g - 47.7 g), and the amount of lignin was 15.1 g (25.9 g - 10.8 g). These values were used as inputs to calculate carbohydrate and lignin recovery.

After precipitation of both lignin fractions (pH 9.5 and 2.5), the solids isolated were characterized, and the values obtained were the outputs shown in the bottom part of Table 2. In the example, the lignin fraction isolated at pH 9.5 represented 1.7 g of carbohydrates and 3.1 g of lignin. In contrast, the lignin fraction obtained at pH 2.5 represented 0.4 g of carbohydrates and 3.2 g of lignin. The intermediate values were obtained by a simple subtraction of each compound dissolved in the black liquor minus the amount obtained in each step of the precipitation. Finally, the recovery of each compound (carbohydrates and lignin) was calculated based on its amount in the black liquor and in the solids precipitated.

RESULTS AND DISCUSSION

Pulping

The present work evaluated pulp and black liquor samples of hardwood (sweetgum) and softwood (pine) at different points of kraft pulping. The cooks were performed to different levels by varying H-factor. Pulping results for sweetgum and pine are shown in Table 3.

Table 3. Pulping Results for Sweetgum and Pine: H-Factor, Pulp Yield, Residual Effective Alkali (rEA), and Percent of Solids in the Black Liquor

| Cook Time (min) | Sweetgum | | | | Pine | | | |
|-----------------|----------|----------------|-----------|------------------|----------|----------------|-----------|------------------|
| | H-factor | Pulp Yield (%) | rEA (g/L) | Solids in BL (%) | H Factor | Pulp Yield (%) | rEA (g/L) | Solids in BL (%) |
| 30 | 0 | 85.5 | 12.5 | 8.9 | 0 | 93.2 | 19.2 | 11.1 |
| 60 | 51 | 62.6 | 9.0 | 12.1 | 32 | 69.1 | 17.0 | 13.8 |
| 90 | 273 | 50.7 | 4.7 | 14.1 | 503 | 51.4 | 11.5 | 16.6 |
| 120 | 487 | 48.7 | 3.5 | 14.4 | 983 | 47.4 | 10.0 | 17.3 |
| 150 | 800 | 47.6 | 2.9 | 14.4 | 1400 | 43.5 | 5.9 | 16.6 |

where BL is black liquor

Lower pulp yields were obtained for hardwood at the beginning of the process. Specifically, the total pulp yield of sweetgum after 30 min (0 H-factor; *i.e.* when the target temperature has not yet been reached) was 85.5%, whereas, for pine, it was 93.2%. The greater yield losses in sweetgum are because hardwoods are easier to pulp than softwoods, due to the former's lower lignin content and presence of syringyl units (Santos *et al.* 2011). In addition, at the beginning of conventional kraft cooking, xylan (main hemicellulose in

hardwoods) is partly solubilized in the cooking liquor and many of the side groups and acetic acid residues are cleaved (Viikari *et al.* 2009). On the other hand, after 150 min, the pulp yield for sweetgum and pine were 47.6% (800 H-factor) and 43.5% (1400 H-factor), respectively. Even though initially sweetgum showed greater pulp yield losses, the final pulp yield was superior to pine also because of the relative ease in pulping hardwood compared to pine. Harsher pulping conditions were necessary to obtain pine pulp due to higher starting lignin content, which explains the lower yield.

The effective alkali (as Na₂O) for the sweetgum and pine cooks was 16% (20.5 g/L) and 19% (24.4 g/L) based upon O.D. wood, respectively, which accounts for most of the inorganics added to the process. A minor part of the inorganics was associated with the wood as Non-Process Elements (NPEs). The ions OH⁻ and HS⁻ are consumed by lignin and carbohydrate hydrolytic reactions; hence, the residual effective alkali (rEA) decreased over time. Within 150 min, the rEA was 2.9 g/L in the sweetgum black liquor (800 H-factor) and 5.9 g/L in the pine black liquor (1400 H-factor).

The method used to determine solids content in the black liquor accounts for the organic and inorganic fractions present in the liquor; thus, an increase over the process was expected because of the degradation and dissolution of wood compounds. The solids ranged from 8.9% (0 H-factor) to 14.4% (800 H-factor) in sweetgum and from 11.1% (0 H-factor) to 16.6% (1400 H-factor) in pine.

The goal of kraft pulping is to preserve the carbohydrates content as high as possible. Unfortunately, carbohydrates degrade as delignification reactions occur. The composition analysis of sweetgum and pine wood chips and pulps are shown in Table 4.

Table 4. Characterization of Sweetgum and Pine Wood Chips for Carbohydrates, Lignin and Ash at Time “0” Followed by their Resultant Pulps for All Other Times Throughout Kraft Pulping Of 100 g (O.D.) of Wood

| Cook Time (min) | Parameter (g) | | | | | | | |
|-----------------|---------------|-------|----------|------|--------------|---------------|-----|-----|
| | Cellulose | Xylan | Galactan | GM | Total Lignin | Klason Lignin | ASL | Ash |
| Sweetgum | | | | | | | | |
| 0 | 43.5 | 14.8 | 1.2 | 5.1 | 25.9 | 23.5 | 2.4 | 0.4 |
| 30 | 38.4 | 12.3 | 0.8 | 3.6 | 21.6 | 19.1 | 2.5 | 1.2 |
| 60 | 36.0 | 9.9 | 0.7 | 1.2 | 10.8 | 9.5 | 1.3 | 0.8 |
| 90 | 33.5 | 8.7 | 0.3 | 0.9 | 2.9 | 2.1 | 0.8 | 0.6 |
| 120 | 33.5 | 8.5 | 0.3 | 0.9 | 1.4 | 0.8 | 0.7 | 0.6 |
| 150 | 33.2 | 8.6 | 0.3 | 1.1 | 1.2 | 0.5 | 0.7 | 0.6 |
| Pine | | | | | | | | |
| 0 | 40.0 | 6.1 | 3.3 | 16.4 | 31.7 | 30.9 | 0.8 | 0.7 |
| 30 | 38.7 | 5.8 | 2.3 | 14.6 | 28.7 | 28.1 | 0.6 | 1.8 |
| 60 | 36.1 | 4.9 | 1.4 | 6.4 | 19.2 | 18.8 | 0.4 | 1.4 |
| 90 | 35.1 | 3.6 | 1.0 | 6.2 | 6.7 | 6.3 | 0.4 | 0.9 |
| 120 | 35.4 | 3.5 | 0.9 | 5.1 | 3.9 | 3.5 | 0.3 | 0.9 |
| 150 | 32.8 | 3.4 | 0.7 | 4.6 | 3.3 | 3.0 | 0.3 | 0.7 |

Where GM is glucomannan, Total Lignin is a sum of Klason Lignin (acid-insoluble lignin) and acid-soluble lignin (ASL).

Time “zero” shows the characterization of the wood chips, while times 30 to 150 min are characterizations of the pulps produced. The residual carbohydrates content (*i.e.*, cellulose, xylan, galactan, and glucomannan), lignin, and ash in the pulp were calculated based on the content measured and pulp yield. Thus, the characterization presented in Table 4 depicts the degradation of each wood compound over the entire kraft pulping process.

The degradation of the main wood compounds of sweetgum and pine are graphically represented in Fig. 3, where the values are the residual content (g) of lignin, cellulose, and hemicelluloses over the kraft pulping process.

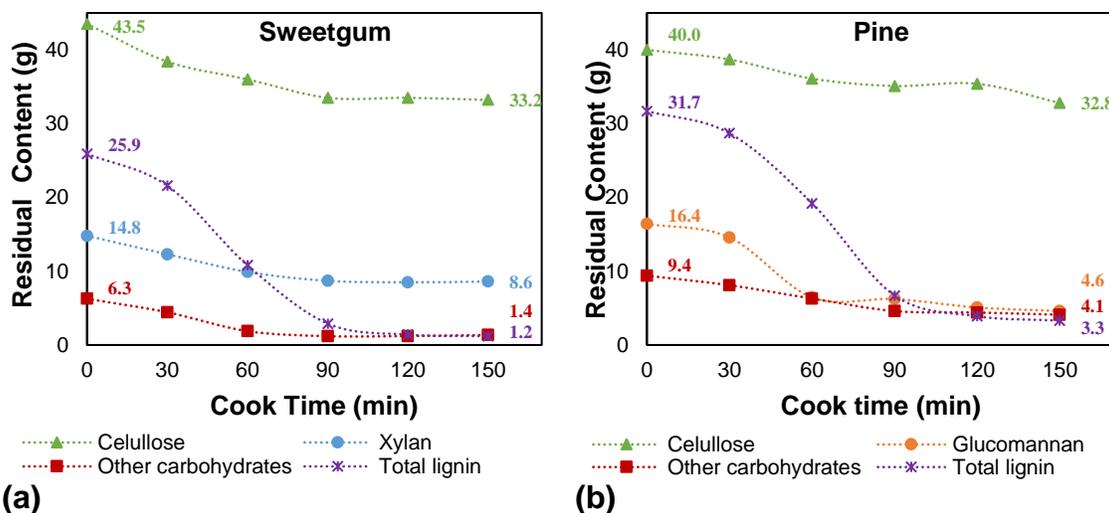


Fig. 3. Residual lignin and carbohydrate contents (g) for (a) sweetgum and (b) pine throughout kraft pulping of 100 g (O.D.) of wood

A large fraction of hemicellulose components are degraded and dissolved in the black liquor throughout kraft pulping; however, xylan (main hemicellulose in hardwoods) and glucomannan (main hemicellulose in softwoods) behave differently. The glucomannan is rapidly degraded and dissolved in the black liquor, whereas xylan is more resistant (Gellerstedt 2009). For instance, xylan contents of 14.8 g and 6.1 g were found in 100 g of sweetgum and pine wood chips, respectively. At the end of the pulping process, the residual amount in sweetgum was 8.6 g, and in pine was 3.4 g. The total loss of xylan was 41.6% in sweetgum and 44.3% in pine. With respect to glucomannan, the starting amount in sweetgum was 5.1 g, whereas, in pine, it was 16.4 g. After pulping, the final contents were 1.1 g and 4.6 g in sweetgum and pine, respectively. The total loss of glucomannan was 79% in sweetgum and 72% in pine. Thus, Fig. 3a shows how xylan is more resistant to the pulping process than the other hemicelluloses and Fig. 3b shows how rapidly glucomannans are degraded through the process. Furthermore, in the early phases of kraft pulping, many of the xylan side groups are cleaved; these hydrolytic reactions consume alkali and contribute to carbohydrate loss (Viikari *et al.* 2009), which may account for the significant decrease in rEA (Table 1) and pulp yield (Fig. 3).

On the other hand, the loss of cellulose was less prominent in both raw materials. It is well known that cellulose is resistant to kraft pulping because of its packing (crystallinity). In contrast, hemicelluloses are much less uniformly arranged (more exposed) and thus heavily degraded during pulping (Viikari *et al.* 2009). The predominant carbohydrate degradation reaction, called endwise peeling, consists of successive depolymerization of the carbohydrates (starting from the reducing end group). At elevated

temperatures (between 160 and 170 °C), alkaline hydrolysis becomes important because it forms more reducing groups by the random cleavage of the glycosidic bonds in polysaccharides (Alén 2011b).

Moreover, cellulose has a much higher degree of polymerization than hemicelluloses (Sixta 2006). Thus, due to cellulose's higher molecular weight and crystalline structure, it is not as significantly degraded during the pulping process compared to the other carbohydrates. As a result, the retained carbohydrate yield of cellulose is significantly higher than that of the other carbohydrates (hemicelluloses). A cellulose loss of 23.7% was observed in sweetgum, whereas in pine the total loss was of 12.9%.

The delignification process over kraft pulping occurs in three distinct phases (initial, bulk, and residual) (LéMon and Teder 1973). The main delignification reactions/removal occur over the first two phases. Up to 120 min, approximately 97% of the sweetgum lignin was removed (487 H-factor), while about 89% of pine lignin was removed (H-factor of 983). Even though the pulping conditions applied to pine were harsher than the conditions applied to sweetgum, the delignification of sweetgum was greater than pine, which reinforces the superior pulpability of hardwoods over softwoods. The residual phase, which is less selective towards lignin degradation, dominates after about 90 to 95% delignification (Sjödahl 2006). This phase was observed for both samples after approximately 20 min of cooking, in which less than 2% of lignin was removed.

Lignin Precipitation and Characterization

Two lignin fractions were precipitated from the black liquor generated; one was precipitated at pH 9.5 and the other at pH 2.5. Lignin precipitation is typically followed by filtration; however, due to its colloidal nature, the filtration step is a challenge. Complete or partial plugging of the filter cake has been reported, which requires large filter areas (Tomani 2010) and leads to high levels of impurities in the lignin (Öhman *et al.* 2007). The separation of the lignin from the black liquor was carried out by centrifugation to mitigate this problem for laboratory studies.

In the course of kraft pulping, lignin undergoes relatively drastic degradation reactions, for instance, cleavage of β -O-4 linkage (main linkage in lignin), which results in the liberation of phenolic hydroxyl groups. These groups increase the hydrophilicity of lignin fragments (Hubbe *et al.* 2019) and lead to lignin dissolution in the black liquor. It has been determined that the protonation of the phenolic hydroxyl groups occurs over about pH 9 to 11. So, with decreasing pH to this range, lignin solubility decreases, resulting in precipitation. In addition, further lowering pH to around 2, the carboxylic acid groups in lignin (pK_a 3 to 5) are also protonated, which enhances precipitation (Alén 2011a). Therefore, lignin precipitation experiments are based on the concepts of pK_a and protonation.

Sweetgum analysis

In addition to lignin, other degradation products are found in the black liquor that can also be co-precipitated with lignin as impurities. The characterization of wood chips and pulps has already been presented above; thus, it was possible to calculate the content of a given compound in the black liquor by the difference between its content in the wood and the pulp.

The material balance of the precipitation experiments for sweetgum is shown in Table 5. After pulping 100 g (O.D.) of wood chips, the solids in the black liquor were measured according to the standard "TAPPI/ANSI T 650 om-15" protocol and converted

to a weight basis. Since the two lignin fractions (at pH 9.5 and 2.5) were obtained from the same black liquor sample, the solids in the black liquor presented in pH 2.5 section are a subtraction of the solids originally found in the black liquor and the solids precipitated at pH 9.5. The lignin in the black liquor was calculated from the difference between the lignin content in the wood and the pulp, at a given time/H-factor.

It was observed that the solids in the black liquor increased as pulping progressed, which was due to degradation and dissolution of wood compounds. After 30 min of pulping (0 H-factor), 38.9 g of solids were found in the sweetgum black liquor, which were a mixture of organic and inorganic compounds. Out of the 38.9 g, 4.3 g were accounted for by the difference between the lignin content in the wood and in the pulp. After 150 min (800 H-factor), an increased mass of solids was found (68.2 g,) and 24.7 g was accounted for by lignin.

Table 5. Material Balance of Lignin Precipitation from Sweetgum Black Liquors

| Cook Time (min) | Parameter (g) | | | | | | | | |
|-----------------|------------------|------------------|---------------------|--------|-------|--------------|---------------|-----|-----|
| | Solids in the BL | Lignin in the BL | Solids precipitated | Glucan | Xylan | Total Lignin | Klason Lignin | ASL | Ash |
| pH 9.5 | | | | | | | | | |
| 30 | 38.9 | 4.3 | 0.6 | 0.1 | 0.3 | 0.1 | 0.1 | 0.0 | 0.0 |
| 60 | 55.5 | 15.1 | 5.5 | 0.5 | 1.2 | 3.1 | 2.8 | 0.2 | 0.1 |
| 90 | 66.2 | 23.0 | 12.4 | 0.7 | 1.3 | 9.0 | 8.4 | 0.6 | 0.3 |
| 120 | 68.1 | 24.5 | 14.7 | 0.8 | 1.4 | 10.9 | 10.4 | 0.5 | 0.3 |
| 150 | 68.2 | 24.7 | 12.3 | 0.5 | 1.1 | 9.4 | 9.1 | 0.3 | 0.3 |
| pH 2.5 | | | | | | | | | |
| 30 | 38.3 | 4.2 | 0.8 | 0.0 | 0.2 | 0.3 | 0.3 | 0.0 | 0.0 |
| 60 | 50.0 | 12.0 | 4.2 | 0.0 | 0.3 | 3.2 | 3.0 | 0.2 | 0.0 |
| 90 | 53.8 | 14.0 | 3.6 | 0.0 | 0.1 | 3.2 | 3.0 | 0.2 | 0.0 |
| 120 | 53.4 | 13.5 | 4.4 | 0.0 | 0.2 | 4.0 | 3.8 | 0.2 | 0.0 |
| 150 | 55.9 | 15.3 | 8.4 | 0.0 | 0.4 | 7.8 | 7.5 | 0.3 | 0.1 |

Weight based on pulping 100 g of wood chips. Where BL is black liquor, Total lignin is a sum of Klason lignin (acid-insoluble lignin) and acid-soluble lignin (ASL).

Furthermore, the total amount of solids precipitated (lignin, carbohydrates, and ash) by acidification increased over the process. After 30 min (0 H-factor), only 0.6 g were precipitated during the carbonation of the sweetgum black liquor (acidification to pH 9.5), whereas at 120 min (487 H-factor), 14.7 g were precipitated. The same trend was observed throughout the precipitation of the lignin fraction at pH 2.5 (acidification with HCl). This increase was expected since more organic compounds were found in the black liquor throughout the process due to hydrolytic reactions.

In general, at higher pH, the fraction of lignin that precipitates has a higher molecular weight, whereas, at lower pH, the lignin that precipitates has a lower molecular weight (García *et al.* 2009; dos Santos *et al.* 2014; Kumar *et al.* 2016). A decrease in the amount of lignin precipitated at pH 9.5 between 120 to 150 min (487 and 800 H-factor, respectively) was observed, followed by an increase in the fraction obtained at pH 2.5. This likely occurred due to further degradation of the lignin dissolved in the black liquor into

smaller molecules and further lignin depolymerization over the pulping process.

Even though significant amounts of carbohydrates are not expected to precipitate with lignin, sweetgum lignins isolated at pH 9.5 were heavily contaminated with carbohydrates. For instance, at 30 min (0 H-factor), 0.6 g of solids were isolated after carbonation, of which 0.1 g was glucan, and 0.3 g was xylan, whereas only 0.1 g was found to be lignin. On the other hand, the lignin isolated at pH 2.5 showed superior purity, *i.e.*, less carbohydrates and ash. It is well known that lignin precipitated at higher pH is less degraded (higher molecular weight); therefore, it can be safely assumed that the carbohydrates associated with these lignins are also less degraded (Zhu *et al.* 2015). Thus, at pH 9.5, the carbohydrates are less degraded, less soluble, and hence they can be precipitated along with lignin. Whereas, at pH 2.5, less amount of carbohydrates is remaining, and they are more degraded/soluble and do not precipitate. Another possibility is the lignin and carbohydrates are chemically bonded (LCCs), which leads to precipitation of lignin and carbohydrates at the same time.

It is important to mention that higher lignin yields have been reported with straightforward filtration recovery when compared with centrifugal recovery; however, filtration takes a longer time due to the colloidal nature of the lignin precipitate (Namane *et al.* 2015).

Pine analysis and comparison with sweetgum

The present work intended to establish a baseline comparison between the precipitation of lignin from hardwood and softwood black liquors. Thus, the precipitation, characterization, and material balance for both hardwood and softwood black liquors were performed under similar operating conditions. The material balances for the precipitation experiments are shown in Table 5 for hardwood and Table 6 for pine.

Table 6. Material Balance of Lignin Precipitation from Pine Black Liquors

| Cook Time (min) | Parameter (g) | | | | | | | | |
|-----------------|------------------|------------------|---------------------|--------|-------|--------------|---------------|-----|-----|
| | Solids in the BL | Lignin in the BL | Solids precipitated | Glucan | Xylan | Total lignin | Klason Lignin | ASL | Ash |
| pH 9.5 | | | | | | | | | |
| 30 | 47.7 | 3.0 | 0.4 | 0.0 | 0.0 | 0.3 | 0.3 | 0.0 | 0.0 |
| 60 | 62.8 | 12.4 | 4.6 | 0.0 | 0.0 | 4.3 | 4.2 | 0.0 | 0.1 |
| 90 | 78.4 | 25.0 | 6.9 | 0.0 | 0.2 | 6.4 | 6.2 | 0.2 | 0.1 |
| 120 | 82.7 | 27.8 | 19.4 | 0.0 | 0.4 | 16.4 | 16.1 | 0.4 | 0.4 |
| 150 | 83.0 | 28.4 | 21.0 | 0.0 | 0.4 | 19.4 | 19.0 | 0.4 | 0.5 |
| pH 2.5 | | | | | | | | | |
| 30 | 47.3 | 2.7 | 1.2 | 0.0 | 0.0 | 1.0 | 1.0 | 0.0 | 0.0 |
| 60 | 58.2 | 8.1 | 3.0 | 0.0 | 0.0 | 2.6 | 2.6 | 0.1 | 0.0 |
| 90 | 71.5 | 18.6 | 16.9 | 0.0 | 0.5 | 13.9 | 13.5 | 0.5 | 0.2 |
| 120 | 63.3 | 11.4 | 9.0 | 0.0 | 0.3 | 7.6 | 7.3 | 0.2 | 0.1 |
| 150 | 62.0 | 9.0 | 7.1 | 0.0 | 0.2 | 6.4 | 6.2 | 0.2 | 0.1 |

Where BL is black liquor, Total lignin is a sum of Klason lignin (acid-insoluble lignin) and acid-soluble lignin (ASL).

During the pulping of pine, the solids content of black liquor increased, which is in accordance with the sweetgum experiments. After 30 min of the pulping of 100 g (O.D.) of pine wood chips (0 H-factor), 47.7 g of solids were found in the black liquor (organic and inorganic); while after 150 min (1400 H-factor), 83.0 g of solids were found. The solids content at 30 min (0 H-factor) was reasonably higher in pine black liquor (47.7 g) than in sweetgum (38.9 g). This surplus of solids has an inorganic origin (white liquor) since the alkali charge was greater, and not much degradation was observed in the pulped pine chips at this point.

The total amount of solids precipitated from pine black liquor increased over the process, which is also in accordance with the sweetgum experiments. After 30 min of pulping (0 H-factor), 0.4 g of solids were obtained at pH 9.5, whereas at 150 min (1400 H-factor), same pH, the recovery was 21 g. In addition, the purity of the pine lignin was superior to the sweetgum lignin due to less carbohydrate and ash contamination. For instance, the total solids precipitated over the carbonation of sweetgum black liquor obtained at the end of the pulping process (800 H-factor, 150 min) was 12.3 g, where about 1.9 g was contamination (carbohydrates and ash). On the other hand, out of the 21 g of solids obtained at the end of the pulping of pine wood chips (1400 H-factor, 150 min), only around 0.9 g were accounted for by contamination. In addition, the increase in lignin recovery throughout the pulping process could also be explained by lignin concentration. In low lignin concentration samples, the lignin molecules are surrounded by significantly more water molecules than in high lignin concentration samples, which might influence lignin interactions/agglomerations (Helander *et al.* 2016) and hence affect lignin recovery. The results of lignin concentration are not shown; however the same liquor to wood ratio was applied to all pulping experiments and the collected black liquors were evaporated to 20% solids content. Thus, a higher lignin content in the black liquor translates to higher lignin concentration.

Overall, it was observed that the precipitation of the lignin fraction at pH 2.5 contributed to a considerable increase in lignin recovery (Fig. 4). This is in agreement with earlier investigations, which have shown that yield of precipitated lignin increased by decreasing pH (García *et al.* 2009; Theliander 2010; dos Santos *et al.* 2014; Zhu *et al.* 2014; Sewring *et al.* 2019).

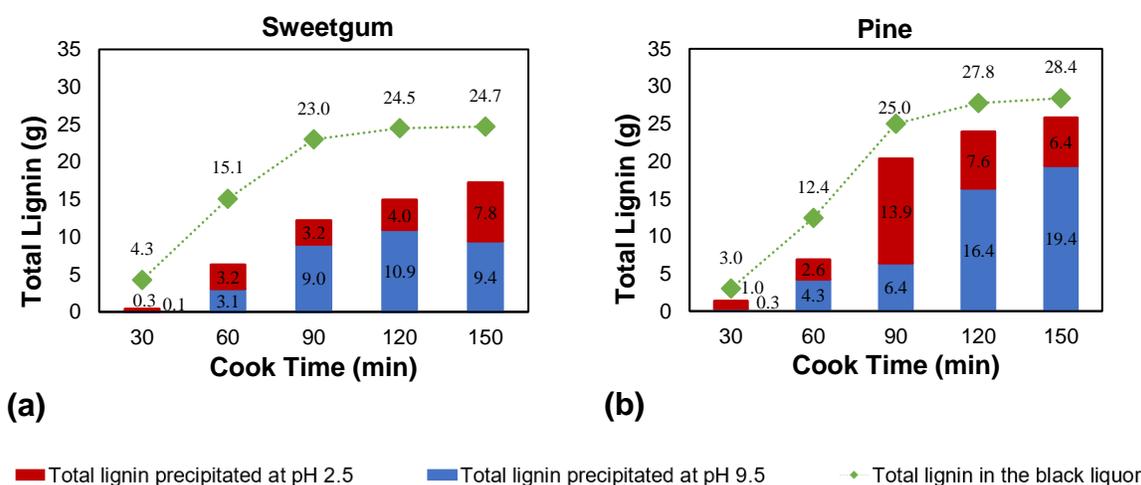


Fig. 4. Total lignin content in the black liquor and Total lignin precipitated at pH 9.5 and 2.5 from (a) sweetgum and (b) pine samples throughout kraft pulping

At the onset of the pulping, the yield of lignin fraction obtained at pH 2.5 was higher than the lignin fraction recovered at pH 9.5. It has been reported that lignin with high molecular weight precipitates at pHs around 8 to 11, and lignin with low molecular weights precipitate at lower pH (dos Santos *et al.* 2014; Kumar *et al.* 2016). In addition, it is known that mainly low molecular weight lignin is removed during the initial phase of delignification (Gellerstedt and Lindfors 1984). As the kraft pulping continues, lignin fractions of higher molecular weight are removed and solubilized in the black liquor (Gellerstedt *et al.* 1984). Moreover, it is known that condensation of lignin fragments occurs by repolymerization during the pulping process, causing an increase in the molecular weight as the process continues (Shrotri *et al.* 2017). Therefore, initially, more lignin is obtained at pH 2.5 than at pH 9.5, and as the pulping proceeds, the yield of lignin obtained at pH 9.5 increases, while yield at pH 2.5 drops.

As softwood lignin precipitation methods have been well documented in both the literature and in commercial practice, it was assumed that those methods could be used as a template for hardwood lignin precipitation. However, this study showed that the behavior of sweetgum and pine lignin as a function of precipitation was considerably different. Firstly, the recovery of lignin from pine black liquors was greater than the recovery from sweetgum black liquor; which is in accordance with previous investigations that claims superior yields from softwoods over hardwoods (Öhman *et al.* 2007; Santos *et al.* 2011; 2012; Zhu *et al.* 2014, 2015). Furthermore, Table 7 depicts the percentage of carbohydrates and lignin recovered via precipitation at both pH 9.5 and 2.5. As shown in the table, significant quantities of the sweetgum carbohydrates were precipitated, and relatively lower levels of lignin were obtained. For the pine liquor, only low amounts of the carbohydrates present in the black liquor were isolated with lignin via precipitation. For both the sweetgum and pine, the percentage of lignin precipitated increased as the cook progressed, but much superior lignin yields were obtained for the pine liquors at all conditions evaluated.

Table 7. Percentage of Carbohydrates and Lignin Precipitated from the Collected Sweetgum and Pine Black Liquors throughout the Cooking Process

| Cook Time (min) | Sweetgum | | Pine | |
|-----------------|-------------------|------------------|-------------------|------------------|
| | Carbohydrates (%) | Total Lignin (%) | Carbohydrates (%) | Total Lignin (%) |
| 30 | 6.6 | 9.3 | 0.5 | 45.5 |
| 60 | 12.2 | 41.8 | 0.6 | 55.4 |
| 90 | 10.1 | 52.9 | 4.0 | 81.4 |
| 120 | 11.2 | 61.1 | 3.7 | 86.2 |
| 150 | 9.5 | 69.7 | 2.5 | 90.9 |

The total lignin recovery presented in Table 7 was calculated based on the sum of the amount of lignin precipitated at pH 9.5 and 2.5 divided by the calculated lignin content in the black liquor. The maximum lignin recovery was obtained from black liquor samples generated at the end of the kraft pulping process. The total lignin recovery of sweetgum was 69.7% (800 H-factor), whereas the total lignin recovery of pine was 90.9% (1400 H-factor). Overall, the yield of lignin obtained from pine was greater than from sweetgum, mainly because part of the sweetgum lignin remained soluble in the supernatant due to the contamination with carbohydrates. The percentage of carbohydrates precipitated was calculated based on the amount of carbohydrates measured in the lignin fractions (pH 9.5

and 2.5), and the amount dissolved in the black liquor, which could be obtained by the difference between the residual content of carbohydrates in the produced pulp and the content in the black liquor.

The presence of lignin-carbohydrate complexes (LCCs) is a plausible explanation for the low yields achieved by sweetgum. Although these linkages exist in small amounts in lignocellulosic materials, it is speculated that almost all lignin is associated with polysaccharides (Lawoko *et al.* 2005; Du *et al.* 2013). The multiple –OH groups from carbohydrates will contribute to hydrophilicity, rendering the lignin more soluble in water (Hubbe *et al.* 2019). In addition, the LCCs are suggested to play a crucial role in recalcitrance during biomass processing and fractionation (Giummarella *et al.* 2019). For the analyses performed so far, it cannot be claimed that the carbohydrates that were precipitated with the sweetgum lignin were chemically bonded to it; however, it is plausible that they were chemically associated. Indeed, considerably more carbohydrates were detected in the sweetgum lignin versus pine. Moreover, the greater loss of cellulose by sweetgum during the kraft pulping might also be related to this association between carbohydrates and lignin. In addition, incorporation of xylan into lignin agglomerates as they form could cause a reduction in the further growth/agglomeration of particles due to increased electrostatic repulsive forces and/or steric effects, resulting in smaller particles being formed when compared to less xylan in the system (Sewring *et al.* 2019).

CONCLUSIONS

1. Lignin recovery from black liquor and lignin purity increased with the increase of H-factor. The recovery at pH 2.5 was higher at the beginning of the process; however, as pulping proceeded, the recovery at pH 9.5 increased, while at pH 2.5, it decreased.
2. The recovery of sweetgum lignin (hardwood) showed low yields since considerable levels were still soluble in the black liquor after acidification. In addition, these lignins presented low purity due to high contamination with carbohydrates.
3. Pine lignin (softwood) was more easily precipitated and displayed superior purity.
4. All lignin precipitated at pH 2.5 were purer than the fraction obtained at pH 9.5, and the former fraction contributed to a considerable recovery enhancement.
5. The total recovery of the sweetgum lignin (summing both fractions) was 69.7% at 150 min (800 H-factor), whereas for pine was 90.2% at 150 min (1400 H-factor).
6. Overall, the recovery of pine lignin was superior to the recovery of sweetgum lignin with respect to yield and purity.

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