Quantification of hardwood black liquor contamination in pine black liquor

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ABSTRACT: The presence of hardwood black liquor contamination in pine black liquor can negatively impact brownstock washer and evaporator operation, as well as reduce soap separation and yield. It is also believed to negatively impact commercial kraft lignin production. It was desired to develop a method of quantitatively determining the amount of low-level hardwood liquor contamination in pine black liquor.

A method employing pyrolysis-gas chromatography mass spectrometry (py-GCMS) was developed to perform the desired measurement. Laboratory cooks with carefully controlled blends of pine and hardwood chips were prepared, and the resulting liquor was measured using this technique. Additionally, samples of pine and hardwood black liquors were blended in known quantities and analyzed. All these samples were submitted as blind samples. The resulting analysis suggests the py-GCMS method was able to accurately determine the level of hardwood contamination between 1% to 10% hardwood liquor using a low-level calibration curve prepared with coniferyl alcohol and sinapyl alcohol as standards.

Application: This method provides a path for mills to determine the quality or the level of contamination of the black liquor. The result can be used to understand certain negative impacts, such as process upsets in pulp mill, evaporator, and lignin precipitation operations and low black liquor soap yield.

When pine black liquor becomes contaminated with hardwood liquor, process upsets may occur in pulp mill, evaporator, and lignin precipitation operations [1-3]. Black liquor soap yield also decreases due to hardwood liquor contamination [4,5]. Liquor contamination can occur via multiple pathways, including padding liquor in digesters, liquor leaking through valves, and hardwood and softwood chips getting unintentionally blended in the woodyard. Often, when hardwood liquor contamination occurs, it is not immediately known to operations. Rather, various pieces of production equipment start behaving erratically, resulting in production upsets such as foaming or reduced soap yield. When pure pine liquor is being sent to a precipitation plant to produce lignin, the presence of hardwood liquor is believed to negatively impact the production rate of lignin being processed as well.

Currently, there is no widely accepted method to determine the level of hardwood liquor contamination in pine liquor. As such, there is a desire for a reproducible test to quantitatively determine the amount of hardwood lignin contained within the pine black liquor to better understand root causes of some operational and soap yield upsets. Although hardwood, softwood, and grass contain *p*-coumaryl lignin (H type) [6], one of the major differences between hardwood and pine lignin is the presence of syringyl groups in hardwood lignins (S type). Pine lignin contains guaiacyl lignin (G type), while hardwood lignin contains both S type and G type lignin. Syringyl lignin contains two methoxy groups on the benzene ring, while guaiacyl lignin only has one methoxy group on the benzene ring. These two G and S type structures can be represented by their lignin precursors, coniferyl alcohol and sinapyl alcohol, respectively. **Figure 1** shows the difference in base units of G and S type lignin [7-9].

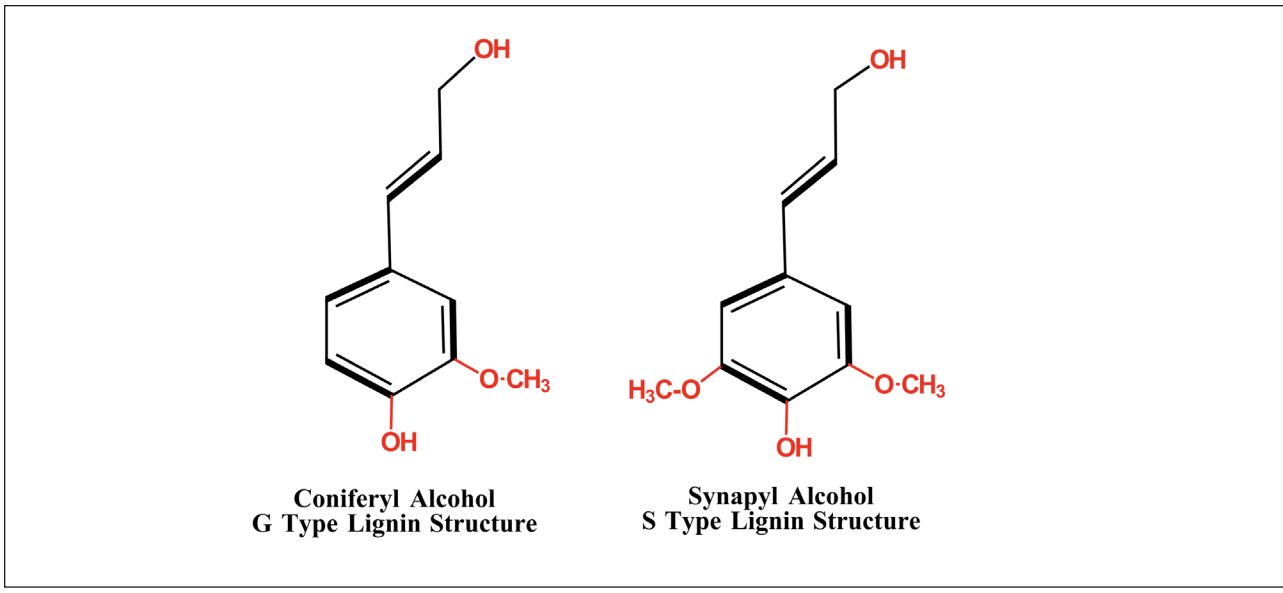
Different methods are available to determine the presence of S and G lignin. Some examples include phloroglucinol-hydrochloric acid (HCl) staining, Klason lignin, nitrobenzene oxidation, and the Fourier transform infrared (FTIR) spectroscopy techniques. These techniques are discussed in the following sections [10-15], along with a new technique introduced in the current study that employs pyrolysis-gas chromatography mass spectrometry (py-GC-MS).

Phloroglucinol-HCl staining technique

The phloroglucinol-HCl or Wiesner stain is a staining approach to determine the presence of lignin. The stain solution is made of 0.3 g phloroglucinol in 10 mL absolute ethanol; the resulting solution is mixed with 5 mL of concentrated HCl to produce the Wiesner stain. A drop of Wiesner stain on a sample containing lignin will turn red-violet. Even if the concentration of the lignin is determined using the phloroglucinol-HCl and an ultraviolet-visible (UV-Vis) spectrophotometer, the ratio of the lignin S and G remains unknown with this approach [10,11].

Klason lignin technique

Klason lignin is another approach to quantify lignin. The method consists of using sulfuric acid to hydrolyze the car-



1. Lignin precursors: coniferyl and sinapyl alcohols for the main repeat unit structures of guaiacyl (G) and syringyl (S) type lignin.

bohydrate portion of the wood or pulp. It is not known if the Klason approach can be used on black liquor or precipitated lignin, and the results of this approach would not provide the proportion of lignin S and G [12,13].

Nitrobenzene oxidation technique

Lignin determination by the nitrobenzene oxidation approach consists of oxidizing a dry sample (mainly pulp and precipitated lignin) in nitrobenzene and sodium hydroxide. The resulting product is washed and tested on gas chromatograph (GC) to determine syringaldehyde (S) group and vanillin (V) group. The S/V is determined by the molar ratio of the amount of syringaldehyde divided by the sum of vanillin and vanillic acid. This approach distinguishes the differences between the lignin types and is similar to the S/G ratio [14].

FTIR technique

There is also an FTIR method that uses a potassium bromide (KBr) pellet containing 1% finely divided lignin sample analyzed in the range of 4000–400 cm^{-1}. Syringyl absorbance is predominant at 1317 and 830 cm^{-1}, while guaiacyl structures predominate at 1230 cm^{-1}. The ratio of the intensities at 1317 cm^{-1} and 1230 cm^{-1} is usually used to estimate the ratio of S/G in biomass. It is also known that better results are obtained when the intensities at 830 cm^{-1} and 1230 cm^{-1} are used for the S/G ratio determination [15].

Py-GCMS potential for determining pine lignin contamination

Pyrolysis-gas chromatography mass spectrometry has been used to determine lignin in wood chips; the technique consists of cryo-milling wood block into a finely powdered sample. The powder is directly injected as-is into a pyrolizer to determine the lignin components in the wood [16-17].

In our study, it was thought that analyzing for the presence of S type lignin could be used as a method of determining hardwood contamination of a pine lignin sample, as pine does not contain S type lignin structures. It was decided to evaluate the potential for using py-GCMS as a tool for determining relative amounts of hardwood lignin contamination of pine black liquor, as discussed here.

EXPERIMENTAL METHODS

Reagents

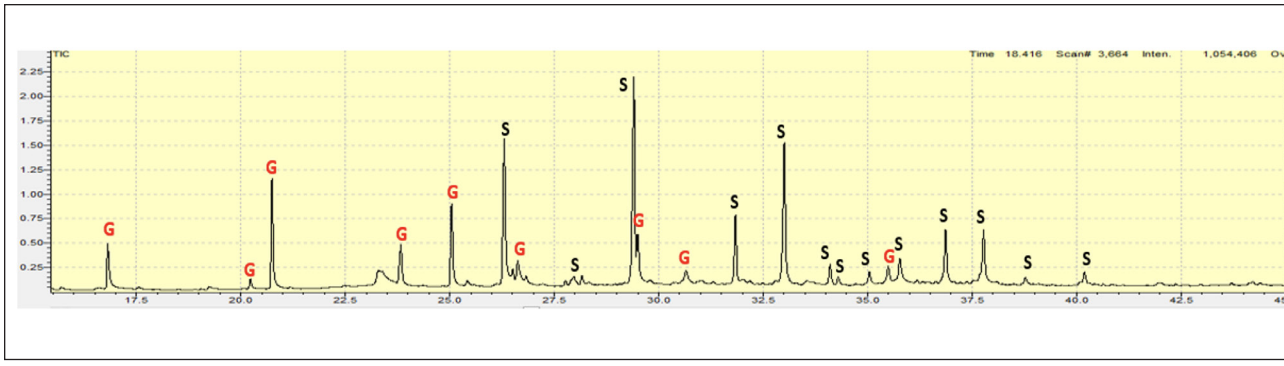
Four main chemicals were used in this study: coniferyl alcohol, synapyl alcohol, HCl, and glacial acetic acid. The coniferyl alcohol and the synapyl alcohol were supplied by Sigma-Aldrich (St. Louis, MO, USA). The HCl and glacial acetic acid were supplied by Thermo Fisher Scientific (Waltham, MA, USA).

Instrumentation

Analyses were performed on a Shimadzu GCMS-QP2010 Ultra, Shimadzu AOC-20, and Frontier PY-3030. The column (UltraAlloy-5; 40 m x 0.25 mm; inner diameter [ID] 0.25 um) was run with a helium flow of 1 mL/min; split ratio 50 at a temperature of 45°C for 4 min; 4°C/min to 240°C, hold 20 min. The injector was operated at 200°C, ion source at 250°C, and interface at 290°C. Scans were performed between 40–600 amu (atomic mass unit). The pyrolizer settings were 550°C for the furnace, 250°C for the interface, and 0.2 min for time.

Calibration curve

A calibration curve was prepared using four different S/G weight ratios between 0 and 0.12.



2. Pyrogram of mixed sinapyl alcohol (S) and coniferyl alcohol (G). Main peaks are labeled. Overall, the G peaks eluted sooner than the S peaks.

$$X = \frac{m_S}{m_G} \quad (1)$$

where m is the mass in grams of S and G lignin.

Each standard was run on the pyrolizer, and the pyrolysates S and G were identified on the chromatogram. **Figure 2** shows the general profile of the chromatogram (not all peaks are labeled), and **Table I** shows the list of the peaks integrated to determine the amount of synapyl and coniferyl alcohols in the samples. Overall, the chromatogram and Table I show that the G components elute from the GCMS column sooner than the S components. Compounds with lower molecular weight (MW) and lower boiling (bp) point tend to elute first on gas chromatograph [18-21]. This phenomenon is observed with G (MW 180.20 g/mol, bp 163°C–165°C) [22] and its pyrolysates compared to the S (MW 210.23 g/mL, bp 384–385 C) [23,24] and its pyrolysates.

The areas of the pyrolysates S and G on the chromatogram were used to calculate the "area percent ratio S/G" or Y using the following equation:

$$Y = \frac{\Sigma_1^n \alpha_S}{\Sigma_1^m \alpha_G} \quad (2)$$

where α is the area of individual pyrolysate of S and G lignin.

The data from X (Eq. 1) and Y (Eq. 2) were plotted to generate a linear calibration curve $Y = \alpha X + \beta$, as in Eq. 3. The calibration curve (**Fig. 3**) is linear with a correlation coefficient of 0.9934.

$$Y_0 = \alpha X_0 + \beta \quad (3)$$

For a given sample to be tested, the S/G area ratio of Y_0 was determined using Eq. 2. From the calibration curve, the S/G weight ratio of the sample (X_0) is calculated as:

$$X_0 = (Y_0 - \beta)/\alpha \quad (4)$$

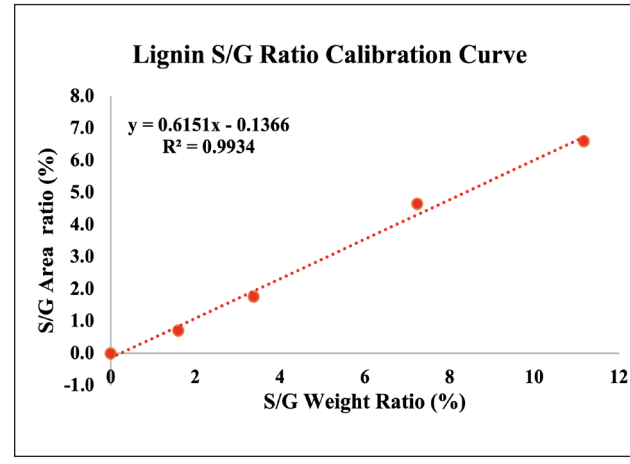
Or, it is calculated by including Eq. 1:

$$X_0 = \frac{m_S}{m_G} = (Y_0 - \beta)/\alpha \quad (5)$$

Lignin precipitation from black liquor for analysis

Black liquor was obtained from the first stage liquor tank of commercial brownstock washers and from lab cooks for analysis. The black liquor was filtrated through a 325 mesh (i.e., 45 µm) screen to remove fibers. The resulting filtrate is used for the lignin precipitation reaction. Approximately 500 mL of well mixed black liquor was poured into a 2-L glass beaker. The beaker was placed on a hot plate, and an overhead Teflon coated mixer was affixed. The black liquor was mixed vigorously without splashing (the mixing also helps knock down the foam). Drips of 6 N HCl followed by pH measurement were performed until the pH reached 2 (approximately 120 mL of HCl was used). In the event of excessive foam, acid addition was stopped to allow foam to dissipate or water spray was used to break up the foam.

Once the final pH was reached, the hot plate was turned on, and the beaker was heated to 70°C; a precaution was taken to keep the temperature always below 80°C while stirring. The sample was heated and stirred for 30–45 min at 70°C to allow the lignin particles to coagulate. After 45



3. Lignin syringyl/guaiacyl (S/G) ratio calibration curve.

ID	Retention Time, min	Pyrolysate Name	Origin
1	16.85	Phenol, 2-methoxy-	G
2	20.27	m-Cresol	G
3	20.78	p-Cresol	G
4	23.86	4-Ethyl-guaiacol	G
5	25.07	2-Methoxy-4-vinylphenol	G
6	26.35	Phenol, 2,6-dimethoxy-	S
7	26.54	3-Allylguaiacol	G
8	28.00	Benzaldehyde, 4-hydroxy-3-dimethoxy-	G
9	28.20	Phenol,2-methoxy-4-(1-propenyl)-	G
10	29.42	3,5-Dimethoxy-4-hydroxytoluene	S
11	29.52	Trans-Isoeugenol	G
12	29.88	Phenol, 2-methoxy-4-propyl-	G
13	31.87	Benzene, 1,2,3-trimethoxy-5-methyl-	S
14	33.04	3′,5′-Dimethoxyacetophenone	S
15	34.13	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	S
16	34.38	1,4-Dimethoxy-2-methyl-5-(prop-1-en-2-yl) benzene	S
17	35.43	Benzene, 1,2,4-trimethoxy-5-(1-propenyl)-, (Z)-	S
18	35.54	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	S
19	35.83	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	S
20	36.12	4-((1-E)-3Hydroxy-1-propenyl)-2-methoxyphenol	G
21	36.44	3-(2-Methoxy-5-methylphenyl) acrylic acid	S
22	36.92	2,6 Dimethoxy-4-(prop-1-en-1-yl) phenol	S
23	37.05	Homo-Syringaldehyde	S
24	37.39	4-((1E)-3-Hydroxy-1-propenyl-2-methoxyphenol	G
25	37.68	(E)-4-(3-hydroxyprop-1-en-1-yl)-2-methoxyphenol	G
26	37.94	Coniferyl aldehyde	G
27	38.37	(E)-4-(3-hydroxyprop-1-en-1-yl)-2-methoxyphenol	G
28	39.49	Benzene, 1,2,3-trimethoxy-5-(2-propenyl)-	S
29	40.15	Trans-Sinapyl alcohol	S
30	40.26	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	S
31	42.06	5-(3-Hydroxypropyl)-2,3-dimethoxyphenol	S
32	42.64	Trans-Sinapyl alcohol	S
33	43.80	Trans-Sinapyl alcohol	S
34	44.24	3-(3′,5′-dimethoxy-4′-hydroxyphenyl)-E-2-propenal	S
35	44.68	Trans-Sinapyl alcohol	S
36	46.64	Sinapic acid methyl ester	S

I. Pyrolysates of sinapyl alcohol (S) and coniferyl (G) alcohol.

Actual wt% HWD black liquor solids (laboratory blend)	0.0	1.0	2.0	5.0	10.0	20.0
Predicted wt% HWD black liquor solids using py-GCMS	0.00	0.93	1.90	5.14	11.14	28.98

II. Actual vs. predicted amounts of hardwood (HWD) contamination in pine liquor samples (py-GCMS: pyrolysis gas chromatography mass spectrometry).

minutes, the hot plate was turned off and the mixer was left running until the sample cooled down to about 60°C for safety reasons.

Next, the solution in the beaker was filtered using a Büchner funnel and Whatman P8 filter paper (Cytiva; Marlborough, MA, USA). The solid cake was removed from the funnel when cracks appeared on its surface. The cracked solid cake was placed into a glass beaker containing 1 L of deionized water that has been pre-adjusted to pH 2 using 6 N HCl.

The overhead mixer was gently used for about a minute to disperse the solids, and the resulting solution was filtrated again using a fresh filter paper. The cracked solid cake was removed and placed into a glass beaker containing 1 L of deionized water that has been pre-adjusted to pH 3.5 using glacial acetic acid. The mixer was gently used for about a minute to disperse the solids and the resulting solution was filtrated again using a fresh filter paper. The solid obtained at this stage was placed into a Ziploc bag and stored in the freezer until analysis.

Laboratory samples prepared with known hardwood contamination

Pure pine chips and mixed southern hardwood chips were obtained from chippers feeding the mill. The chips were hand selected, moisture contents were determined gravimetrically, and the samples were carefully blended with 2 wt%, 5 wt%, and 10 wt% on oven dry hardwood in the pine chips. Samples of pure pine and pure mixed hardwood chips were also prepared. Each of these samples was cooked in an M/K laboratory digester (M/K Systems Inc.; Frisco, TX, USA) to representative kappa numbers. The resulting black liquor was collected, the lignin was precipitated, and the samples were sent for analysis in randomly coded containers.

Blended liquor samples

Samples of pine black liquor and hardwood black liquor were obtained from the mill and volumetrically blended in the laboratory to represent hardwood intrusion into the pine black liquor. A series of five blends and the two pure liquor species were prepared. The blended liquors were precipitated according to the previously mentioned procedure and tested for hardwood lignin. As with the previous laboratory pulping samples, the samples were randomly coded when sent for analysis.

Stability study

Three sets of the precipitated lignin samples from the laboratory-produced black liquor samples were tested daily (omitting weekends) over a 14-day period to determine the stability of the precipitated lignin. Days 3, 4, 10, and 11 were weekend days and therefore not tested. Very low standard deviations were obtained for each of the three lignin samples analyzed.

DISCUSSION OF RESULTS

Once a good correlation curve was determined, the method was tested by obtaining black liquor prepared from a series of known and carefully controlled laboratory cooks performed in an M/K digester. The controlled laboratory cooks were performed with hand blended pine and hardwood chips of known weights. The lignin from each of the resulting black liquors was precipitated according to the procedure described previously and submitted as blind samples for py-GCMS evaluation. The blind samples contained 2.0 wt%, 5.0 wt%, and 10.0 wt% hardwood in the pine chips, respectively. The py-GCMS analyses, conducted in duplicate and averaged, determined the amount of hardwood lignin to be 1.9%, 5.0%, and 10.9%, respectively. In general, at these low levels of hardwood lignin, the test method was able to accurately predict the amount of hardwood lignin present in the predominantly pine black liquor.

Next, samples of mill pine and hardwood black liquors being sent to the evaporators were obtained. Hardwood liquor was used to "contaminate" the pine liquor for testing purposes. Samples containing 0 wt%, 1 wt%, 2 wt%, 5 wt%, 10 wt%, and 20 wt% of hardwood black liquor solids were prepared. The resulting blended liquors were precipitated and submitted for blind testing. **Table II** shows the comparison between the prepared liquors and the predicted results from py-GCMS. These results suggest that the py-GCMS methodology is quite good at predicting hardwood lignin content in pine liquors up to about 10% contamination. Above the 10% range, the method tends to overpredict the percentage of hardwood and requires switching to a midrange calibration curve to obtain accurate results. As the mill is only interested in determining incidental hardwood contamination, the low-level calibration curve should be adequate, and the test method should provide an acceptable method for analysis.

Finally, the stability of the testing method was examined by taking samples of the precipitated lignin from the three blended laboratory cooks and measuring the weight per-

Day	1	2	5	6	7	8	9	12	13	14	Std. Dev.	AVG	Min	Max
Sample X1	1.9%	2.1%	2.0%	2.3%	2.3%	2.1%	2.3%	2.3%	2.4%	2.3%	0.0017	2.2%	1.9%	2.4%
Sample X2	5.0%	4.6%	5.0%	5.3%	5.1%	5.0%	5.2%	5.3%	5.2%	4.9%	0.0021	5.1%	4.6%	5.3%
Sample X3	10.9%	11.2%	10.5%	11.2%	10.7%	10.8%	11.3%	10.7%	11.0%	10.6%	0.0028	10.9%	10.5%	11.3%

III. Stability of lignin samples over a 14-day sampling period.

cent hardwood lignin every weekday over a 2-week period (14 days). Days 3, 4, 10, and 11 were weekend days and not measured. The variability was determined for each of the three samples. All these test values are shown in **Table III**. It was determined that the precipitated lignin was stable over the 14-day period of the study.

Critiques

Another way to determine the S/G ratio other than the approach used in this study is to determine or quantify one component (S or G) and divide its weight by the total weight of the sample. This approach seems less arduous; however, this simpler alternative is prone to error since the total weight of the precipitated lignin includes residual compounds such as inorganics (sodium, sulfate, carbonate, etc.) [25, 26], *p*-coumaryl alcohol [27,28], carbohydrates [29,30], traces of fatty acids, and traces of rosins [31]. The recommended way to determine the lignin ratio is to determine both S and G in the lignin to avoid the interferences of residual compounds. In this study, one calibration equation was generated from the candidate pyrolysates (Table I); another approach would be to use the same pyrolysates and generate two calibration curves, one for S and the other for G. The results from these two curves would be used to determine the S/G ratio. This approach also avoids the interferences of residual components in the precipitated lignin.

S/G ratio variation in hardwoods

It is well known that the S/G ratio of hardwoods varies both among different species (**Table IV**) [32-36] and within specific species [37]. As a result, obtaining an exact per-

Species	S/G Ratio[1]	S/V Ratio[2]
Red oak (*Quercus rubra*)	2.13	2.50
White oak (*Quercus alba*)	2.28[3]	2.42
Sugar maple (*Acer saccharum*)	1.4[4]	
Red maple (*Acer rubrum*)	1.2	
Sweetgum (*Liquidambar styraciflua*)	1.61	2.7
Cottonwood (*Populus deltoides*)	1.41	
Quaking aspen (*Populus tremuloides*)	2.0[4]	
Yellow birch (*Betula alleghaniensis*)	2.0[4]	2.39
White birch (*Betula papyrifera*)	2.71[5]	3.00
Red alder (*Alnus rubra*)	1.20	
Acacia (*Acacia mangium*)	1.15	
E. nitens	2.59	
E. globulus	2.73	
E. urophylla	1.76	

[1] From Santos et al. [32], unless otherwise noted.
[2] From Gomes et. al [33].
[3] From M. Chen et al. [36].
[4] From Nicholson et al. [35].
[5] From S. Chen et al [34].

IV. Syringyl/guaiacyl (S/G) or syringyl/vanillin (S/V) ratios of various hardwoods.

Species	Red Oak	White Oak	Cottonwood	Sweetgum
Lignin content, %	22.8	23.1	21.5	22.8
S/G	2.13	2.28	1.41	1.61
% in Mill 1 blend	28	35	22	15
% in Mill 2 blend	31	28	18	23
% in Mill 3 Blend	33	26	10	31
Blended Chip Properties for Each Mill (assuming 1 kg ovendry blended chips)				
	Mill 1	Mill 2	Mill 3	
Total S lignin, g	148.4	148.0	149.1	
Total G lignin, g	77.8	78.5	78.4	
Combined pile S/G	1.91	1.89	1.90	

V. Estimating mixed hardwood syringyl/guaiacyl (S/G) ratio for different species blends obtained from three southeastern U.S. mills.

centage of hardwood lignin contamination within a softwood black liquor using the S/G ratio is not completely accurate. However, as shown in Table IV, the S/G of typical mixed hardwoods pulped within the southern U.S. (e.g., various oaks, cottonwood, sweet gum, etc.) only vary from about 1.4 to 2.3. These species are themselves blended within the mixed hardwood chip supply, and the blended average chip pile S/G should not vary substantially for mixed southern hardwood chips. As an example, actual southern hardwood chip blends were obtained from three different pulp mills located in the southeastern U.S. and analyzed for predominant wood species percentages. Each of these mills predominately obtained red and white oaks, sweetgum, and cottonwood. Percentages of these four species for the three mills are shown in **Table V**. By using the average lignin content for each species (also shown in Table V) and the S/G ratio for each species shown in Table IV, it is possible to estimate the S/G ratio for the mixed hardwood chips that are pulped at each of these three mills. These values were 1.91, 1.89, and 1.90 for the three mills, respectively. When the liquor contamination levels being measured were only 10% or less, the resulting changed in the S lignin content due to species variation was exceptionally small.

In areas where mostly eucalyptus species or birch species are pulped, it would be possible to follow the method developed here and adjust the baseline calibration for the higher S/G present in the predominant species being pulped. Additionally, for southern mixed hardwoods, as we are only examining small levels of hardwood contamination of less than 10%, the contribution of varying S/G for specific species should have only small-to-negligible impacts on the overall test results.

CONCLUSIONS

It is possible to detect low levels of hardwood lignin in a pine black liquor system by examining the S and G lignin content of the lignin precipitated from that black liquor. Pure pine black liquor contains only G type lignin, whereas hardwood black liquor contains both G and S type lignin. Therefore, if an analysis is performed that contains S type lignin, there should be some amount of hardwood lignin in the pine liquor.

The py-GCMS testing protocol outlined here can be used to determine low levels of hardwood lignin in a pine black liquor system. The protocol includes sampling the liquor, precipitating the lignin, and running the py-GCMS analysis to determine the S and G lignin content. Contamination levels between 0 and 10% hardwood can be determined using the low-level calibration curve with the ratio of S/G of 0 to 12% obtained from sinapyl and coniferyl alcohols as standards. **TJ**

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ABOUT THE AUTHORS

Mills have been experiencing problems with hardwood black liquor contamination in softwood black liquor, resulting in negative impact for commercial kraft lignin production. The current work attempted to quantify the level of contamination.

It is known that when pine black liquor becomes contaminated with hardwood liquor, process upsets may occur in the pulp mill, evaporator, and lignin precipitation operations. Black liquor soap yield also decreases due to hardwood liquor contamination. Currently, there is no widely accepted method to determine the level of hardwood liquor contamination in pine liquor. This work shows a clear method to determine the level of contamination.

The most difficult part of this study was determining the conditions to test in the laboratory. Several brainstorming sessions and "what if?" scenarios were performed to develop the test conditions.

We found that py-GCMS is sensitive enough to detect low levels of lignin. We also determined that it is possible to detect low levels of hardwood lignin in a pine black liquor system by examining the syringyl (S) and guaiacyl (G) lignin content of the lignin precipitated from that black liquor.

The method provided here offers a path for mills to determine the quality or the level of contamination of the black liquor. The result can be used to understand certain negative impacts, such as process upsets in pulp mill, evaporator, and lignin precipitation operations and low black liquor soap yield. Our next step is to attempt to identify approaches or mechanisms that can be used to mitigate or reverse the negative impacts due to hardwood black liquor contamination in softwood black liquor.



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