Combustion properties of reduced-lignin black liquors

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ABSTRACT: The growing interest in production of green chemicals and biofuels from biomass provides an incentive for pulp mills to identify new possibilities in recovering more wood components from the pulping process. One possibility is to use lignin, separated from black liquor. We undertook this work to determine the combustion properties of reduced-lignin black liquors—two kraft liquors and one soda liquor—in a laboratory-scale, singleparticle furnace. The combustion times, maximum swollen volume, nitric oxide formation, cyanate formation, and sulfur release were measured for the original liquors, the filtrates, and intermediate levels of lignin reduction. Combustion experiments were conducted at 900°C in 10% oxygen. Cyanate formation experiments were carried out by pyrolyzing the droplets at 800°C in 100% nitrogen to form a char. The chars were then gasified at 800°C in a 13% carbon dioxide/87% nitrogen atmosphere to obtain the smelt. Sulfur release was studied by pyrolyzing the samples at temperatures ranging from 300°C to 900°C. Liquors with the lowest lignin content had a smaller maximum swollen volume than the original sample. The devolatilization time was not affected by the lignin removal to any great extent, but lignin removal did have a clear effect on the char burning time. The amount of formed nitric oxide (g N/kg black liquor solids) remained constant or decreased slightly with increasing lignin removal in the kraft liquor samples, while for the soda samples the amount of nitric oxide formed increased. The amount of cyanate decreased clearly when comparing the samples with lowest lignin content to the original liquor samples. The peak sulfur release occurred at 500°C for both kraft liquors. In almost all experiments, the share of sulfur released was highest for the original samples and lowest for the sample with lowest lignin content. These results provide new data on combustion properties for reduced-lignin black liquors and indicate that for lignin removal levels up to about 20%, no significant changes are expected in the combustion behavior.

Application: This work will help mills identify the effect of lignin precipitation on combustion properties of black liquor.

The pulp and paper industry is identifying possibilities in new value-added products from biomass to increase revenues. One possibility is the use of lignin that could be applied to various applications in the chemical industry [1-3]. The removal of lignin is also an option to increase the pulping capacity, if the recovery boiler is the bottleneck of the pulp mill. The separated lignin can be used in the pulp mill to replace fossil fuels used in the lime kiln [4,5] as a first step until new markets open up for lignin as a biomaterial.

Up to 70% of lignin from low dry solids (<30% dry solids) kraft black liquor can be separated by lowering the pH of the black liquor with carbon dioxide (CO₂) to pH 10 [6-8]. One such process based on this concept is the LignoBoost process (**Fig. 1**). Carbon dioxide is added to a stream of black liquor (30-45 wt% dry solids) taken from the evaporation plant. The precipitated lignin is then filtered off and the filtrate is pumped back to the evaporation plant. The precipitated lignin is filtered off a second time. The filter cake is washed with warm water acidified with H_2SO_4 ; part of the filtrate is pumped back to the early stages of evaporation and part is used to disperse lignin from the first filtration. The amount of lignin removed from the black liquor sent to the process is



1. General layout of the LignoBoost lignin removal process.

approximately 70%. By treating a larger stream of black liquor, more filtrate is produced and then blended back in with the liquor to the recovery boiler. This results in as-fired black liquor with lower lignin content.

Lignin is 30%-45% of the dry solids in black liquor [9].

Hardwood and softwood kraft lignins have higher heating values (i.e., 23-27 MJ/kg), while kraft black liquor has a much lower high heating value (i.e., 13-15 MJ/kg) [10,11]. Therefore, the removal of lignin from black liquor will decrease the high heating value of black liquor. On the basis of the changes in black liquor composition with varying levels of lignin removal, mathematical calculations estimate that up to 20% lignin removal is possible without any considerable changes in recovery boiler operation. Also, the estimated minimum load at which the recovery boiler can operate without support fuel is 40%-50% lignin removal [11,12].

Recovery boiler NO_x emissions come from nitrogen (N) in the black liquor [13]. The N content of lignin is higher than black liquor so black liquor N will be reduced with lignin reduction [10,11]. Thus, one of the questions is whether lignin removal will affect nitric oxide (NO) emissions from black liquor. Lignin is the primary source of organic N in the char [14] and may affect char N more than pyrolysis N. Char N forms the inorganic compound cyanate during char conversion [15,16]; for this reason cyanate formation was studied for different levels of lignin removal.

Roughly 65% of the sulfur (S) in black liquor is present as inorganic compounds (i.e., sulfide, thiosulfate, sulfite, and sulfide) [9,17] and the remaining 35% as a wide variety of organic bound sulfur compounds [18]. With lignin removal, a fraction of the organic bound sulfur is removed from black liquor, meaning that the ratio between inorganic and organic sulfur will be changed.

The S content of the reduced-lignin black liquor increases slightly with increased lignin removal [11,12] because the removed lignin has lower S content than the original black liquor from which it is precipitated. The partial recycling of used acidified solution to black liquor evaporation will further increase the total S content of the black liquor and the share of inorganic S in black liquor.

The S in black liquor is released during pyrolysis mainly as methyl mercaptans, dimethly sulfide, dimethly disulfide, or hydrogen sulfide (H_2 S) [19-22]. The main contributors to volatile sulfur compound formation are sulfide, thiosulfate, and organic sulfur compounds found in black liquor, while sulfite and sulfate do not result in volatile sulfur formation [23,24]. Lignin methoxyl groups reacting with HS- have been hypothesized as a route to mercaptan formation [20,25].

	Soda				
	Lignin Content mg / g d.s.	Kjeldahl N (wt-% d.s.)			
Black liquor	391	0.071%			
8.4% lower lignin	358	0.066%			
30% lower lignin	274	0.063%			

I. Lignin and nitrogen content of the soda liquor samples.

Thus, the impact of lignin removal on S release during the devolatilization stage of black liquor combustion was of interest in this work.

A single-particle reactor was used to determine the impact of lignin removal on the combustion properties of black liquor. The properties studied were maximum swollen volume, combustion times, NO formation during combustion, amount of cyanate in smelt, and release of S during pyrolysis. Intermediate levels of lignin reduction were obtained by mixing the weak black liquors and filtrates.

EXPERIMENTAL

The lignin removal of the soda liquor from hardwood pulping was conducted at Chalmers University of Technology, and the removal of lignin from kraft black liquors from softwood and eucalyptus pulping was conducted at Innventia AB. One original soda liquor sample and two samples with levels of lignin reduction were obtained from Metso Power Oy. The soda liquor was generated in a laboratory cook. The received soda samples had dry solids content of <41% and were dried to >74% dry solids before the tests in the single-particle reactor. The lignin and N contents of the soda liquor samples are given in Table I. The lignin content of soda liquors was determined by UV spectrophotometry, and the total N content of samples was analyzed with a modified Kjeldahl method using the Devarda alloy (CAS No. 8049-11-4) based on Finnish Standards Association (SFS) 5505 "Wastewater inorganic and organic nitrogen determination."

Both the softwood and hardwood (Eucalyptus globulus) kraft black liquors used in this study were processed in bench-scale equipment, similar to what has been used earlier [6]. The process was operated as follows. Industrial kraft black liquors (~40% DS) were used and the pH was lowered to about 10 by addition of CO_2 (g), causing the lignin to precipitate (Fig. 2). The precipitated lignin was separated by filtration (chamber press filter), referred to as filtration 1. The lignin filter cake was then resuspended at pH 2-3, using sulfuric acid solution. The lignin slurry was filtered once more (filtration 2) and the separated lignin cake was washed with acidified water at pH 2-3. After washing, the lignin cake was dewatered by pressing and by blowing compressed air through the filter cake. All filtrates were collected and mixed. These mixtures were used to represent the filtrate mixture that would be obtained in a full-scale LignoBoost plant.

Two kraft liquor samples (one softwood and one eucalyptus) before lignin removal and two filtrates were obtained. The softwood filtrate had $54.6\pm5\%$ lower lignin content than the softwood black liquor and the eucalyptus filtrate had $43.6\pm5\%$ lower lignin content than the eucalyptus black liquor. The received samples had dry solids content of <25%. For both black liquors, the original sample and filtrate were mixed to obtain two more samples with different levels of lignin content. The lignin, S, and N contents of the obtained and mixed kraft liquor samples are shown in Table II. The samples were dried in an oven at 105° C to a dry solid content



2. Schematic figure of the bench-scale equipment used for lignin removal.

of approximately 85% before the tests in the single-particle reactor.

The lignin content shown in **Table II** for the kraft liquors was analyzed using TAPPI T 222 om-02 "Gravimetric determination of acid-insoluble lignin" and UV spectrophotometry (acid soluble lignin). The total N content of selected samples was analyzed with a modified Kjeldahl method using the Devarda alloy (CAS No. 8049-11-4) based on SFS 5505; the S content was analyzed using SCAN-N 38:10 "Acid-soluble metals."

Combustion, cyanate formation, and S release experiments were conducted in a laboratory-scale quartz glass reactor as illustrated in **Fig. 3** [26]. The temperature and the atmosphere in the quartz glass reactor can be adjusted. Six droplets weighing 10 ± 0.5 mg of each sample were suspended on platinum hooks and combusted at 900°C in a 10% O₂/90% N₂ atmosphere. The formed NO emissions were measured with a Model 200EM chemilumenescence analyzer (Teledyne Technologies; Thousand Oaks, CA, USA). The combustion was recorded with a video camera to determine the maximum swollen volume and the combustion times.

The maximum swollen volume of the droplet is estimated by capturing an image from the recorded video. The captured two-dimensional image is compared to an area of a circle or



3. Schematic drawing of the quartz glass reactor used in the experiments.

	Lignin Content mg/ g d.s.	Softwood Sulfur Content wt-% d.s.	Kjeldahl N (wt-% d.s.)	Lignin Content mg / g d.s.	Eucalyptus Sulfur Content wt-% d.s.	Kjeldahl N (wt-% d.s.)	
Black liquor	366	6.11%	0.062%	429	5.10%	0.086%	
10% lower lignin	329.4*	6.56%*	0.060%*	386.1*	5.76%*	0.082%*	
25% lower lignin	274.5*	7.25%*	0.057%*	312.75*	6.76%*	0.077%*	
Filtrate	166	8.58%	0.052%	242	7.99%	0.070%	
* Calculated based on the analysis of black liquor and filtrate.							

II. Lignin and sulfur content of the kraft black liquor samples before evaporation.

an ellipse, which is then used to calculate the volume of a corresponding sphere or ellipsoid. In this work, the maximum swollen volume is represented as cm^3/g of dry solids.

The combustion of black liquor droplets can be divided into four stages: (1) drying, (2) devolatilization, (3) char burning, and (4) smelt coalescence [27]. The times for the different combustion stages were determined from the recorded video. The drying time was not determined in these experiments, because the sample dried before it entered the combustion chamber. Devolatilization time is defined as the time from the appearance of the flame to the disappearance of the flame. The droplets often ignited as they entered the combustion zone; thus, pyrolysis times can be slightly longer (by about 0.5 s) than what is observed. The char burning time is defined as the time from the point where the visible flame disappears to the point where smelt coalescence occurs.

The cyanate formation in the samples was determined by pyrolyzing six droplets $(10\pm0.5 \text{ mg})$ of each sample in the quartz glass reactor at 800°C in 100% N₂ for 10 s to form a char. The chars were then gasified at 800°C in 13% CO₂/87% N₂ to obtain smelts. The formed smelts were dissolved in ion exchange water using a ratio of 1.25 mg smelt:1 mL ion exchange water and filtered. The filtrates were analyzed for cyanate with ion chromatography using a Metrosep Anion Dual 2 column and conductivity detector (Metrohm AG; Herisau, Switzerland) [28].

The S release for the kraft liquor samples was measured in the quartz glass reactor by pyrolyzing six droplets (10 ± 0.5 mg) of each sample at 300°C, 500°C, 700°C, and 900°C in 100% N₂ atmosphere. After the quartz glass reactor a flow of pure oxygen was added to the flue gas. The oxygen content in the flue gas was around 4–5 vol% and was measured with a Servopro 4900 continuous emissions analyzer (Servomex; Crowborough, UK). The flue gas flow containing oxygen was then introduced to an SCC-K catalytic converter (ABB; Zurich, Switzerland) to oxidize released sulfur species to sulfur dioxide (SO₂). The released S was measured as SO₂ with an ABB AO2020 infrared analyzer. The total amount of S released was calculated based on the SO₂ measurement and the total flue gas flow before dilution with oxygen [26].

RESULTS AND DISCUSSION

Combustion characteristics of reduced-lignin black liquors

The combustion times; maximum swollen volume; and distribution between volatile matter, fixed carbon, and smelt for the softwood kraft liquor samples is shown in **Fig. 4** and for the eucalyptus samples in **Fig. 5**. The devolatilization time was around 1 s for all of the samples, and no clear difference between devolatilization time and the level of lignin content in the samples was detected. This was consistent with the idea that the dissolved hemicelluloses are the main source of volatile products in black liquor combustion [14]. For the softwood samples the char burning time and total combustion time decreased with increasing lignin removal, while the op-





4. Combustion times (top) and maximum swollen volume (middle) from experiments conducted at 900°C at 10% oxygen/90% nitrogen. Distribution of volatile matter, fixed carbon, and smelt (bottom) calculated based in weighed initial samples, chars, and smelts from the cyanate formation experiments of softwood kraft liquor samples. Error bars represent one standard deviation of six droplets.



5. Combustion times (top) and maximum swollen volume (middle) from experiments conducted at 900°C at 10% oxygen/90% nitrogen. Distribution of volatile matter, fixed carbon, and smelt (bottom) calculated based in weighed initial samples, chars, and smelts from the cyanate formation experiments of eucalyptus kraft liquor samples. Error bars represent one standard deviation of six droplets.



6. Maximum swollen volume images of the kraft liquor samples.

posite was observed for the eucalyptus sample. This reduced char burning time was most likely due to the combined effects of slightly increased swelling and the reduced organics in the black liquor, specifically the lignin that will contribute to char formation. Increased lignin removal decreased the share of fixed carbon and increased the share of smelt as seen in Figs. 4 and 5. The eucalyptus black liquor had considerably larger maximum swollen volume than the softwood black liquor. The swelling for the eucalyptus black liquor samples decreased with increasing lignin reduction, which may be the reason for slightly higher average char burning times despite lower organic content. Alén et al. [29] showed that hardwood lignin swelled more than softwood lignin because the presence of xylan increases swelling. The ratio between hemicelluloses and lignin affects the swelling, and at a certain ratio maximum swelling occurs. This could be one reason for the difference in the average maximum swollen volume pattern for the eucalyptus and softwood samples. In both cases, the filtrate swelled considerably less than the original sample. The high standard deviations seen in the maximum swollen volume can be explained by nonuniform swelling of black liquor and use of two-dimensional images for estimating volume. Figure 6 shows captured maximum swollen volume images for different kraft black liquor samples.

The combustion times; maximum swollen volume; and distribution between volatile matter, fixed carbon, and smelt of soda liquor with different lignin content are shown in **Fig. 7**; the capture maximum swollen images are shown in **Fig. 8**.

The devolatilization time and the share of volatile matter slightly increased with increasing lignin removal. The char burning time and total combustion time increased and the maximum swollen volume decreased with increasing lignin



7. Combustion times (top) and maximum swollen volume (middle) from experiments conducted at 900°C at 10% oxygen/90% nitrogen. Distribution of volatile matter, fixed carbon, and smelt (bottom) calculated based in weighed initial samples, chars, and smelts from the cyanate formation experiments of soda liquor samples. Error bars represent one standard deviation of six droplets.



8. Maximum swollen volume images of the soda liquor samples.

removal for the soda liquor samples. The amount of smelt increased with increasing lignin removal, while the amount of fixed carbon decreased. The char burning times clearly depend on the maximum swollen volume and the amount of fixed carbon left in the char.

NO formation

The NO formation (as g N/kg dry black liquor) for the eucalyptus and softwood samples are shown in **Fig. 9**. For both black liquors, the NO formation decreased with increasing lignin removal. Part of the black liquor N is removed with lignin, which lowers the N content of the lignin-reduced black liquor compared with the original black liquor samples shown in Table II. The conversion of fuel N to NO was roughly 40% for the eucalyptus samples and roughly 45% for the softwood samples. This includes NO formed during pyrolysis and NO from char burning. In a recovery boiler, much of the char N will exit the recovery boiler as cyanate in the smelt.

The NO formation (as g N/kg dry black liquor) slightly increased for the soda liquor with 30% lower lignin content compared to the original soda liquor, as shown in **Fig. 10**. An equal amount of NO was formed from the 8.4% lower lignin sample and original sample. In the soda liquor samples, N content also decreased with increasing lignin removal, while the amount of formed NO increase remains unknown. The conversion of fuel N to NO was roughly 45% for the original



9. Average nitric oxide formation of softwood and eucalyptus kraft liquor samples. Experiments conducted at 900°C at 10% oxygen/90% nitrogen. Error bars represent one standard deviation of six droplets.



10. Average nitric oxide formation of soda liquor samples. Experiments conducted at 900°C at 10% oxygen/90% nitrogen. Error bars represent one standard deviation of six droplets.

soda sample and increased to approximately 55% for the 30% lower lignin sample.

Cyanate of reduced-lignin black liquors

Cyanate formation (as mg N/kg smelt) for the softwood and eucalyptus samples is shown in **Fig. 11**. The amount of formed cyanate from the 10% lower lignin eucalyptus sample slightly increased when compared with the original sample, while the amount of cyanate formed from the 10% lower lignin softwood sample and original sample are equal. In both kraft liquors, less cyanate was formed from the 25% lower lignin and filtrate samples compared with the original black liquor samples. The fuel N to cyanate conversion for the eucalyptus samples was between 40% and 50%, and the lowest



11. Cyanate formation after pyrolysis (10 s at 800°C at 100% nitrogen) and gasification (800°C in 13% carbon dioxide/87% nitrogen) to smelt for eucalyptus and softwood kraft liquor samples. Error bars represent one standard deviation of six ion chromatography analyses.



12. Cyanate formation after pyrolysis (10 s at 800°C at 100% nitrogen) and gasification (800°C in 13% carbon dioxide/87% nitrogen) to smelt for soda liquor samples. Error bars represent one standard deviation of six ion chromatography analyses.

conversion occurred for the original black liquor sample. Roughly 47% of the softwood filtrates N was converted to cyanate. For the rest of the softwood samples, the fuel N to cyanate conversion was between 57% and 62%. It has been shown that reaction between alkali salts (i.e., sodium and potassium carbonate) and the char N results in cyanate formation [30]. The reason for the increase in cyanate formation from the eucalyptus liquor sample with a 10% lower lignin content is not clear. The ratio between inorganic and organic compounds in the fuel and the amount of inorganic compounds in the char or simply a higher char N content may be possible explanations, but further work would be needed to clarify this question.

Figure 12 shows the cyanate formation (as mg N/kg smelt) for the soda liquor samples. The amount of formed



13. Sulfur release of softwood black liquor samples during pyrolysis (100% nitrogen) at different temperatures. Error bars represent one standard deviation of six droplets.

cyanate slightly increased for the 8.4% lower lignin sample when compared with the original sample. Almost no cyanate was formed from the 30% lower lignin sample. One reason behind the low cyanate formation is that soda liquor samples did not form a smelt at these conditions. The remaining residue still looked partially swollen and thus the char was not fully converted to smelt. Previous studies show that when gasification is conducted at 800°C, maximum conversion occurs when almost 100% of the char is converted [16]. The levels of cyanate formed represent 14% of the fuel N converted to cyanate for the black liquor and the 8.4% lower lignin sample and only 2% for the 30% lower lignin sample.

Sulfur release of reduced-lignin black liquors

Sulfur release during pyrolysis was measured at different temperatures for the softwood samples (Fig. 13) and the eucalyptus samples (Fig. 14). Softwood and eucalyptus samples showed S release peaks at 500°C and decreases with increasing temperature. This has also been observed in previous studies [20,21]. For the softwood black liquor and the 10% and 25% lower lignin samples, the share of S released was quite similar when the pyrolysis was conducted at 500°C, 700°C, and 900°C. However, at 300°C, the share of S released was clearly higher for the 10% and 25% lower lignin samples than for the original black liquor sample. The share of S released from the softwood filtrate sample was clearly lowest of all the samples when the pyrolysis was conducted at 500°C and 700°C. For the eucalyptus samples, the share of S released was highest for the black liquor sample in all of the pyrolysis experiments and lowest for the filtrate sample, except when the pyrolysis was conducted at 900°C. For the S release experiments conducted for the eucalyptus samples, the share of S released was lower for the liquors with lower lignin content.

The removal of a portion of the organic sulfur with the



14. Sulfur release of eucalyptus black liquor samples during pyrolysis (100% nitrogen) at different temperatures. Error bars represent one standard deviation of six droplets.

precipitated lignin, along with the recycling of H_2SO_4 acidified washing solution back to the black liquor, affects the distribution of sulfur species found in black liquor. Previous studies have shown that at most only a very small fraction of the SO_4^2 -results in S release during black liquor pyrolysis [23,24]. Therefore, the share of S released from lignin-reduced liquors was expected to be lower compared with the original black liquor before lignin removal. While this was observed for the softwood black liquor samples with 10% or 25% lower lignin where S release on black liquor dry solids was the same or increased slightly.

CONCLUSIONS

This research gives new information regarding the combustion properties of reduced-lignin black liquors. The removal of lignin decreased the N content of all of the liquor samples. The use of acidified warm-water H₂SO₄ solution in washing of lignin increased the sulfur content of kraft liquor samples. Lignin removal also reduced the organic content of the black liquor and can affect both swelling and char burning. In all samples, the char burning time was affected by lignin removal, while no clear difference could be seen in the devolatilization time. These changes in combustion time were small and will not result in any observable change in char burnout in a recovery boiler. The changes in maximum swollen volume were fairly significant and could slightly affect carryover, but sheet breakup and droplet formation from the liquor spray need to be studied before any predictions can be made about the effect of swelling changes on carryover.

The NO formation was not greatly affected by lignin removal, and NO emissions from the recovery boiler on a dry solids basis are not expected to be significantly affected by lignin removal. However, on a per ton of pulp basis, NO emissions should go down as the flow of as-fired black liquor solids/ton of pulp will decrease. The concentration of cyanate in the smelt will likely be quite similar to the original black liquor, at least at 10% lignin reduction. The lower furnace temperature and air distribution are expected to influence cyanate decomposition; therefore, lignin reduction also may indirectly influence the amount of cyanate exiting the boiler with the smelt.

Assuming the temperature at which devolatilization happens in the recovery boiler is the same, S release from reduced lignin black liquor is expected to be the same or slightly lower than for the original black liquor. This clearly can be seen at all temperatures for the eucalyptus black liquor. For the softwood liquor this is less clear, but when looking at S release at 900°C for the softwood black liquor, there is little difference with lignin reduction. Older boilers with lower temperatures at the gun level and char bed will need to adjust firing with reduced-lignin black liquor to keep up the temperature; otherwise, S emissions could increase due to a cooler lower furnace, which can result in higher S release from black liquor. The influence of lignin removal on S release should be studied in more detail to better understand what role, if any, lignin has on the formation of volatile sulfur compounds.

On the basis of this work, the combustion of reduced-lignin black liquors in the recovery boiler furnace is possible without any major changes. Mill trials with reduced black liquor firing would provide more details on variables such as sheet formation and droplet formation during spraying. **TJ**

ACKNOWLEDGEMENTS

The authors acknowledge the Graduate School in Chemical Engineering (GSCE) for the scholarship supporting Niklas Vähä-Savo. This work has been carried out within the Future fuels for Sustainable Energy Conversion (FUSEC) project (2011-2014) as part of the activities of the Åbo Akademi Process Chemistry Centre. Support from the National Technology Agency of Finland (Tekes), Andritz Oy, Metso Power Oy, Foster Wheeler Energia Oy, UPM-Kymmene Oyj, Clyde Bergemann GmbH, International Paper Inc., and Top Analytica Oy Ab is gratefully acknowledged.

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ABOUT THE AUTHORS

Lignin removal from black liquor and lignin usage are going to increase in the near future. Understanding how reduced-lignin black liquor burns is important for smooth implementation of this technology.

We have a long history at Åbo Akademi University of characterizing the combustion properties of different black liquors. Our earlier work provided a platform for characterizing reducedlignin black liquor. This work used established techniques but raised some interesting questions, such as why the nitrogen chemistry doesn't change more with lignin reduction. The sulfur release was also higher than expected for the reduced-lignin black liquors.

Determining the sulfur release was the most difficult part of this work. We were most surprised by the comparatively high sulfur release with the reduced-lignin black liquors. These results do not conform to what was expected based on our current understanding of sulfur release.

In implementing a new technology in the chemical recovery cycle, mills need to know how the process will affect the rest of the cycle. How the black liquor burns is one important piece of information. This work indicates that from a combustion standpoint, reduced-lignin black liquors with 10%–20% removal should behave similarly to normal black liquor. However, mills will need to think about how they spray the black liquor and air distribution. Reduced-lignin black liquor has less char carbon, which will affect the char bed and reduce efficiency and potentially sulfur dioxide emissions if the lower furnace temperature drops significantly.

Short of a mill trial, perhaps the most beneficial next step would be computational fluid dynamics modeling of the carbon/air distribution when firing reduced-lignin black liquor. This would give mills some indication of how the firing conditions should be adjusted, including spraying and air distribution. Sulfur release and additional experiments with the nitrogen chemistry are interesting topics for further work.

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