



Final Report: Sky-REC Co-combustion of mixed fuels – Phase 2

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Summary

This project was designed to provide some initial information to questions following the SKY-REC Co-combustion of mixed fuels project. The questions of interest are:

- 1. At what addition level does the mixture burn more like wood than black liquor?
- 2. What is the fate of nitrogen in a BL + wood mixture does the char have more cyanate?
- 3. What are the burning characteristics of reduced lignin black liquor?
- 4. What is the fate of nitrogen in lignin lean black liquor?
- 5. What is the impact of wood on the combustion properties of lignin lean BL?
- 6. How much of the nitrogen in biosludge nitrogen is lost for biosludge; biosludge + black liquor after 60 minutes of heat treatment at an agreed upon high solids concentrator temperature followed by concentration of the liquor?
- 7. How does a 5 wt% d.s. biosludge addition affect black liquor combustion?
- 8. Does biosludge addition change the cyanate concentration in smelt?

Wood and biosludge were the two fuels of interest for further work. Some preliminary work was also made with a reduced lignin black liquor. For phase 1 of this project, a single black liquor was used. In this project, the same black liquor was used for the mixtures with wood. A second liquor was used for the biosludge work and a third liquor was used for the lignin depletion tests. This was because there was an insufficient quantity of the original liquor for the biosludge work and the reduced lignin black liquor came from another study. For all liquors, the unmodified liquor was also tested as a reference. In addition to data for wood, we have in some instances done some additional work with bark and in one case peat. These additional tests were funded outside of this project, but included where appropriate to provide some additional insight.

There were three changes to the reactor set up compared with the phase one work. The hook in this work hangs from a platinum wire extended out from a quartz glass tube rather than from platinum wire between two quartz glass tubes. This results in a number of differences. The first is that if the fuel swells in the upward direction, which it often did, we can see it. With the previous set-up we had to estimate the amount of swollen droplet between the quartz glass tubes. Second, the portion of the fuel between the quartz glass tubes was not considered in the burnout time. Finally, the quartz glass tubes clearly resulted in some back mixing. The second change was that we replaced the old NO analyzer. It appears that with the new analyzer/set-up, we get a higher value for NO, but the trend with fuel addition is similar. Finally, we discovered during the trimming of the new analyzer that the flow meters to the reactor were off. The actual flow to the reactor was 261 l/h rather than the target 220 l/h. This accounts for a portion of the difference in the NO values, but not all. For these reasons we re-ran all of the wood-black liquor mixtures, including 13 and 26% wood.

The wood mixtures looked more like solid fuels than liquid fuels, which caused some variation in the biomass - black liquor distribution in the droplets used in the combustion experiments. This can explain the high standard deviations that were obtained in some of the results, particularly the

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burning times where a larger piece of wood would take longer to burn out. Black liquor mixed with biosludge and lignin depleted black liquor looked like typical black liquor fuel.

Below is a brief summary to the experimental results related to each question.

1. At what addition level does the mixture burn more like wood than black liquor?

There was no sharp transition as there had been with 26% peat, though the 50 wt-% d.s. wood appeared to result in a significant increase in combustion time and therefore 35 wt-% wood was also studied. Combustion times for the 26% and 35% wood mixtures were similar and longer than for 13%, but shorter than for 50%. For all wood addition levels, devolatilization times appeared to be shorter and char burning times were significantly longer. Thus increasing the amount of wood would probably result in an increasing amount of char in the char bed and may require a change in air distribution.

2. What is the fate of nitrogen in BL+wood mixture - does the char have more cyanate?

The wood used has more nitrogen than the black liquor on a dry solids basis. Therefore, adding wood resulted in black liquors with a nitrogen content higher than the original black liquor. Because the nitrogen content of wood is lower than bark and peat, this effect is less pronounced. The question here was whether increasing the fuel nitrogen content would also increase the cyanate concentration. Because bark and peat have more nitrogen, we also looked at the impact of these fuels. Wood, bark and peat all resulted in more cyanate, with peat resulting in the largest increase. This is consistent with the nitrogen content of the mixtures, with the peat-BL mixture having the highest nitrogen content. Bark had the lowest increase despite the bark-BL mixture having more nitrogen than the wood-BL mixture. The increase with wood or bark probably would not be seen in a modern recovery boiler. The high lower furnace temperature would likely result in a portion of this added cyanate being oxidized/decomposed and therefore not seen in the exiting smelt. For a very high nitrogen fuel like peat, any difference would be more pronounced. The implication of this work and some subsequent on-going work is that cyanate formation occurs via the alkali carbonate catalysis route.

3. What are the burning characteristics of reduced lignin black liquor?

Our lignin lean black liquor was generated in our lab by bubbling CO₂ through the liquor to lower the pH. Analysis of the lignin lean black liquor provided conflicting results as to the success of the lignin depletion. It is probable that in addition to lignin we also precipitated some hemicelluloses. Therefore these results should be considered preliminary rather than representative of the commercial process. The pH of the black liquor was raised by added NaOH so that the residual alkali was essentially the same for both the original and reduced lignin black liquor. The swelling significantly decreased in the reduced lignin black liquor and the char burning time increased accordingly. Alén et al. [1] showed that both lignin and hemicelluloses together are important to swelling and whether the observed reduction is a result of lignin removal, hemicellose removal, both or another phenomena requires more investigation.





4. What is the fate of nitrogen in lignin lean black liquor?

Because lignin contains more nitrogen based on literature we expected a reduction in both the NO formed and the amount of cyanate formed. We did see a reduction in NO of about 10 to 15%, and a larger reduction in cyanate.

5. What is the impact of wood on the combustion properties of lignin lean BL?

Wood was added to replace the lost energy value of the black liquor. The LHV of the original black liquor and lignin lean black liquor were both measured in this work and the LHV of the wood had been measured in a previous project. Because there was a significant reduction in the LHV with lignin precipitation, the addition of wood was 35 wt-% on a dry solids basis. This addition further increased the combustion time and raised the NO formed by about 20% compared to the original black liquor or about 40% relative to the lignin lean black liquor. This is similar to the 30% increase seen for the mixture of BL-35 wt-% wood indicating that reducing the lignin content of the black liquor that has not had lignin precipitated.

6. How much of the nitrogen in biosludge nitrogen is lost for biosludge; biosludge + black liquor after 60 minutes of heat treatment at an agreed upon high solids concentrator temperature followed by concentration of the liquor?

A black liquor – biosludge mixture containing 5 wt% biosludge was prepared for a Kraft liquor from a Finnish pulp mill and a biosludge from a second Finnish Kraft pulp mill. Three separate mixtures made with the same addition levels were heated to either 105, 130 or 160 °C and held for 60 minutes. After cooling, nitrogen was bubbled through the solution and the gas was bubbled through an 0.05 M H_2SO_4 solution to capture NH₃ for analysis. Very little ammonia was recovered indicating little to no ammonia formation during the heat treatment. These experiments therefore do not explain the apparent loss of biosludge nitrogen seen in some of the earlier mill balances [ex. 2]. A mill balance at Kymi around the concentrator and recovery boiler before and after biosludge addition in the spring would help clarify these findings as the fate of biosludge nitrogen remains unclear.

7. How does a 5 wt% d.s. biosludge addition affect black liquor combustion?

Average combustion times were about the same for all of the heat treated black liquor-biosludge mixtures except for the 160 °C heat treatment where the averate increased due to an increase in the char burning time. Still, there was overlap of the standard deviations indicating that this difference was not statistically significant.

8. Does biosludge addition change the cyanate concentration in smelt?

Biosludge addition resulted in both higher NO and higher cyanate. The NO increase was 24% for the 160 °C heat treatment and 65% for the 130 C heat treatment. Cyanate formation approximately doubled. Experiments at 900 °C, 10% O₂ [3] would separate out NO formation during devolatilization and NO formed due to smelt oxidation. At 1100 °C, this distinction is much harder to make. This distribution may be important to the observation of no increase in NO formation due





to biosludge addition. Of course it should also be noted that the level of biosludge addition here was at least twice that typically added in a mill.

In addition to the above experiments, a wood -black liquor mixture where the wood moisture level was increased to 50% was burned at 1100 °C, 3 vol-% O_2 . The wood addition level was 26 wt-% on a dry solids basis. The wet wood mixture swelled much more than either the dry wood mixture or the original black liquor. The devolatilization + char burning time was about the same as for the black liquor and significantly less than for the dry wood-black liquor mixture. Finally, the NO was about 7% less than for the dry wood-black liquor mixture.

The phase 2 work supports the conclusion of the phase 1 work that wood addition appears possible and very large wood additions may be possible. It also provided some background for interesting questions around lignin depleted liquors, cyanate formation and the fate of biosludge nitrogen. Clearly more work is needed with lignin depleted black liquor, especially around the characterization of the reduced lignin black liquor. The increase in cyanate formation with the addition of higher nitrogen fuels has provided some new insight into cyanate formation. We have begun investigating this further. The fate of biosludge nitrogen remains unclear and would indicate that a mill trial at a modern mill like Kymi where the concentrator condensate can be sampled would be useful in trying to clarify the question of why biosludge does not seem to result in higher NO concentration in the recovery boiler.

Experimental

In this work three different black liquors were used: BL-468 was the same as used in phase 1 and was mixed was mixed with wood, bark or peat; BL-537 was used for the black liquor-biosludge mixtures and BL-538 was used for the lignin reduction.

Black liquor with 80.4% dry solids content (BL468) was mixed with air dried wood and for a few experiments, bark or peat. For the experiments with moist wood, the air dried wood samples were wetted with ion exchange water to 50% dry solids, so that both dry and wet wood samples were used in these experiments. All of these fuel mixtures looked more like solid fuels than liquid fuel. Information on fuel mixtures and experiments conducted are shown in Table 1. The nitrogen content of BL468 and biofuels mixed with BL468 are shown in Table 2.

Table 1. Dry solids of fuels, mixtures and the experiments conducted

Sample	Dry solids%	mass fraction biomass	mixture	combustion	cyanate
	(wt% d.s)	in mixture (wt% d.s)	(wt% d.s)	11	1
BL468	80.40%		80.40%	X	X
bark	92.28%	50.0% / 35.0%	85.91% / 84.53%	X	
bark	92.28%	25.6%	83.41%		Х
bark	49.95%	25.6%	69.52%	X	
wood	92.23%	50.0% / 35.0%	85.88% / 84.51%	X	
wood	92.23%	25.6%	83.40%		Х
wood	49.95%	25.6%	69.48%	X	-
peat	96.55%	25.6%	84.51%	1	X





Table 2. Nitrogen content of black liquor 468 and biofuels

Fuel	N (g/kg) d.s.
Black liquor 468	0.08
Bark	0.4
Wood	0.2
Peat	2.06

Black liquor 537 (BL537) with 81.93% dry solids content was mixed with an 2.1% dry solid biosludge at a 95 wt-% to 5 wt-% dry solids bases. The mixture had a dry solids content of 28.23%. Information on the fuel components is shown in Table 3.

Table 3. Dry solids, Kjeldahl-N and NH₃-N of BL537 and biosludge

Sample	Dry solids	Kjeldahl-N	NH ₃ -N
	(wt-% d.s)	g/kg d.s.	g/kg d.s.
BL537	81.93%	0.9	
Biosludge	2.10%	47	3.8

It was calculated that the mixture contained 3.2 g/kg d.s nitrogen (Kjeldahl-N) and 0.19 g/kg d.s. NH₃. The mixture was divided into the three batches (weighing between 70 and 80g). The batches were heat treated for 60 min in a sealed vessel at three different temperatures: 105° C, 130° C and 160° C. After the heat treatment the vessel was purged with nitrogen and the vent gas was lead through an acid trap containing 0.05M H₂SO₄, in order to capture the released NH₃. The acid trap was analyzed for NH₃ with a WTW NH 500/2 ion selective electrode. Information of the three batches nitrogen content and NH₃ distribution are shown in Table 4.

Table 4. Nitrogen content and NH₃ content in the three heat treated batches

sample	Kjeldahl-N in mixture	NH ₃ in mixture	NH ₃ captured in acid trap	NH ₃ "missing"
	G	g	g	g
105C 60min HT	0.067926	0.004027	0.001327	0.002699
130C 60min HT	0.066128	0.003920	0.000970	0.002950
160C 60min HT	0.070492	0.004179	0.000980	0.003198

After the heat treatment the three batches were concentrated up to approx. 80% dry solids for the combustion tests. Information on the three batches dry solid contents and experiments conducted are shown in Table 5. For comparison cyanate formation and combustion characteristics of BL537 was performed.





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sample	mixture dry solids after concentration	combustion	cyanate
	(wt% d.s.)		
105C 60min HT	81.21%	Х	
130C 60min HT	81.50%	Х	
160C 60min HT	80.86%	X	Х

Black liquor 538 is a Kraft black liquor from the same mill as BL 537, but pulled on a day later. Lignin was precipitated by bubbling CO₂ through the black liquor diluted to 30% dry solids (140 g dry solids in a batch) and held at 65 °C. Sintered glass was used to disperse the CO₂ bubbles in the black liquor. The final pH was measured to be 9.63. The liquor was allowed to set for 1 week in an attempt to maximize lignin depletion. The analysis results provide mixed results for the amount of lignin precipitated. The measured lignin content in the reduced lignin black liquor is 25.1 wt % compared to 29.2 wt % for the liquor before lignin depletion. The heating value data, Table 6, indicates that more lignin than this was removed, but additional analysis is needed to clarify these conflicting results. Table 7 gives the CHN (ASTM D 5373) and BL538 and lignin.

Table 6. Data on black liquor, lignin depleted black liquor and lignin depleted black liquor with wood addition

	Dry solids	LHV
Sample	(wt % d.s)	(MJ/kg)
BL538	83.05 %	10.04
BL538RL(+3.8 wt-% NaOH)	84.87 %	5.68
BL538RL(+3.8 wt-% NaOH)+dry wood (65.31-34.69)	87.29 %	10.04

Table 7. C,H,N analysis (ASTM D 5373); *Kjeldahl N

-	Dry solids	С	Η	Ν
Sample	(wt % d.s)	(%)	(%)	(%)
BL538	30.00 %	31.0	3.1	0.097*
BL538RL	25.95 %	21.8	2.6	< 0.1
Lignin	94.0 %	62.0	5.4	< 0.1

Combustion and cyanate formation experiments were conducted in a single particle furnace, which is a quartz glass reactor where the temperature and atmosphere can be adjusted. The single particle furnace is described in detail by DeMartini et.al [1]. Droplet size used during combustion and cyanate formation experiments was between 11 and 17 mg. The combustion experiments were conducted at 1100°C and 3.3% O_2 in N_2 . The total gas flow was 264.7 l/h and 23.2 l/h of the nitrogen flow into the reactor is lead through the sample insertion port, in order to cool down the sample and prevents any reactions before insertion. The CO, CO₂ and SO₂ emissions were measured with an on-line infrared analyzer (ABB AO2020) and NO was measured with a chemiluminescence analyzer (Teledyne Model 200EM). The combustion of the samples was recorded with a video camera.

The recorded combustion videos were used to determine devolatilization and char burning times for the fuel mixtures. Maximum swelling volume of the droplet is estimated by capturing an image





from the recorded video. The captured two dimensional image is compared to a circle or an ellipse, so that the volume of a corresponding sphere or ellipsoid could be calculated.

Cyanate formation in the fuel mixtures was determined by pyrolysing the samples at 800°C 100% N_2 in the single particle furnace for 6 seconds to form a char. The chars were then gasified at 800°C 13% CO_2 87% N_2 to different smelt yields. The smelt yield was calculated from weight loss of the samples, by comparing the weight of the smelt samples to the char samples. The samples were gasified to five different smelt yields. Each smelt yield consisted of 6 samples. After the pyrolysis and gasification the samples were washed with ion exchanged water and filtrated. The procedure was to take three samples from each smelt yield and wash it with 6ml ion exchange water, giving two washing solutions for each smelt yield. The washing solutions were analyzed for OCN⁻ with ion chromatography (IC) which had a Metrosep Anion Dual 2 column.

Results

1. At what addition level does the mixture burn more like wood than black liquor?

Increasing wood generally resulted in longer char burning and total combustion times while devolatilization times were about the same for all wood addition levels, Figure 1. The combustion times for the 13 and 26% wood addition levels were based on new mixtures with the modified reactor set-up. There was no sharp transition as there had been with 26% peat, though 50% wood did represent another significant increase in combustion time relative to 26% and 35% wood. There was not a clear trend between level of wood addition and average swollen volume, Figure 2.



Figure 1. Devolatilization, char burning and total combustion times for 4 different addition levels of dry wood with black liquor.



Figure 2. Average swollen volume for BL 468 and BL-wood mixtures at 4 different levels.

2. What is the fate of nitrogen in BL+wood mixture - does the char have more cyanate?

As found in the phase 1 work, adding wood increases the NO formed due to an increase in fuel-NO, Figure 3. Cyanate also increased for a wood-BL mixture relative to wood, Figure 4. Only the 26 wt% wood mixture was tested from the wood mixtures. To verify this result, both a bark-BL and peat-BL mixture were tested and showed increased cyanate formation, Figure 5. The largest increase in cyanate came with peat mixture which also has the highest fuel nitrogen. The bark-BL mixture has a higher nitrogen content than the wood mixture but did no result in a higher cyanate formation in these tests.



Figure 3. NO formation as gN/100 g dry fuel for increasing levels of wood addition.



Figure 4. Concentration of cyanate in char vs. char gasification at 800 °C in 13% CO₂ / 87% N₂. Chars were formed by pyrolysis at 800 °C for 6 s in 100% N₂.



Figure 5. Concentration of cyanate in char vs. char gasification at 800 °C in 13% CO₂ / 87% N₂. Chars were formed by pyrolysis at 800 °C for 6 s in 100% N₂.

- 3. What are the burning characteristics of reduced lignin black liquor?
- 5. What is the impact of wood on the combustion properties of lignin lean BL?

The swelling significantly decreased in the reduced lignin black liquor, Figure 6, and the char burning time increased accordingly, Figure 7. Wood did not have much impact on swelling, but did result in longer residence times, most likely due to small sticks of wood.







Figure 7. Devolatilization, char burning and total combustion times of BL 538, the reduced lignin BL and the reduced lignin BL + wood.

4. What is the fate of nitrogen in lignin lean black liquor?

Because lignin contains more nitrogen based on literature we expected a reduction in both the NO formed and the amount of cyanate formed. We did see a reduction in NO of about 10 to 15%, Figure 8, and a larger reduction in cyanate, Figure 9.



Figure 8. NO formation as gN/100 g dry fuel for reduced lignin black liquor with and without the addition of wood to replace the heating value.



Figure 9. Concentration of cyanate in char vs. char gasification at 800 °C in 13% CO₂ / 87% N₂. Chars were formed by pyrolysis at 800 °C for 6 s in 100% N₂.

6. How much of the nitrogen in biosludge nitrogen is lost for biosludge; biosludge + black liquor after 60 minutes of heat treatment at an agreed upon high solids concentrator temperature followed by concentration of the liquor?

As shown Table IV, very little NH_3 was captured after heat treatment indicating that vey little was formed. This is also consistent with the higher NO formation observed, Figure 10.



Figure 10. NO formation as gN/100 g dry fuel for BL-biosludge samples that were heat treated for 60 minutes at one of three temperatures.

7. How does a 5 wt-% d.s. biosludge addition affect black liquor combustion?

The biosludge black liquor mixture had to be concentrated to 80% solids before combustion. The concentrated mixture looks like black liquor. Combustion times for the mixtures were within a few seconds of the combustion time for the original black liquor, Figure 11 despite a large difference in the average swollen volume, Figure 12.



Figure 11. Devolatilization, char burning times for BL-biosludge samples that were heat treated for 60 minutes at one of three temperatures.



Figure 12. Swollen volume of BL 538, and the heat treated biosludge mixtures.

8. Does biosludge addition change the cyanate concentration in smelt?

Cyanate formation was measured for only the liquor treated at 160 °C. A significant increase in cyanate formation was observed, Figure 13.



Figure 13. Concentration of cyanate in char vs. char gasification at 800 °C in 13% CO₂ / 87% N₂. Chars were formed by pyrolysis at 800 °C for 6 s in 100% N₂.





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