Co-firing Black Liquor and Biomass

Summary

The objective of this work was to determine if mixing other biofuels in with black liquor would alter the combustion characteristics of the black liquor. The four biofuels mixed with black liquor were bark, wood chips, peat and biosludge. The specific variables followed were swelling, carbon evolution (CO_2+CO), and NO formation tendency. We found that there were changes in all of these, but not for all mixtures and that the level of added fuel made a difference.

The largest changes in swelling were seen for peat and bio-sludge addition. The cause of these changes is not clear as 13,2 % and 25,5 wt % peat addition resulted in higher and lower swelling respectively when compared to the black liquor. Similarly, the 0,8 % biosludge mixture resulted in more swelling, while the swelling of the 1,8 % biosludge mixture had swelling similar to the black liquor.

The char burning stage is on average increased only slightly by the addition of bark, wood chips and biosludge, but more significantly by peat, especially the 25,5 wt% peat mixture. This was caused in part by the significantly lower swelling of the this mixture. Peat also had a significant impact on NO formation, resulting in an increase in NO formed during both the devolatilization and char burning stages. The other fuels did not result in a significant change in the NO formed.

The mixtures (except the black liquor + biosludge sample) looked more like a wet solid fuel rather than a liquid fuel containing entrained solids and therefore it is probable that there is some variation in the exact distribution of the biofuel and black liquor in the droplets studied. At least some future combustion tests will be carried out with the fuel being ground into a finer powder if possible to improve fuel homogeneity.

There are a number of interesting open topics with regards to the combustion chemistry of biomass mixed with black liquor. They include:

- distribution of nitrogen between the gas phase and smelt
- sulfur, sodium, potassium and chloride release
- distribution of volatiles and fixed carbon

In the next piece of this work we would like to look more closely at the nitrogen chemistry of bark and bio-sludge addition, specifically the smelt. Both should result in an increase in the nitrogen content of the black liquor, but neither resulted in an increase in the NO formed. We would run interrupted pyrolysis and char gasification tests to better understand the fate of this nitrogen. For example, does it result in more cyanate in the smelt. We would also be interested in running two biosludges if deemed appropriate – one from a mill and the other a municipal biosludge that a mill might burn. In this way, a biosludge could represent a larger biomass stream for co-combustion.

Report Prepared by:
Nikolai DeMartini
Senior Researcher
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Experimental

The four biofuels tested were bark, wood chips, peat and biosludge (pre-dried). The individual fuels were mixed as received and the dry solids of the fuels and mixtures are given in Table I.

Table I. Dry solids of fuels and mixtures.

Sample	Dry solids	Size description	Mass Fraction Biomass in Mixture (wt % d.s.)	Mixture (wt % d.s.)
BL	80,4	liquid		80,4 %
bark	95,0	< 1 mm	13,2 % / 25,6 %	82,1/83,7
wood chips	95,9	4 mm	13,3 % / 26,9 %	82,2/84,1
peat	94,2	ground	13,3 % / 25,5 %	82,0/83,5
bio-sludge	21,9	viscous liquid	0,82 % / 1,84 %	78,7/76,6

Pictures of the mixtures are given in Figure 1. Aside from the biosludge, the other fuels resulted in a fuel that more closely resembled a wet solid fuel than a liquid fuel with entrained solids. Fuel homogeneity was of concern when preparing the droplets.

Six droplets of each fuel mixture were burned at 1100 °C in 3 % O_2 in the droplet furnace at Åbo Akademi, Figure 2. Combustion was recorded with a digital video camcorder. A picture of the droplet at maximum swelling was analyzed to obtain an estimate of the swollen droplet volume. On-line analyzers were used to follow carbon ($CO+CO_2$) and NO evolution during the droplet combustion.

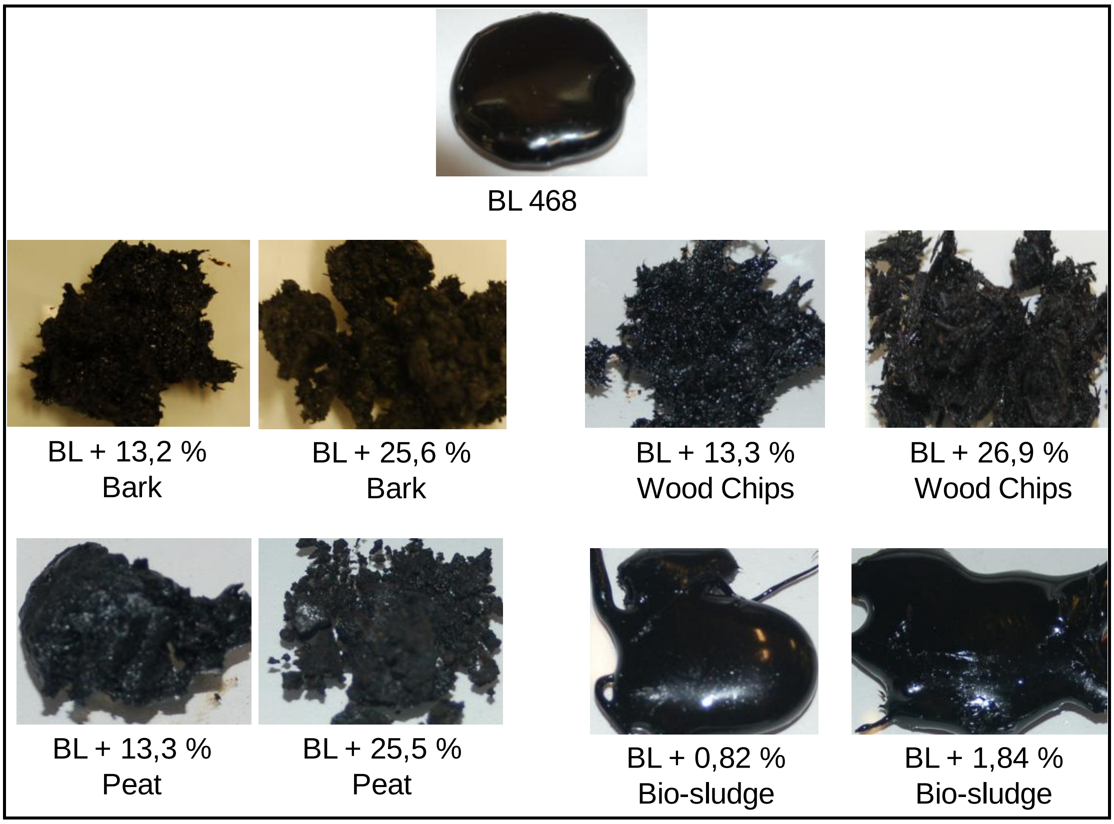

Figure 1. Photos of the fuel mixtures.

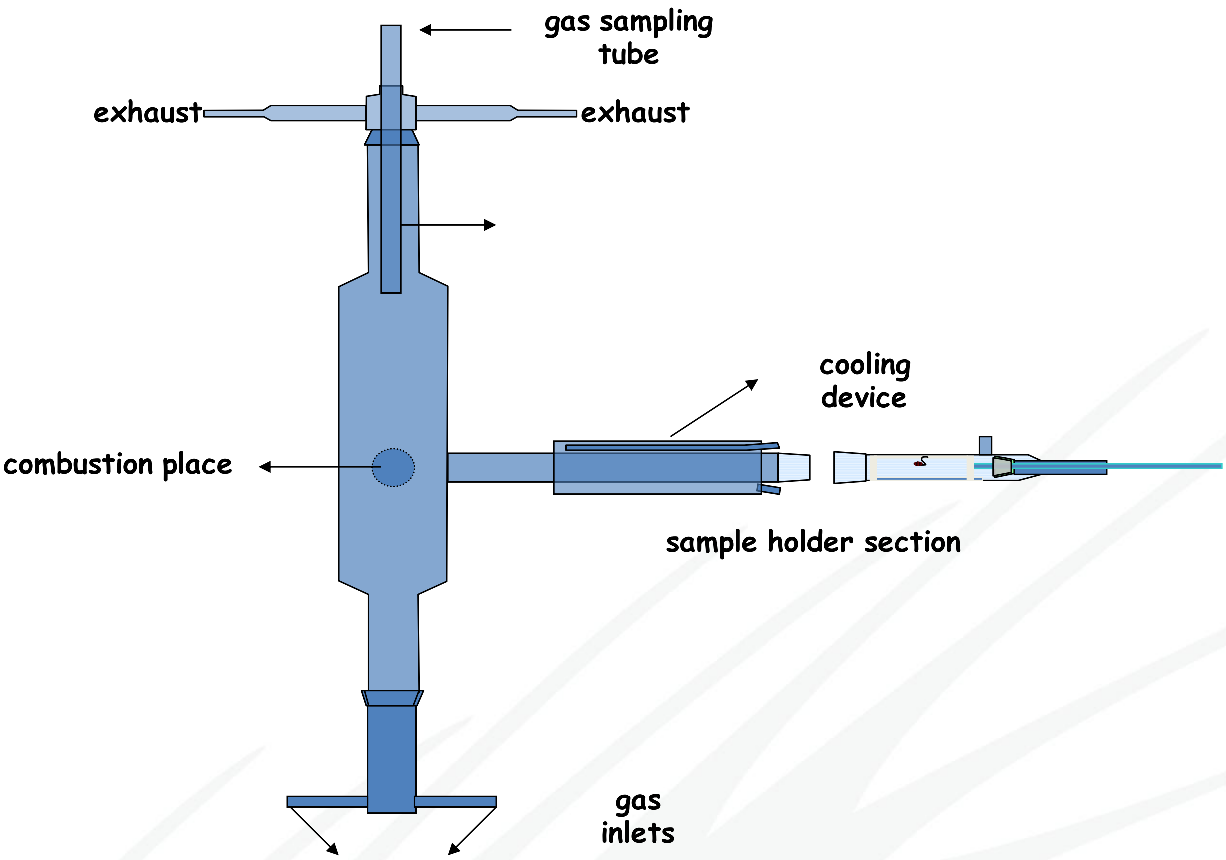

Figure 2. Diagram of droplet furnace used in this work.

Results and Discussion

Swelling. Average swelling changed most significantly with peat addition and 0,82 bio-sludge addition, Figure 3. The cause of the significant change in swelling for the two levels of peat addition is not clear, but this swelling change is likely at least partially responsible for the much longer char conversion time for the mixture with 25,5 wt % peat discussed in the next section.

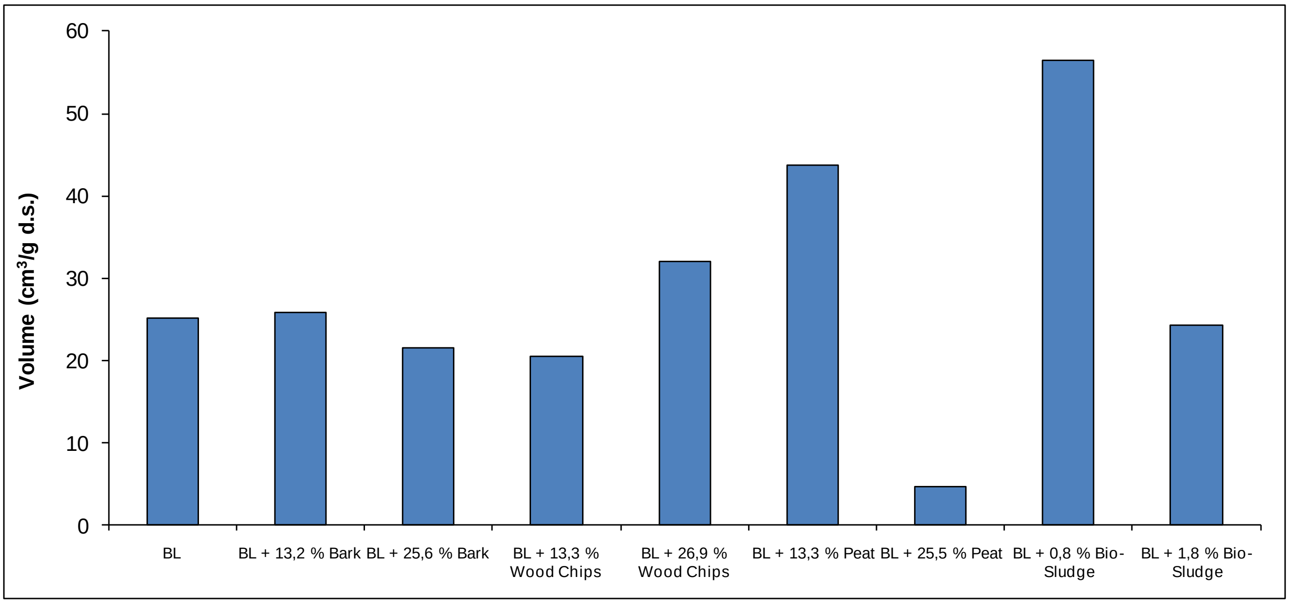

Figure 3. Average swelling of the black liquor and mixtures.

Gas Evolution. All of the mixtures exhibited longer char burning times on average than the black liquor, Figure 4. This is most pronounced for the mixtures with peat. It would appear from the curves for peat that less material is volatilized and the significant increase in char burning time is both because of more fixed carbon and the reduced swelling though these effects have not been separated.

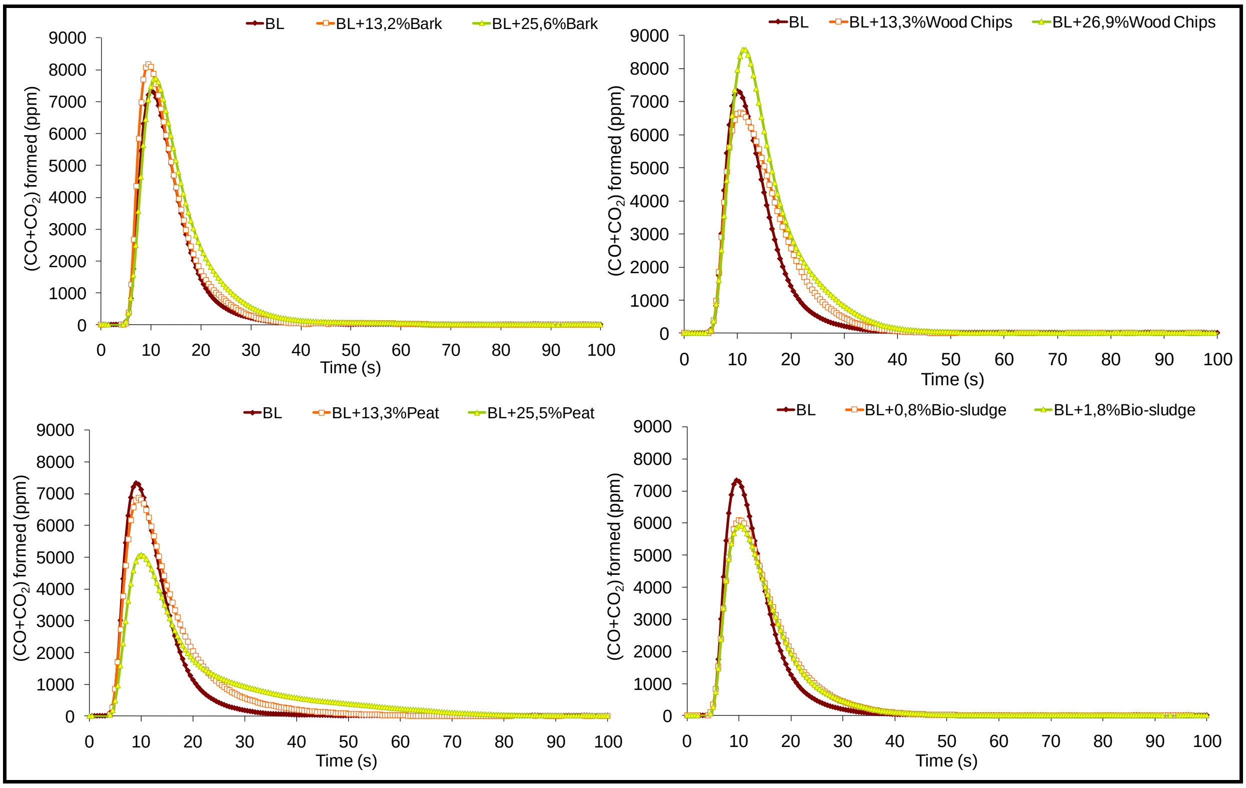

Figure 4. Carbon evolution as CO + CO_2 (avg. for 6 droplets) for the black liquor and the mixtures burned at 1100 °C with 3% O_2 in N_2.

The videos were also used to determine the average times for devolatilization and char burning, Figure 5. The devolatilization time was the time from the beginning of the flame to the end of the flame and the char burning stage was taken as the time from the end of the flame to smelt coalescence. Drying is not included as the high temperature in the reactor resulted in significant drying of the samples before insertion into the reactor despite the nitrogen cooling. Combustion times were 30-50% longer when compared with the black liquor for all samples except the mixture with 13,2% bark and 25,5% peat. Most of this increase in the reaction time occurs in the char burning phase and may be due to the fact that the alkali is not as intimately mixed with the biomass fuels as it is with the organics in the black liquor thereby resulting in a difference in the catalysis of the fixed carbon during the char conversion reactions. The addition of 13,2% bark does not affect the total combustion time based on the droplet results, but addition of 25,5% peat results in a combustion time 3.5 times longer than for the black liquor.

The only fuel mixture which resulted in a significant change in NO formation was peat, Figure 6. Peat resulted in significantly more NO formation both during devolatilization and char burning. Whether this results in more NO from the recovery boiler will likely depend on air staging and lower furnace conditions. Earlier work has shown that the addition of 0.5 wt. % biosludge to black liquor does not result in an increase in NO formed in the recovery boiler or in OCN with the smelt [1]. The impact of the other fuels on smelt nitrogen was not studied, but would be of interest.

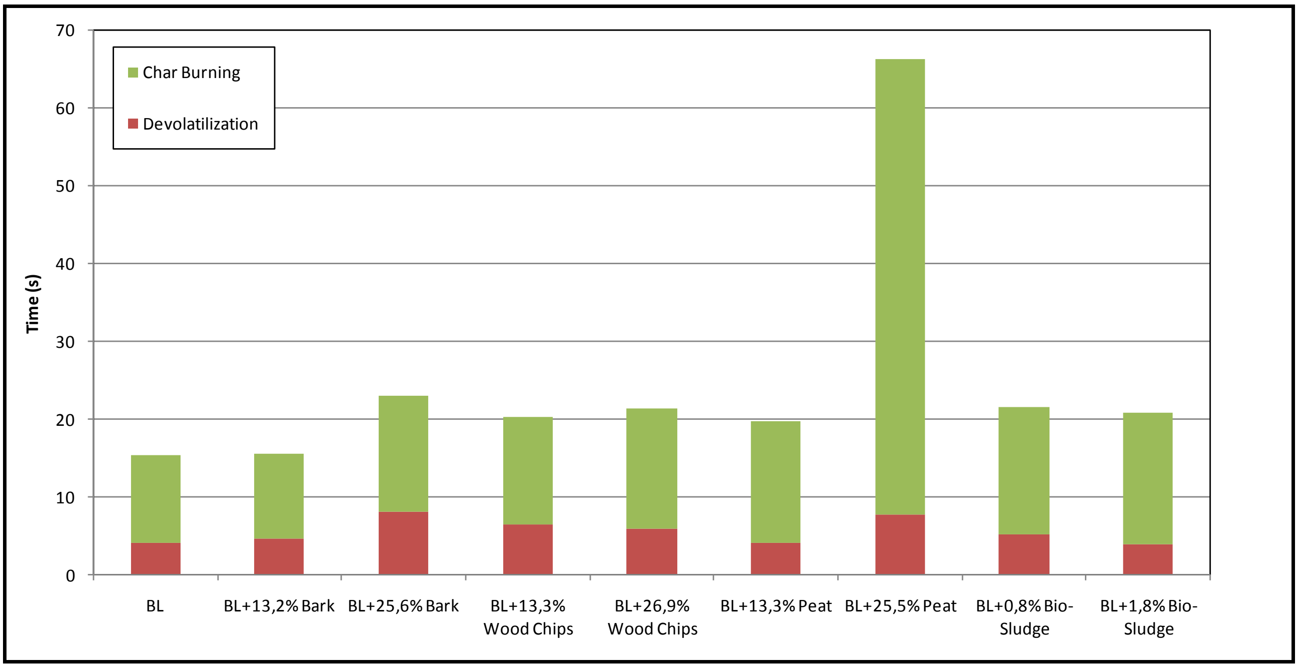

Figure 5. Times of the combustion stages (drying, devolatilization, and char burning) for the fuel mixtures.

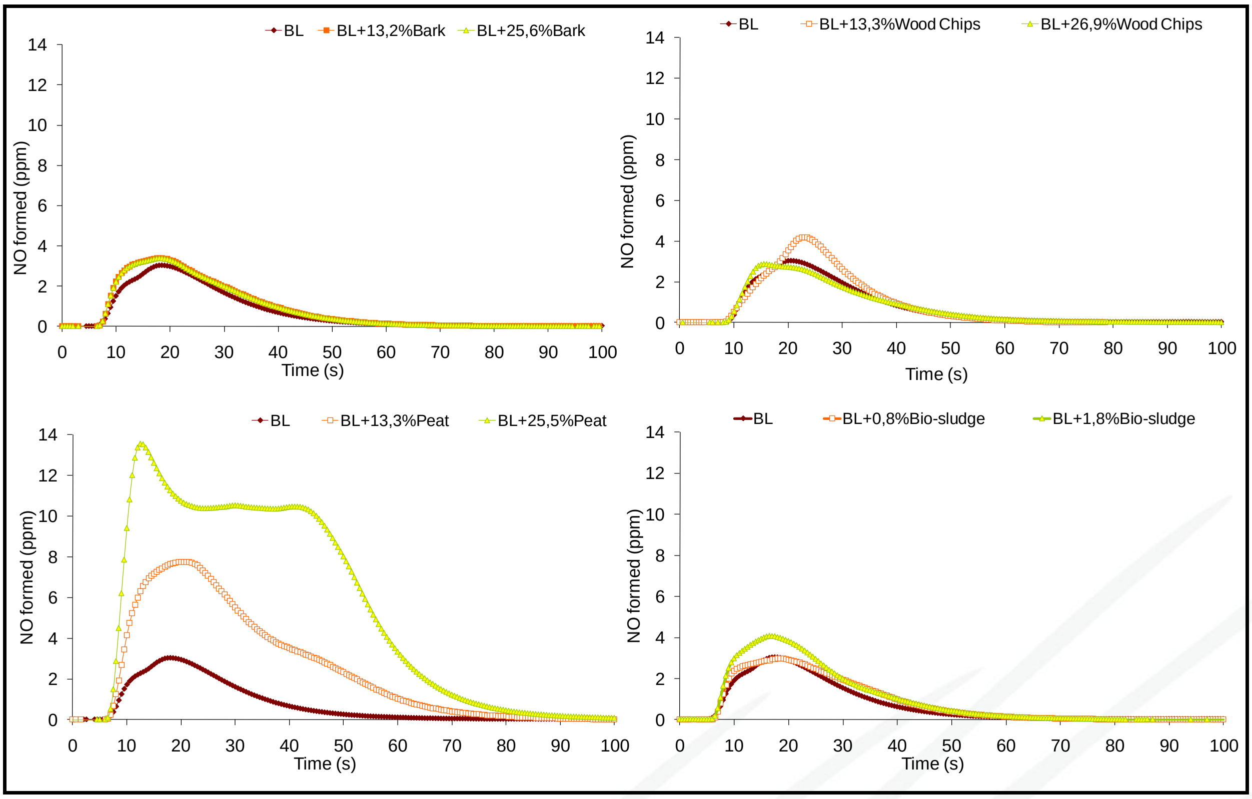

Figure 7. NO formed for the various fuel mixtures relative to black liquor. Mixtures made with 80.4 wt % d.s. black liquor.

References

1. Kymäläinen, M.; Holmstrom, M.; Forssén, M.; Hupa, M. The fate of nitrogen in the chemical recovery process in a kraft pulp mill. Part III. The effect of some process variables. J. Pulp Pap. Sci. 27(9): 317-324 (2001).