CO-FIRING BLACK LIQUOR AND BIOMASS IN A LABORATORY SINGLE DROPLET REACTOR – EFFECTS ON EMISSIONS AND COMBUSTION CHARACTERISTICS

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ABSTRACT

Mills with recovery boilers with excess capacity can potentially mix other biofuels into the black liquor to produce more bio-electricity. This work is a laboratory study of the effect on combustion of mixing other biofuels with black liquor. The four fuels mixed with softwood black liquor were bark, wood chips, peat and biosludge (which some mills already burn with black liquor). Droplets of the mixed fuels were burned at 1100 °C and 3% O_2 in a droplet furnace. Video and on-line gas analyzers for CO, CO_2 and NO were used to measure swelling, combustion times, carbon evolution (CO_2+CO), and NO formation tendency. We found changes in swelling, char burning and NO formation, but the results indicate that mixing biofuels with black liquor may be a reasonable method of producing additional bio-electricity.

INTRODUCTION

For a mill with recovery boiler capacity, there is the possibility of producing additional bioenergy by mixing biofuels such as bark or wood into the as-fired black liquor and co-combusting the fuel in the recovery boiler. This study was conducted with a single particle reactor at Åbo Akademi University to study the impact of the addition of four fuels – bark, wood, peat and bio-sludge – on the swelling, devolatilization and char burning and NOx formation tendency. The fuels were added at two levels of about 13 and 26% for bark, wood and peat and 0.8 and 1.8% for biosludge; all on a dry solids basis.

Biosludge has been successfully added to black liquor in mills with no clear increase in NO [1], or challenges in firing the black liquor [2]. Our combustion tests with biosludge are of the same order of magnitude as burned in mills. Up to 20% sawdust on a dry solids basis [3] and 60% rice husk and rice husk dust [4] on a dry solids basis have been trialed for co-gasification with black liquor in pilot units, but little detailed information was made available in these papers. Black liquor is also a source of interest as an inexpensive catalyst source for coal gasification [e.g. 5] with loadings of 5 to 8 wt% being found to be optimal. This paper is a step forward in helping clarify if it is possible to co-combust black liquor with four possible fuels: bark, wood, peat and bio-sludge.

EXPERIMENTAL

An 80.4% d.s. black liquor was mixed with bark, wood, peat or biosludge to two different dry solids concentrations. All fuel mixtures except the biosludge mixtures looked more like wet solid fuels than liquid fuels, Figure 1. The bark, wood and peat were air dried for previous projects and the biosludge was pre-dried in the laboratory oven at 115 °C to increase the dry solids up to over 20% dry solids before mixing. One advantage of using drier samples was that the final dry solids content of the mixtures burned was within 4% of the initial black liquor dry solids.

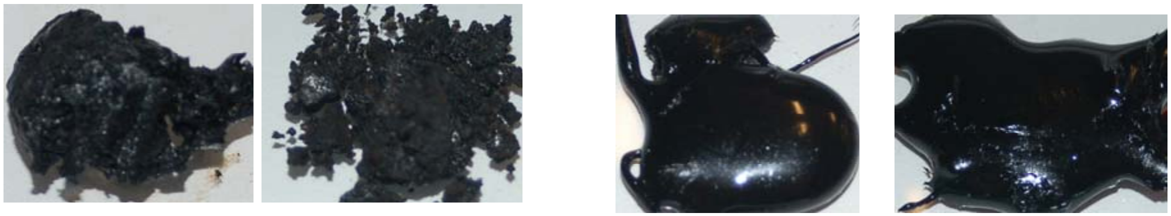
BL

BL + 13,2 % Bark

BL + 25,6 % Bark

BL + 13,3 % Wood

BL + 26,9 % Wood



BL + 13,3 % Peat

BL + 25,5 % Peat

BL + 0,82 % Bio-sludge

BL + 1,84 % Bio-sludge

Figure 1. Fuel mixtures of black liquor with bark, wood, peat or bio-sludge.

Table I. Dry solids of fuels and mixtures.

Sample	Dry solids of fuel	Size description	Mass Fraction Biomass in Mixture (wt % d.s.)	Mixture (wt % d.s.)	Droplet sizes (g) (+/- 1 standard deviation)
BL	80,4	liquid		80,4 %	11.3 +/- 1.7
Bark	95,0	< 1 mm	13,2 % / 25,6 %	82,1/83,7	12.0 (+/- 3.1) 22.0 (+/- 5.9)
Wood	95,9	4 mm	13,3 % / 26,9 %	82,2/84,1	17.5 (+/- 4.6) 18.8 (+/- 4.9)
Peat	94,2	ground	13,3 % / 25,5 %	82,0/83,5	21.1 (+/- 5.8) 22.5 (+/- 3.6)
Bio-sludge	21,9	viscous liquid	0,82 % / 1,84 %	78,7/76,6	14.6 (+/- 1.6) 15.9 (+/- 2.4)

Six single droplets of the initial black liquor and each mixture were burned at 1100 °C in a quartz reactor with a total gas flow rate of 220 L/h and 3% O_2 in N_2, Figure 2. The droplet size range is given in Table I. It was more difficult to maintain a uniform sample size with the mixtures because of the presence of solids. A nitrogen flow of 20 L/h is used to purge the line where the droplet is held before insertion into the reactor. This nitrogen flow keeps the sample from reacting before insertion. On-line infrared analyzers were used to measure CO and CO_2 and a chemilumenescence analyzer was used for $NO+NO_2$ analysis.

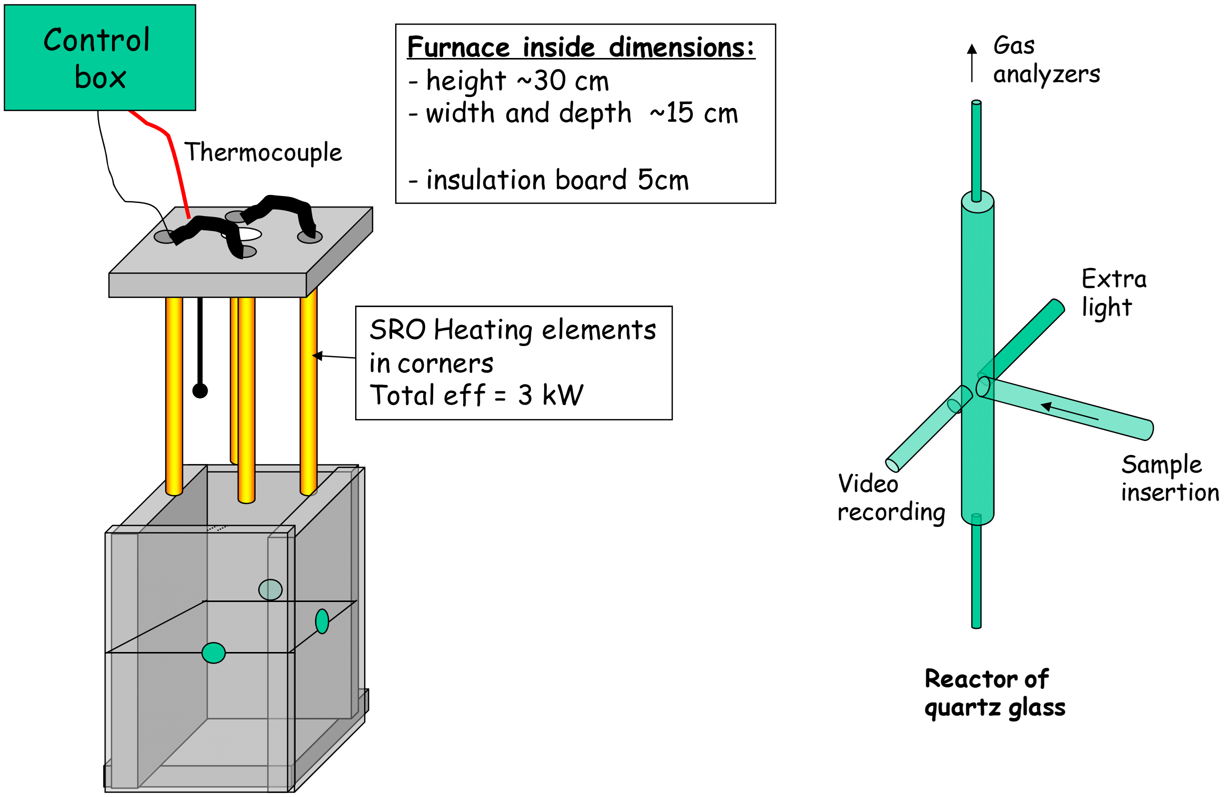


Figure 2. Reactor used for single droplet combustion tests.

Video was taken of the droplet from the point at which it was inserted. Swelling was estimated using the 2 dimensional image of the droplet at the maximum swollen volume. The surface area of the two dimensional image is determined and then the volume is determined based on the volume of a sphere or ellipsoid depending on the shape of the swollen droplet.

The black liquor has only been analyzed for nitrogen as part of another project. The biosludge has not been analyzed at all. An estimate of the nitrogen content of the biosludge is also given in Table II and is based on the concentration of nitrogen in another biosludge sample taken from the same mill for an earlier project. The bark, wood and peat were also analyzed for various elements. The concentrations relevant to this paper are given in Table II.

Table II. N, K, Na, Mg, and Mn concentrations in the fuels on a dry solids basis. *based on different biosludge sample from the same mill for an earlier project.

Element	Black Liquor	bark	wood	peat	Biosludge
N (wt % d.s.)	0.08	0.4	0.2	2.06	6.17*
K (mg/kg d.s.)		1090	1100	270	
Na (mg/kg d.s.)		978	160	171	
Mg (mg/kg d.s.)		599	440	780	
Mn (mg/kg d.s.)		465	87	97	

RESULTS AND DISCUSSION

Swelling. The change in swelling relative to the original black liquor was greatest for peat and biosludge, Figure 3. The swollen volume for the black liquor was 25 cm^3/g. Interestingly; there was an increase in swelling with the addition of 13.3 % peat while swelling decreased dramatically when the amount of peat was increased to 25.5 wt %. The lowest addition of biosludge also caused significant swelling relative to the higher addition level. The causes for the changes in swelling are not clear at this time.

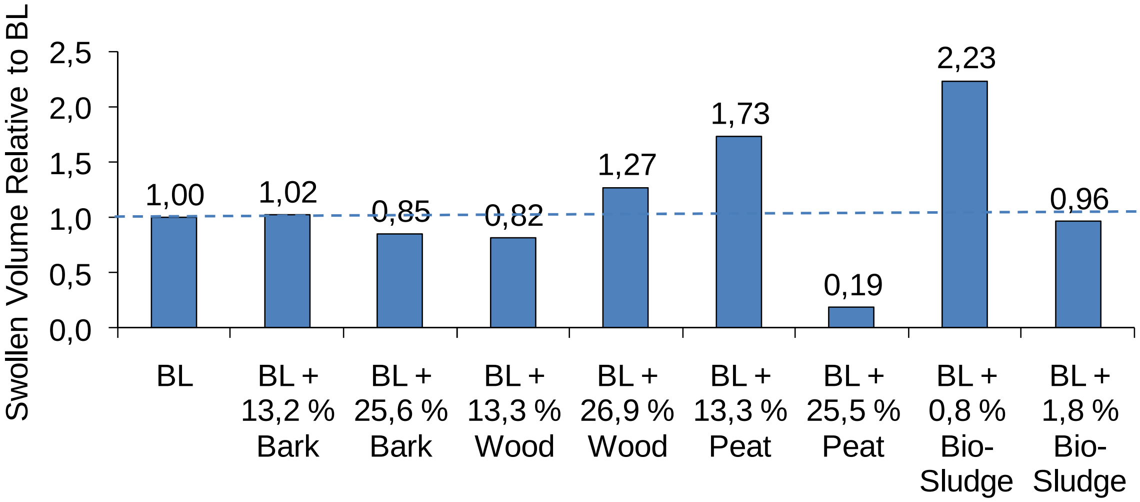


Figure 3. Swelling of mixtures relative to the black liquor.

Combustion times. The stages of black liquor combustion can be divided into drying, devolatilization, char burning and smelt coalescence [6]. The devolatilization and char burning times were measured from the video, though drying times were not included because at 1100 °C, some droplets ignited as soon as they entered the reactor. The devolatilization time was based on the time at which a flame first appears to when it disappears. Char combustion is taken as the time from the disappearance of the flame until smelt coalescence. The times relative to black liquor are presented in Figure 4. The times for devolatilization and char combustion for the black liquor were 4.1 and 11.2 seconds respectively.

The dramatic change in swelling and char burning time for the highest level of peat addition is also seen in the curves for CO+CO2, Figure 5. The initial peak which can be attributed to devolatilization is significantly lower for the highest peat addition level while the amount of carbon released during char burning (indicated by the tail of the peak) is higher. The lower devolatilization peak would indicate less material was volatilized from the highest addition level of peat. This may be part of the cause for the reduced swelling. The reduced swelling in turn would increase the mass transfer resistance during char burning and thus increase the char burning time. But a reduction in the volatiles yield from a peat black liquor mixture is surprising as the volatiles yield for this peat is higher than for the black liquor. In a separate project this peat was volatilized at 900 °C in N_2 for 6 seconds and nearly 60% of the dry mass was released. Thus, the volatiles yield of the black liquor-peat mixture would be expected to have a higher volatiles yield than black liquor alone. Pyrolysis experiments at 1100 °C with various levels of peat addition are needed to help clarify the observed trend during combustion of the black liquor – peat mixtures.

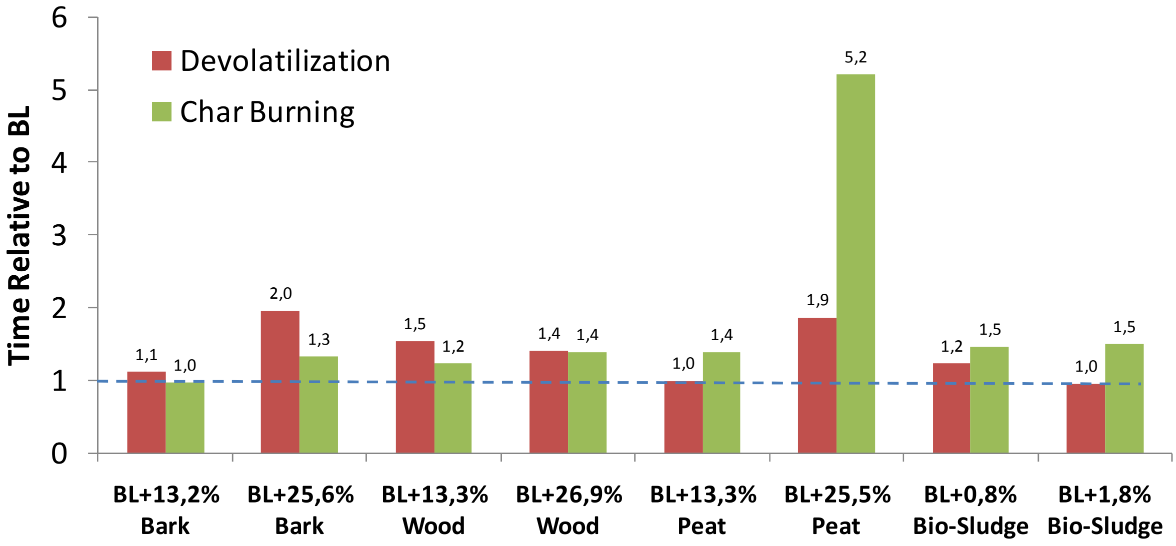


Figure 4. Relative devolatilization and char burning times for the black liquor and mixtures.

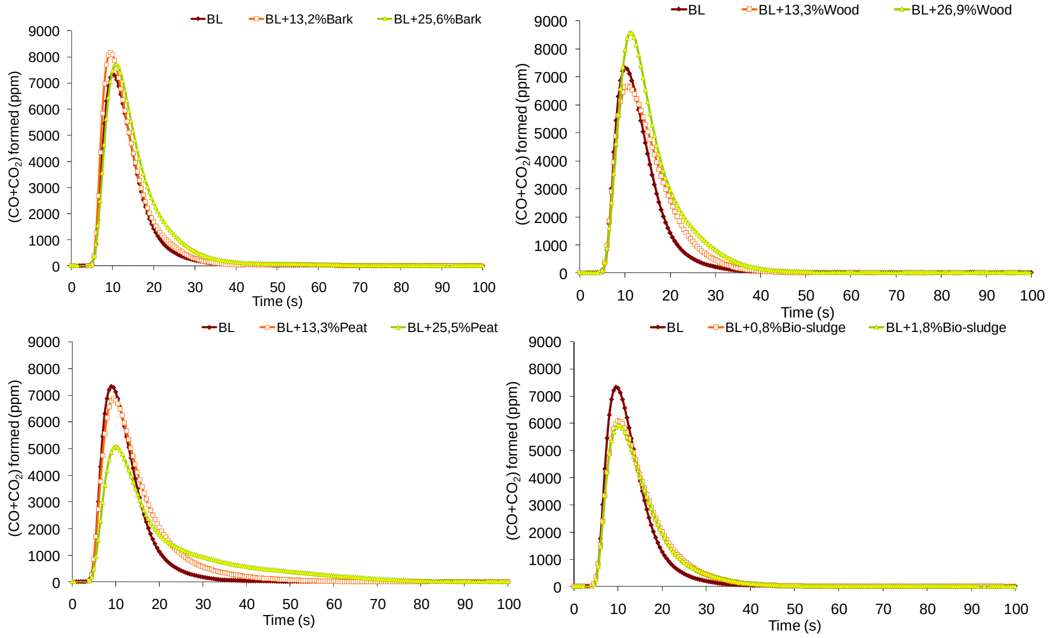


Figure 5. Carbon evolution as CO + CO_2 (avg. for 6 droplets) for the black liquor and the mixtures.

NO Formation. The nitrogen content of the fuel mixtures is higher than the nitrogen content of the black liquor due to the higher concentrations of nitrogen in the added fuels, Figure 6. All mixtures result in a higher NO formation with peat resulting in a significantly higher NO formation due to the higher nitrogen concentration, Figure 7. The ratio of NO formed from combustion of the mixture to the NO formed from combustion of the black liquor is close to the ratio of fuel nitrogen in the mixture compared to the nitrogen content of the original black liquor. Wood, bark and biosludge mixtures all showed the same NO evolution distribution as the original black liquor, while the peat mixtures resulted in much more NO formation during both the devolatilization and char burning stages, Figure 8.

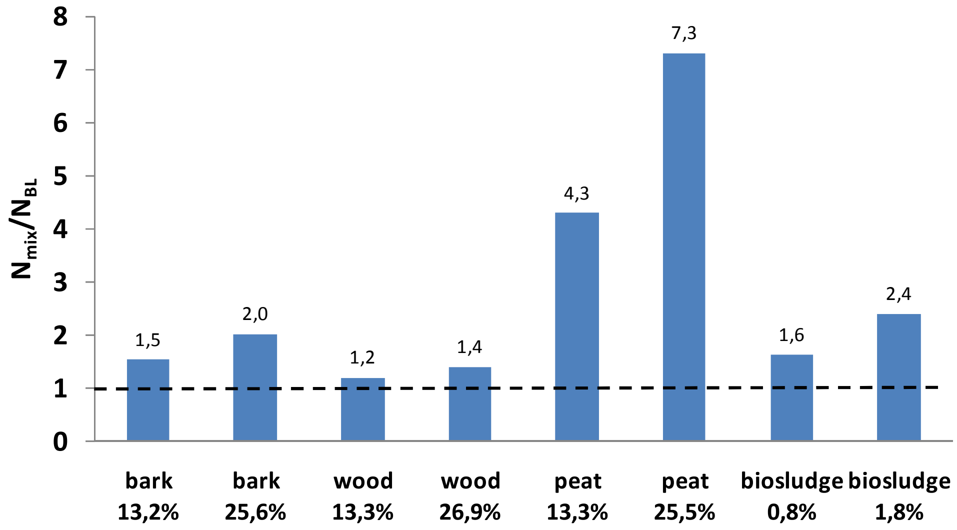


Figure 6. Fuel nitrogen concentration relative to black liquor.

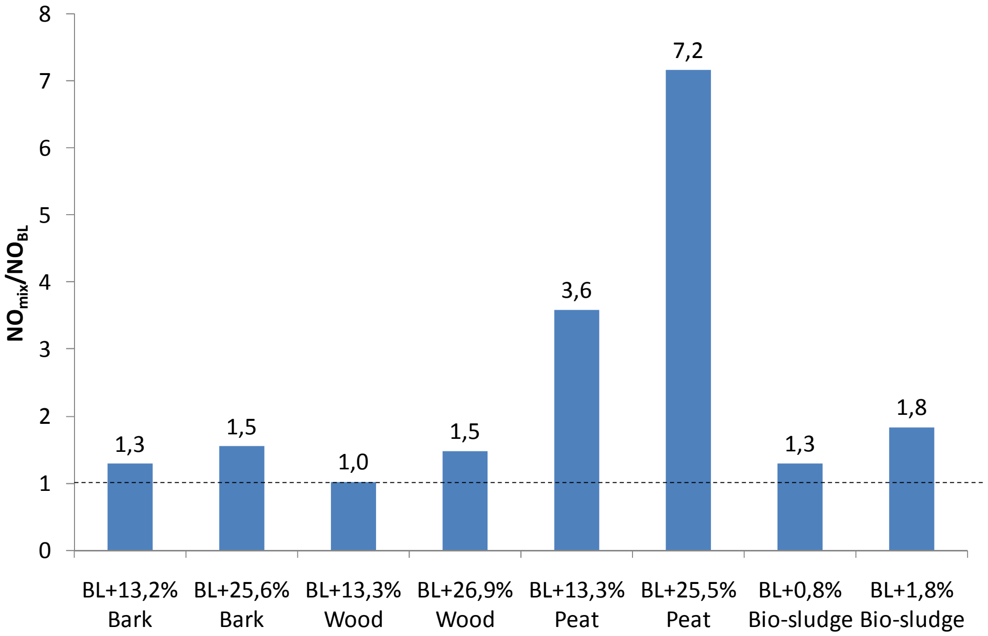


Figure 7. Average NO formation of the mixtures relative to the NO formation of the black liquor.

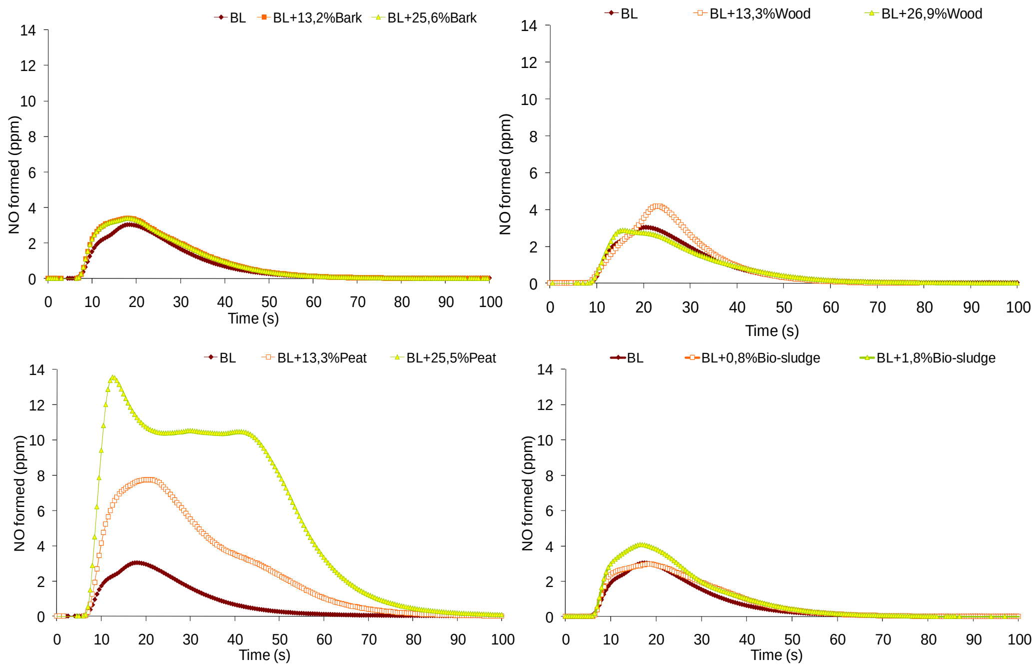


Figure 8. Average NO formation curves for the 6 droplets of the black liquor and mixtures.

Addition of K, Na, Mg, Mn. The addition of other fuels to black liquor will result in the addition of ash forming elements as well. Examples are given for K, Na, Mg, and Mn for the bark, wood and peat used in this study, Figure 9. For example, bark addition with a potassium concentration of 1090 mg/kg d.s. will result in 166 and 375 kg K/1000 metric tons black liquor solids fired at addition levels of 13.2 and 25.6 wt % dry solids respectively. While the addition of these fuels will result in the addition of elements to the recovery cycle, the concentration of potassium and chlorine for example, may be lower in the fuel mixture than in the original fuel which may impact melt characteristics of carryover particles for example. Figure 10 shows the concentration of K in the mixtures assuming a potassium concentration in the black liquor on a dry solids basis of 1 wt%.

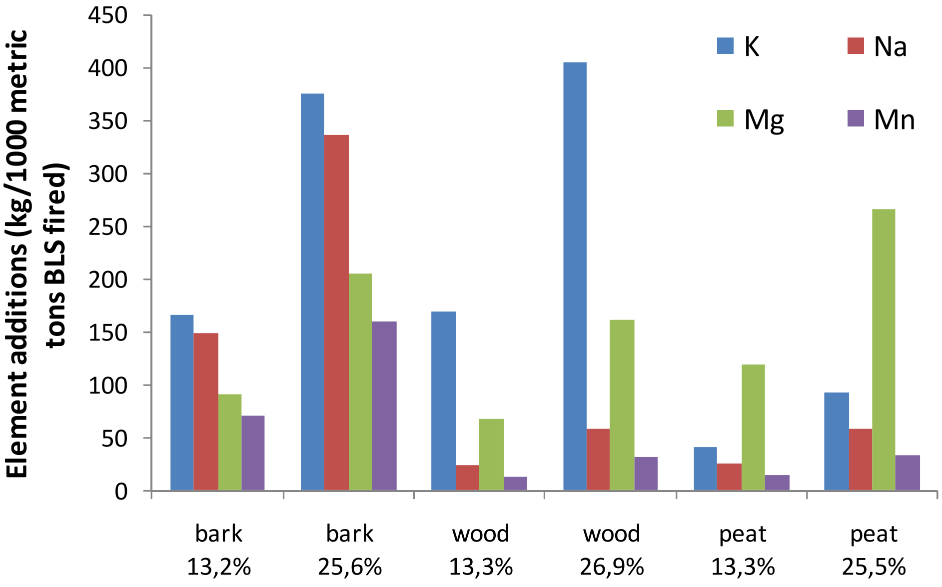


Figure 9. Rate of addition of elements per 1000 metric tons of black liquor dry solids fired.

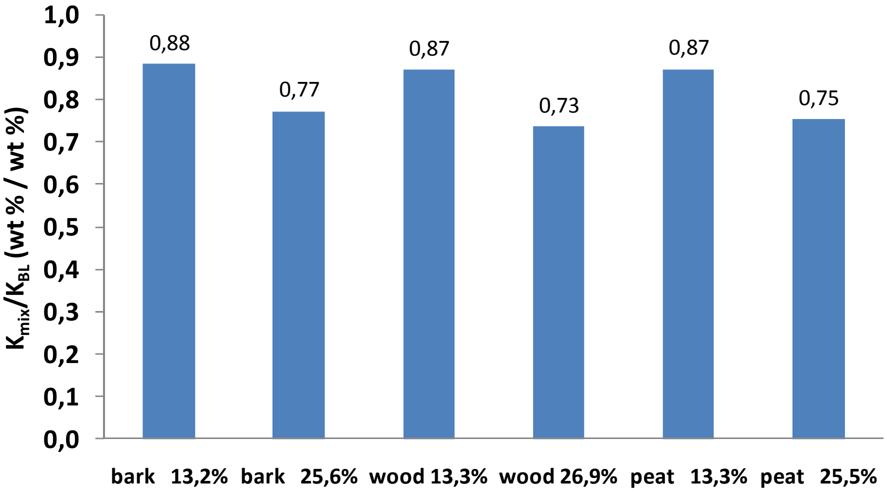


Figure 10. Concentration of potassium in the mixtures assuming a potassium concentration in the black liquor of 1 wt % on a dry solids basis. Potassium was measured in the other fuels.

CONCLUSIONS

The results of this preliminary study indicate that from a combustion chemistry standpoint, there is potential to add biofuels to black liquor for firing of the mixtures in a recovery boiler that has excess capacity to increase the amount of bio-electricity. The mixtures containing bark, wood or biosludge appear to burn much like the original black liquor based on single particle combustion tests. Changes in air distribution should minimize any increase in NO. Peat was the one fuel that appears to significantly alter the combustion behavior of black liquor and would likely need addition levels of no more than 13% on a dry solids basis and more trimming of the recovery boiler. The addition of elements to the recovery cycle can be accurately estimated and accounted for though the release of potassium from mixtures for example should be studied further.

The fuels added here were air dried in the laboratory and therefore quite dry relative to the fuels as mills would receive them. Additional work should be carried out to determine the impact of this moisture on the burning characteristics. Additionally, for the mixtures considered here the black liquor appears to coat the solid material rather than form a solution with suspended solids. At firing temperatures the mixtures could look different, but spraying studies are certainly required to determine how to best feed such mixtures.

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