Co-firing black liquor and biomass in a laboratory single droplet reactor – effects on emissions and combustion characteristics

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ABSTRACT: Mills having recovery boilers with excess capacity can potentially mix other biofuels into the black liquor to produce more electricity from biomass. 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 bio-sludge (which some mills already burn with black liquor). Droplets of the mixed fuels were burned at 1100°C and 3% O_2 in a single particle reactor. Video and on-line gas analyzers for CO, CO_2 and NO were used to measure swelling, combustion times, carbon evolution ($CO+CO_2$), 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 electricity.

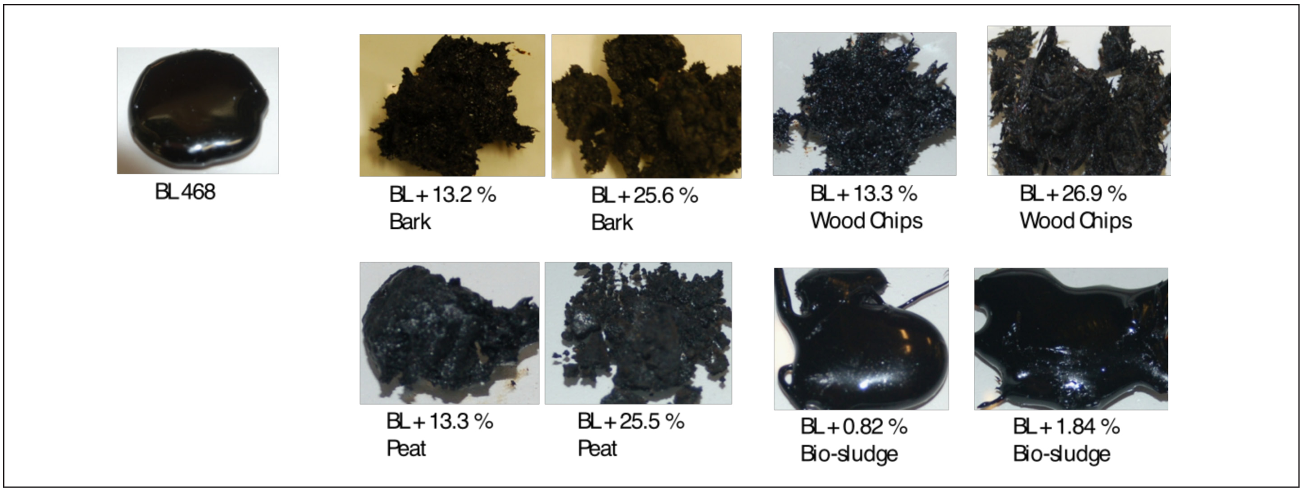
Application: The data in this paper can be used to compare the combustion characteristics (carbon evolutions, NO formation, swelling, devolatilization, and char burning times) of black liquor and black liquor–biomass mixtures.

For a mill with excess recovery boiler capacity, there is the potential for 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 to study the impact of the addition of four fuels – bark, wood, peat and bio-sludge – on the swelling, devolatilization, 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 bio-sludge – all on a dry solids basis.

Bio-sludge 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 bio-sludge 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 no detailed information was made available in these papers. Black liquor is also a source of interest as an inexpensive catalyst source for coal gasification [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 bio-sludge to two different dry solids concentrations. All fuel mixtures except the bio-sludge mixtures appeared closer



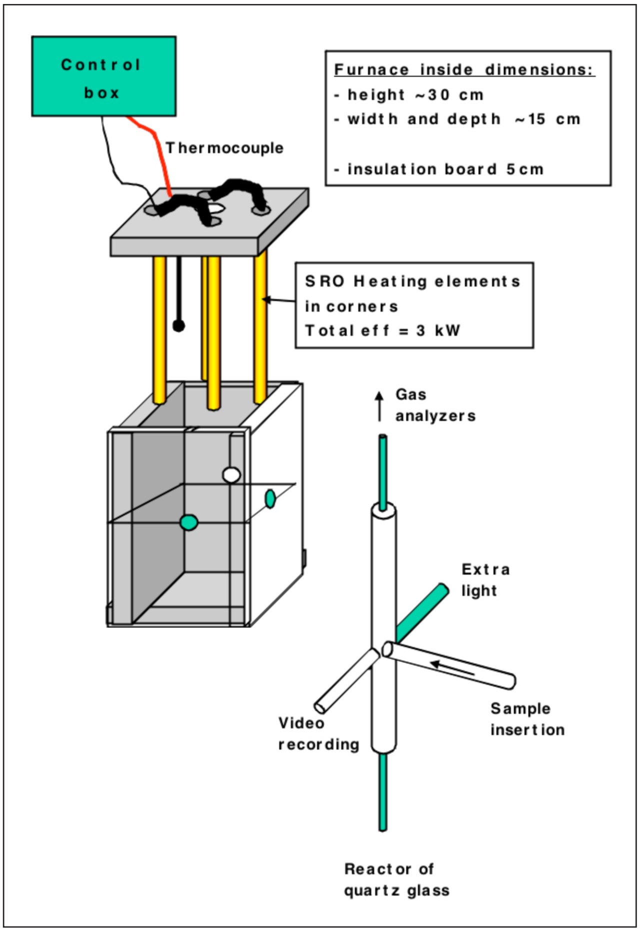
1. Fuel mixtures of black liquor (BL) with bark, wood, peat, or bio-sludge.

to wet solid fuels than liquid fuels (**Fig. 1**). The bark, wood, and peat were air dried for previous projects, and the bio-sludge was pre-dried in the laboratory oven at 115°C to increase the dry solids to more than 20% d.s. 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.

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 (**Fig. 2**). **Table I** gives the droplet size range. It was more difficult to maintain a uniform sample size with the mixtures because of the presence of solid biomass. 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.

Video was taken of the droplet as it reacted. Swelling was estimated using the two-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 had only been analyzed for nitrogen as part of another project. The bio-sludge had not been analyzed at all. An estimate of the nitrogen content of the bio-sludge is also given in **Table II**. This estimate is based on the concentration of nitrogen in another bio-sludge sample taken from the same mill for an earlier project. The bark, wood, and peat were also analyzed for various elements. Table II gives the concentrations relevant to this paper.



2. Reactor used for single droplet combustion tests.

RESULTS AND DISCUSSION

Swelling

The change in swelling relative to the original black liquor was greatest for peat and bio-sludge (**Fig. 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 lower addition of bio-sludge also caused significant swelling relative to the higher addition level. The causes for the changes in swelling are not clear at this time.

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. However, drying times were not included, because at 1100 °C, some droplets ignited as soon as they

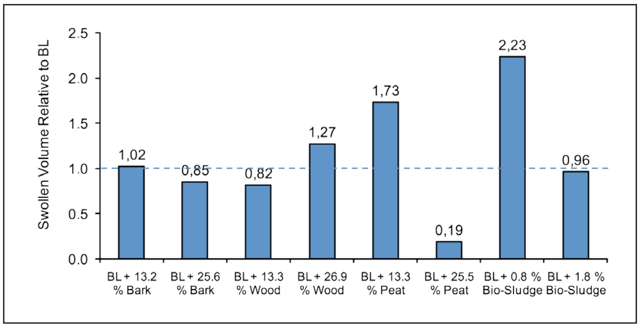
Sample	Dry Solids of Fuel	Size Description	Mass Fraction Biomass in Mixture (wt % d.s.)	Mixture (wt % d.s.)	Droplet Sizes (mg) (+/- 1 standard deviation)
Black Liquor	80.4	liquid		80.4 %	11.3 +/- 1.7 15.4 +/- 0.8 20.4 +/- 0.6
Bark	95.0	< 1 mm	13.2 % / 25.6 %	82.1/83.7	12.0 (+/- 3.1) 22.0 (+/- 5.9)
Wood	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)

I. Dry solids fo fuels and mixtures.

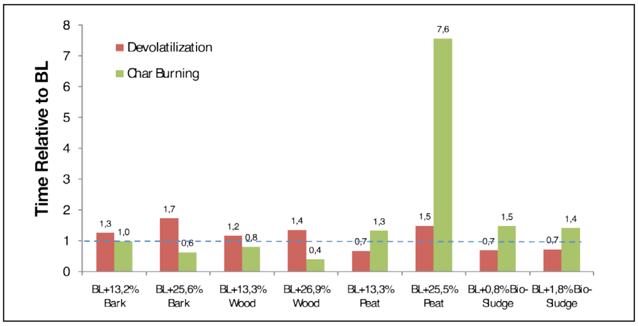
Element	Black Liquor	Bark	Wood	Peat	Bio-sludge
N, wt % d.s.	0.08	0.4	0.2	2.06	6.17*
K, mg/kg d.s.		1090	1100	270	
Na, mg/kg d.s.		978	160	171	
Mg, mg/kg d.s.		599	440	780	
Mn, mg/kg d.s.		465	87	97	

* Based on a different bio-sludge sample from the same mill for an earlier project.

II. N, K, Na, Mg, and Mn concentrations in the fuels on a dry solids basis.



3. Swelling of mixtures relative to the black liquor (BL).



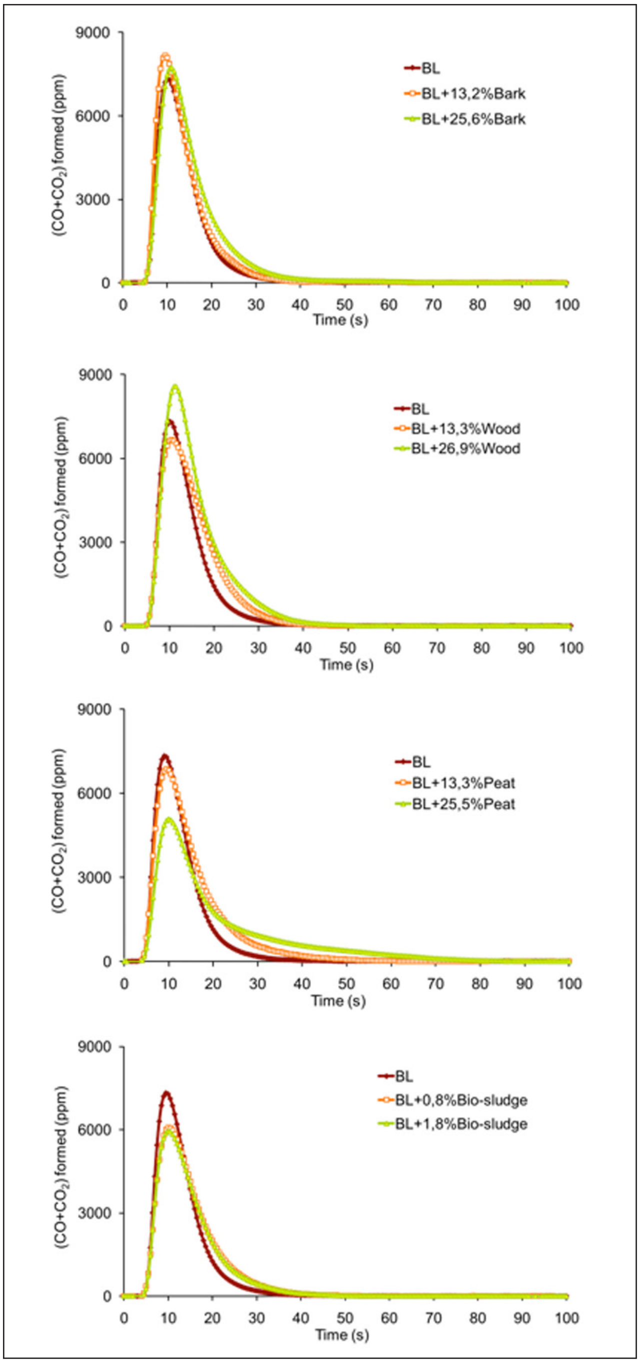
4. Relative devolatilization and char burning times for the black liquor (BL) and mixtures.

Droplet Mass (mg)	Devolatilization (s)	Char Burning (s)
11.3 +/- 1.7	2.51	5.51
15.4 +/- 0.8	2.96	7.77
20.4 +/- 0.6	3.02	7.82

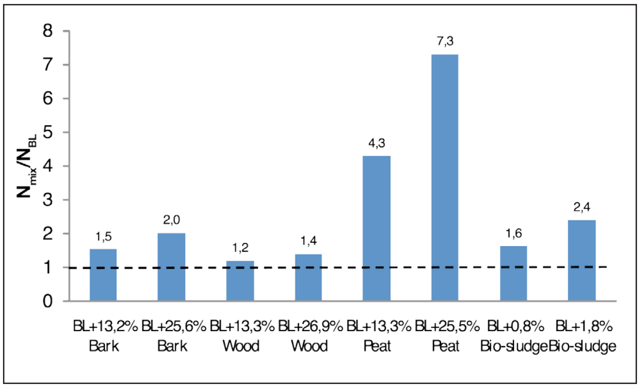
III. Devolatilization and char burning times for three different black liquor masses.

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. **Figure 4** presents the times relative to black liquor.

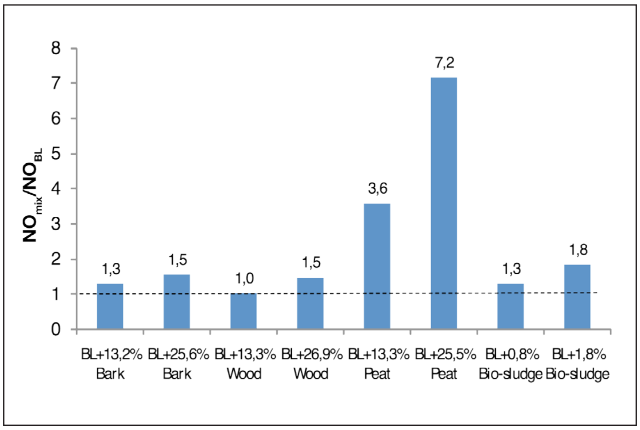
Black liquor droplets of three different masses were burned. The devolatilization and char burning times for the mixtures are compared with those of the black liquor droplet with a similar mass. **Table III** gives the average times for devolatilization and char combustion for the black liquor at



5. Carbon evolution as $CO + CO_2$ (average for 6 droplets) for the black liquor (BL) and the mixtures.



6. Fuel nitrogen concentration relative to black liquor (BL), based on mixture % and the component nitrogen concentrations in Table II.

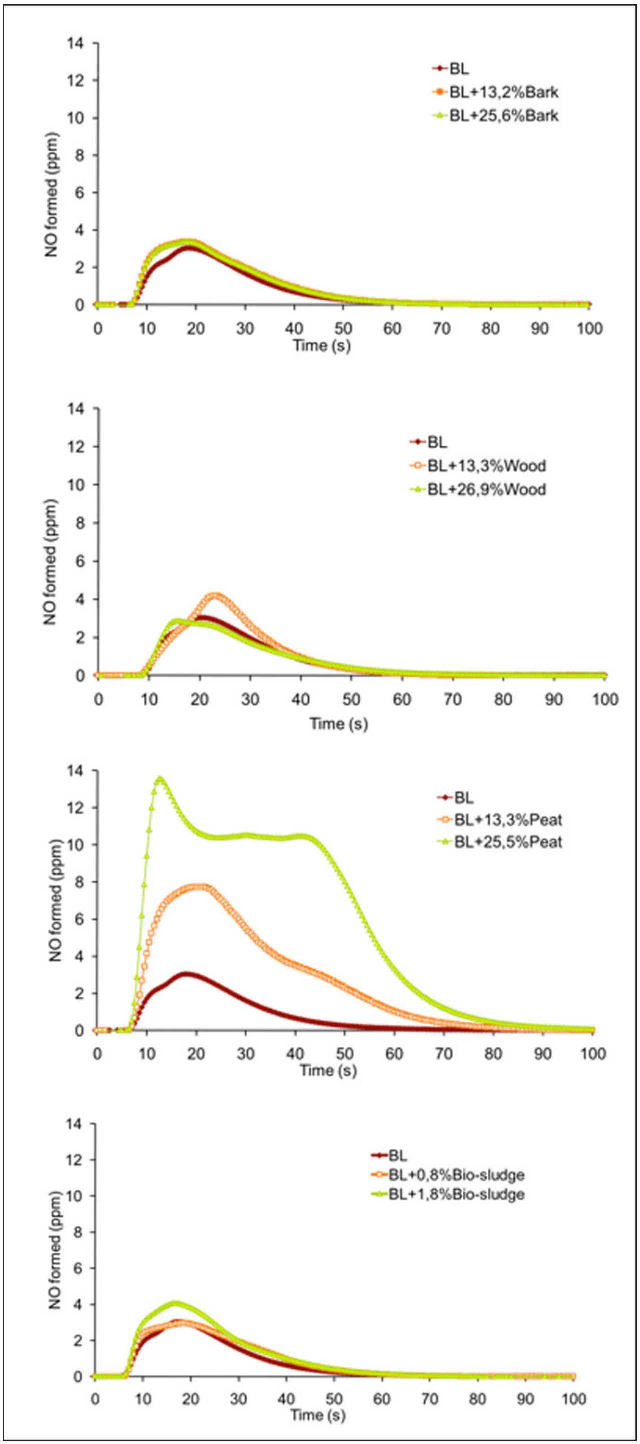


7. Average NO formation in droplet burning tests of the mixtures relative to the NO formation of the black liquor (BL).

three droplet sizes. The dramatic change in the char burning time for the highest level of peat addition is also seen in the curves for carbon release (**Fig. 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.

NO formation

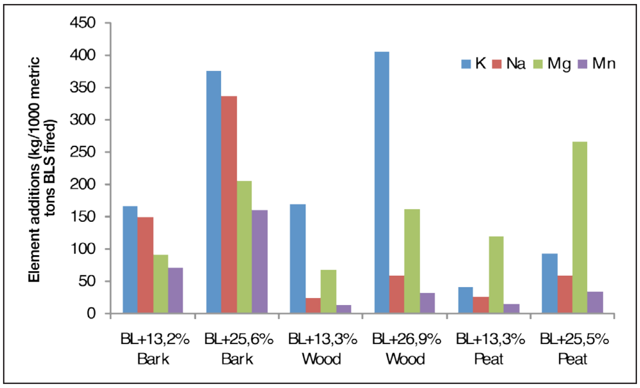
Due to the higher concentrations of nitrogen in the added fuels, the nitrogen content of the fuel mixtures is higher than that of the black liquor (**Fig. 6**). All mixtures result in a higher NO formation, with peat resulting in a significantly higher NO formation due to the higher nitrogen concentration (**Fig. 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 bio-sludge 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 (**Fig. 8**).



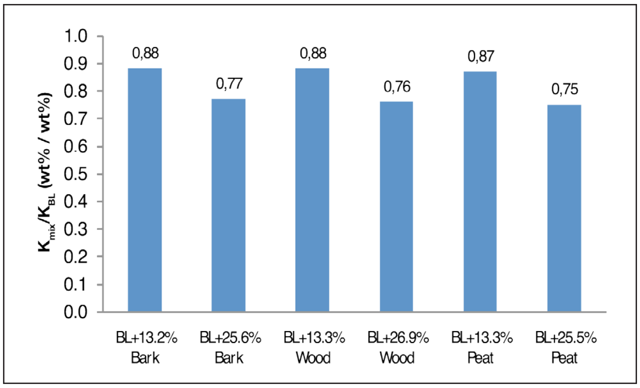
8. Average NO formation curves for the six droplets of the black liquior (BL) and mixtures.

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 (**Fig. 9**). For example, bark addition with a potassium concentration of 1090 mg/kg d.s. will result in 166 and



9. Addition of elements to the recovery cycle per 1000 metric tons of black liquor dry solids (BLS) fired.



10. Concentration of potassium in the mixtures for a black liquor (BL) containing 1 wt % K on a dry solids basis. Table II gives the K concentration for the added fuels.

375 kg K/1000 metric tons black liquor solids fired at addition levels of 13.2 and 25.6 wt % d.s., 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 for a black liquor with a potassium concentration of 1 wt % on a dry solids basis.

CONCLUSIONS

The results of this preliminary study indicate that, from a combustion chemistry standpoint, there is potential to add biofuels to black liquor for combustion in a recovery boiler. The mixtures containing bark, wood, or bio-sludge 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, as well as 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 much drier than the material that would be received by a mill. Additional work should be carried out to determine the impact of this moisture on the burning characteristics. Also, 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. **TJ**

EDITOR'S NOTE

This paper was presented at the 2010 International Chemical Recovery Conference (ICRC) in Williamsburg, VA, where it received a Best Paper Award.

AFTERWARD

Two changes in the data have been made relative to the 2010 ICRC paper. The devolatilization and char burning times for 15 and 20 mg droplets of the black liquor have subsequently been determined. This allowed for more direct comparison with the devolatilization and char burning times for the mixed fuels as those droplets were often larger than 10 mg. This has resulted in changes in Fig 4. Additionally, the Na and K concentrations in wood were inverted in the original paper. The corresponding correction has been made in Table II and Figs. 9 and 10.

ACKNOWLEDGMENTS

The authors wish to thank the Finnish Recovery Boiler Committee and TEKES for their support of this work. The time of Nikolai DeMartini and Patrik Yrjas was financed by Chemcom, a mainly Tekes funded project coordinated by the Process Chemistry Centre at Åbo Akademi University in Turku, Finland. Other funders within Chemcom are: Andritz Oy, Foster Wheeler Energia Oy, International Paper Inc., Metso Power Oy, Oy Metsä-Botnia Ab, Clyde Bergemann GmbH, and UPM-Kymmene Oy. The Junta de Comunidades de Castilla La Mancha is gratefully acknowledged for its financial support of Esperanza Monedero (personal grant: 08/010-A and GACOM-BIO, PCI01-0063).

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Mixing black liquor with biomass offers the opportunity to increase the production of electricity from biomass. We chose this topic because there is a lack of data on the combustion characteristics of black liquor – biomass mixtures. This research uses established techniques to evaluate fuel mixtures, but the evaluation of the mixtures is new.

Fuel homogeneity was the biggest concern in our research. We ran six replicates for each fuel mixture to try and average out droplet-to-droplet variations, which in most cases were small.

Our work yielded some surprising findings. For one, despite the relatively large additions of biomass, the mixtures (with the exception of the highest peat addition) still burned much like the original black liquor. The other was the dramatic change in swelling obtained with the two addition levels of peat and bio-sludge.

There are several scenarios being considered in which mills would supplement the energy input into recovery boilers using biomass. One option is mixing the biomass directly into the black liquor. Our work provides mills with a preliminary evaluation of combustion characteristics and indicates that if the idea is found economically attractive, the technical issues (such as feeding/spraying) are worth further evaluation.

We are following up on this work by studying the impact of other variables and conditions. After that, the next technical step would be to address the mixing and spraying characteristics of various biomasses with high solids black liquor.

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