Effects of added materials on black liquor combustion

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ABSTRACT: Black liquor is often mixed with various types of materials before being burned in a recovery boiler to meet specific needs of kraft pulp mills. A systematic study was conducted using a thermogravimetric combustor to examine how added materials might affect the combustion behavior of black liquors obtained from several pulp mills. The results show that adding soap, caustic, white liquor, and sawdust significantly reduces the liquor swelling tendency, thereby requiring a longer time for the liquor to burn completely. Adding makeup saltcake, precipitator ash, sodium sulfate, and biosludge, on the other hand, has little or no effect on the liquor combustion behavior.

Application: Mills that understand how each added material affects the combustion behavior of black liquor can optimize their recovery boiler operation.

The kraft pulping process uses white liquor, an aqueous solution of sodium hydroxide (NaOH), and sodium sulfide (Na_2S), to digest wood to make wood pulp. It is the most dominant pulping process because of its ability to produce strong pulp and to efficiently recover valuable spent cooking chemicals. The recovery of chemicals is attained by concentrating the spent liquor (weak black liquor) in a series of evaporators and concentrators, burning the concentrated black liquor in a recovery boiler to generate steam and power, and converting the combustion residue (smelt) in the causticizing plant into white liquor for reuse in the pulping process [1].

Before being burned in the recovery boiler, black liquor often is mixed with various materials to meet specific mill needs. Sodium sulfate (Na_2SO_4), sodium bisulfate ($NaHSO_4$), sodium sesquisulfate ($Na_3H(SO_4)_2$), and in some cases, elemental sulfur (S), are added to the black liquor in the mix tank to make up for sodium and sulfur losses, control the mill liquor sulfidity, or both. Precipitator ash from the recovery boiler, which contains mainly Na_2SO_4 and sodium carbonate (Na_2CO_3), is mixed with black liquor in the mix tank to reclaim the sodium and sulfur. Caustic, in the form of NaOH or white liquor, is used to adjust the black liquor viscosity, making the liquor easy to pump and spray into the boiler. Because of its high heating value, tall oil soap (a byproduct from the black liquor evaporation plant) is burned with black liquor to increase the boiler steam production capacity and to recover the sodium and sulfur [2]. Although it is not common, biosludge also has been mixed with weak black liquor and eventually burned in recovery boilers as a means for sludge disposal [3]. In mills where recovery boilers are not thermally limited, burning sawdust and other types of biomass with black liquor to produce additional steam has been suggested. Depending on the amount added, these materials inevitably alter the liquor composition and properties, and hence combustion characteristics.

Understanding black liquor combustion properties and factors affecting them is of great importance in recovery boiler operation. Although black liquor combustion has been extensively studied over the past three decades [4-15], only a few studies have dealt with the effects of specific added materials [6,7,13,14]. In all studies, experiments were carried out by either suspending a small black liquor droplet (5–12 mg) on a platinum wire, or placing a larger amount of liquor sample (300–500 mg) in a metal tray and observing how the sample burned in a preheated muffle furnace. While the single droplet technique simulates well the combustion of black liquor droplets in the recovery boiler, it does not provide good quantitative results. This is because small droplets burn so quickly (within a few seconds) that it is difficult to capture accurately the change in sample volume and appearance during combustion. The tray technique does not simulate the combustion condition in the boiler well, but it allows the combustion to occur more slowly and makes it easier to follow.

This research work consists of two parts. Part 1 involves constructing a thermogravimetric (TG) combustor that can be used to examine more accurately the combustion behavior of various spent pulping liquors (e.g., kraft, soda, dissolving pulp, or sulfite liquor) and solid biofuels (e.g., lignin, wood, bark, or biosludge). Part 2 involves the use of the TG combustor to systematically investigate the effects of added materials (e.g., tall oil soap, caustic, white liquor, saltcake, precipitator ash, or biosludge) on black liquor combustion. Part 1 work has been discussed in detail in previous publications [15,16]. This paper discusses the key results obtained from Part 2 and their practical implications where applicable.

Liquor	Mill Type	Solids Content, wt% dry	Ash Content, wt% dry	REA Content, wt% as Na_2O dry	Heating Value, MJ/kg dry
A	Kraft	68.3	37.8	2.8	13.2
B	Kraft	77.2	43.7	1.8	13.0
C	Kraft	77.9	44.6	3.8	13.2
D	Kraft	70.8	43.1	5.0	13.6
E	Kraft	74.5	42.5	2.3	13.4
F	Dissolving pulp	70.9	46.6	1.4	12.4

I. Solids, ash, and residual effective alkali (REA) content and heating value of black liquor samples

THE EXPERIMENTS

Black liquors

Black liquor samples were obtained from five kraft pulp mills (liquors A–E) and a dissolving pulp mill (liquor F). **Table I** summarizes the solids content, ash content, residual effective alkali (REA) content, and heating value of these samples.

Added materials

The added materials used in this study were tall oil soap, NaOH, Na_2SO_4, white liquor, precipitator ash, biosludge, and sawdust. The soap was obtained from a black liquor storage tank of the same kraft mill as liquor A. The soap had pH 13.1, solids content of 53.3 wt%, ash content of 28.7 wt%, and a higher heating value of 18.0 MJ/kg on dry basis. The NaOH and Na_2SO_4 were analytical grade chemicals. The white liquor was obtained from a kraft mill with a total titratable active alkali (TTA) of 130 g/L sodium oxide (Na_2O). The biosludge was obtained from an ammonium (NH_4)-based sulfite pulp mill with a solids content of 1.4 wt%. On a dry basis, it contained 5.1 wt% ash and had a heating value of 21 MJ/kg. The sawdust was a commercial pulverized pine with a particle size of < 0.8 mm.

Experimental procedures

The experiments were performed using the TG combustor developed in Part 1 of this research. As shown in **Fig. 1**, the combustor consisted of an electric furnace with a quartz glass observation window, a high-precision balance, a camcorder, a gas control system, and a data acquisition system. For each test condition, a black liquor sample was uniformly mixed with a known amount of additive (e.g., soap or caustic). The dry solids content of the mixture was adjusted to 70 ± 1 wt% before testing by either drying the mixture in an oven or diluting it with an appropriate amount of water. Because water can greatly affect the combustion behavior, it was important to keep all test samples at the same initial dry solids content so that the results can be readily compared.

For each test, a sample weight of 0.3 ± 0.01 g was used. The sample was placed on a stainless steel type 316 tray (3 cm outside diameter) hung on a nichrome hook underneath the balance. After the sample tray was appropriately tared and stabilized, the camcorder was turned on. The furnace, preheated and controlled at 830°C, was quickly pushed up so that the sample tray was submerged in the middle. As the sample burned on the tray, its appearance during the combustion was continuously recorded by the camcorder through the glass window, while its weight was continuously recorded by the balance. During the test, air was passed through the furnace from the bottom at a constant flow rate of 1 L/min to ensure complete combustion and to help purge the combustion gas out of the furnace.

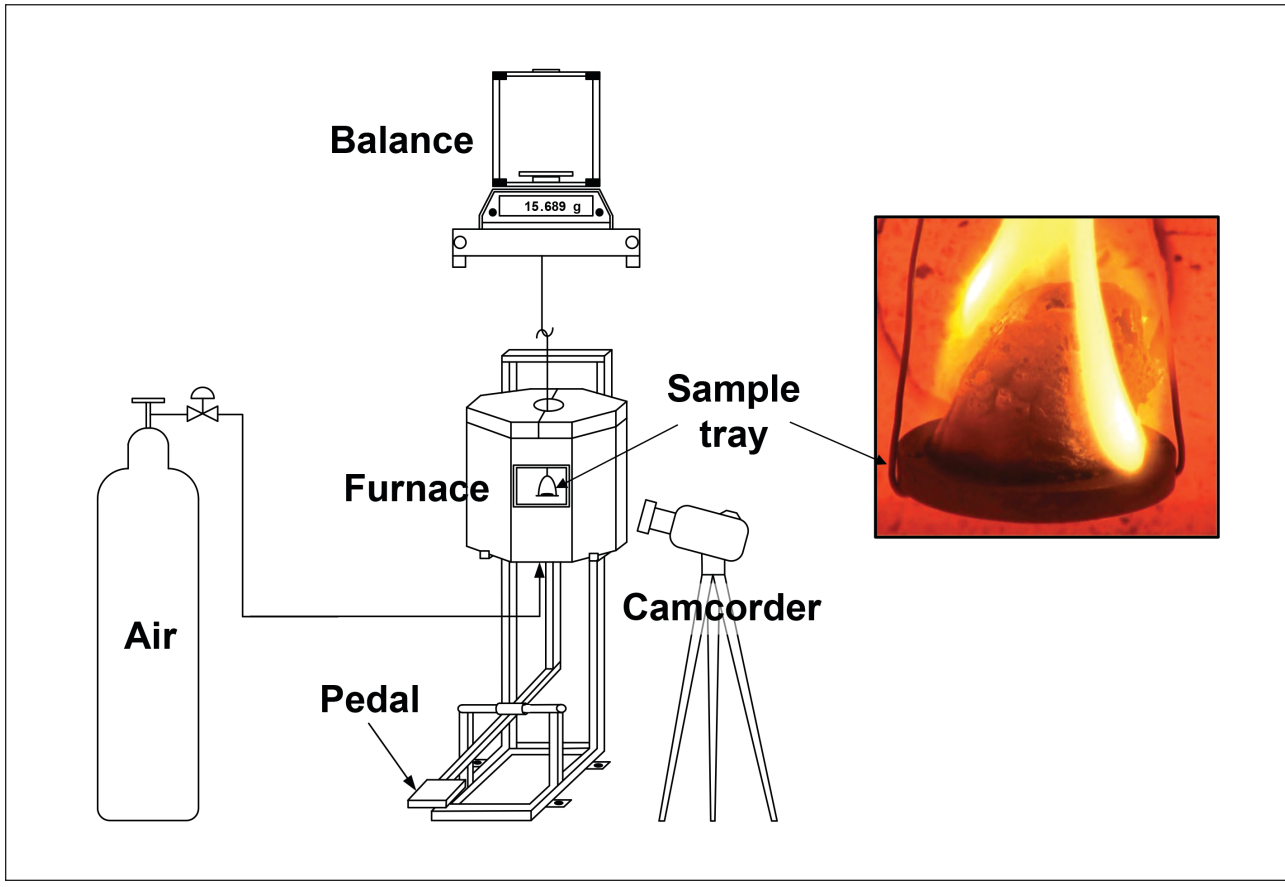
Detailed description and operating procedures of the TG combustor can be found in previous publications [15,16]. Because of the combustor's ability to directly measure sample weight, it can be used to obtain many important properties, including maximum swollen volume, drying time, volatile burning time, char burning time, total combustion time, volatile content, char content, and ash content.

In this study, we chose to use only two intrinsic values that could be used to characterize the combustion behavior of a black liquor sample: (1) the maximum swelling (or maximum swollen volume) of the liquor during combustion and (2) the total time required for the sample to completely combust. These values were obtained by analyzing the two-dimensional video images obtained by the camcorder as well as the weight loss profile of the sample registered by the balance. The maximum swelling was defined as the largest swollen volume the sample could reach during the test. The total combustion time was defined as the duration from when the sample was submerged into the furnace to when it completely burned and its weight became constant. For each test condition, three to five identical experiments were performed to obtain the average and standard deviation values for the maximum swelling and the total combustion time.

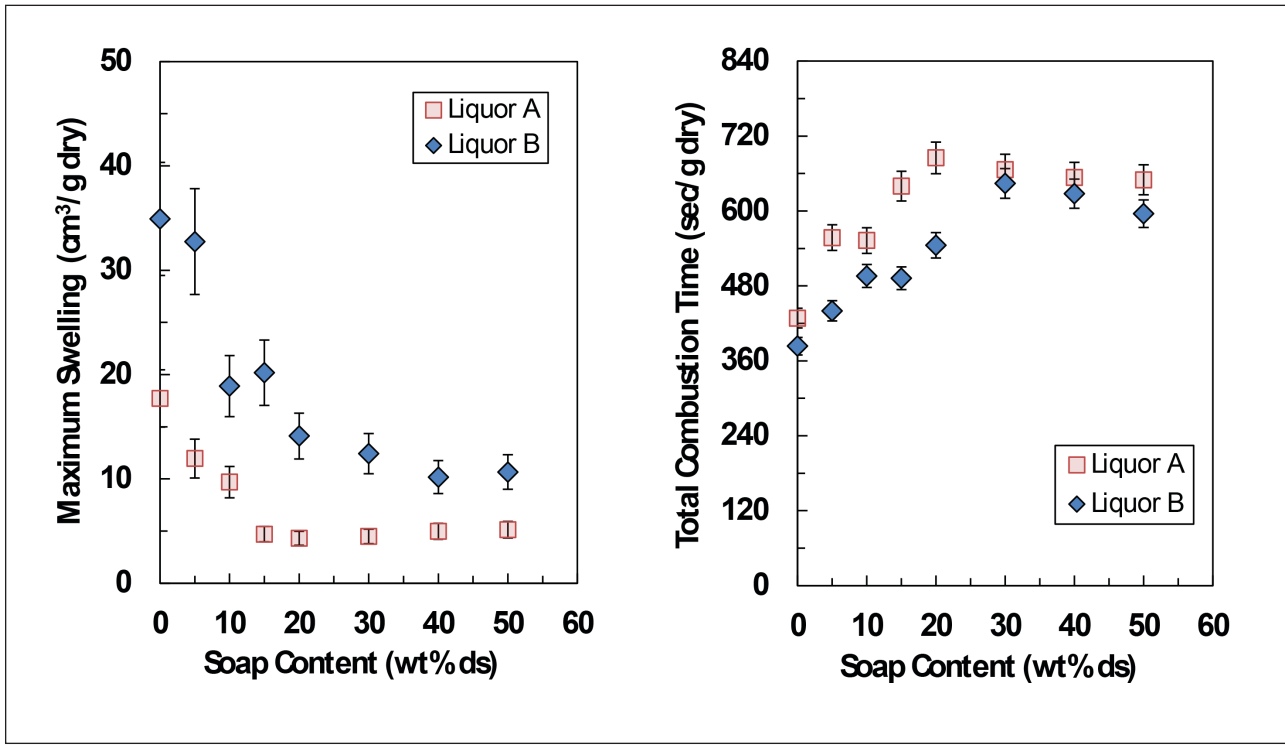
RESULTS AND DISCUSSION

Effect of tall oil soap

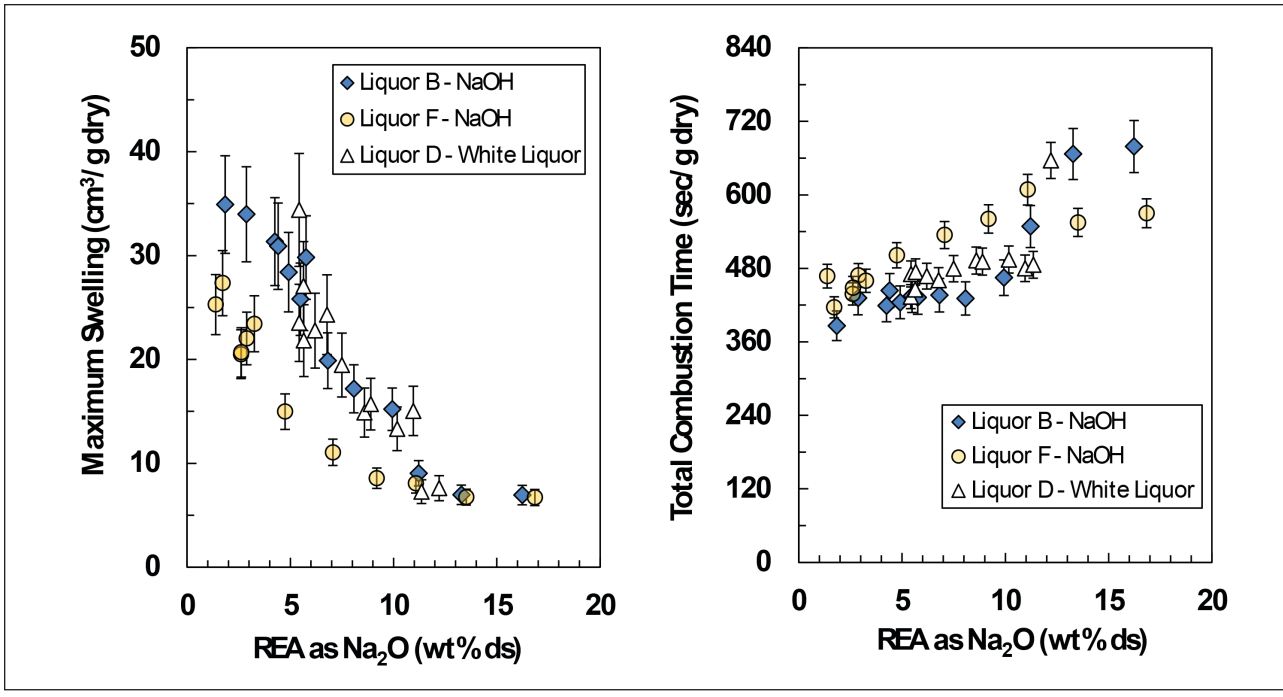
The effect of tall oil soap addition was examined on two kraft black liquors: a low swelling liquor (liquor A) and a high swelling liquor (liquor B). The results are shown in **Fig. 2**. The amount of soap added to the liquors is expressed as wt% dry solids (ds), while the maximum swelling is expressed as cm^3/g



1. Thermogravimetric (TG) combustor.



2. Effect of soap content on maximum swollen volume (left) and total combustion time (right) for black liquors A and B. Furnace temperature = 830°C; liquor dry solids (ds) content before burning = 70 wt%.



3. Effect of REA content on maximum swollen volume (left) and total combustion time (right) for black liquors B, F, and D. Furnace temperature = 830°C; liquor dry solids content before burning = 70 wt%.

and the total time required for complete combustion is expressed as s/g on a dry basis.

For liquor A, without soap addition (i.e., 0 wt% ds soap content), the maximum swelling was about 18 cm^3/g. With soap addition, the maximum swelling decreased sharply to the lowest value of 5 cm^3/g with an increase in soap content. No additional adverse effect of soap was found beyond 20 wt% ds. Similar results were found for liquor B. In this case, the maximum swelling decreased sharply from 35 cm^3/g at 0 wt% ds soap content to about 12 cm^3/g with soap content >20 wt% ds. The results agreed well with the findings of Hupa et al. [6] and Milanova [7]. However, they were not in agreement with those reported by Niemi et al. [13], who compared the combustion behaviors of only two black liquors, one without soap addition and the other with only 2 wt% ds soap addition.

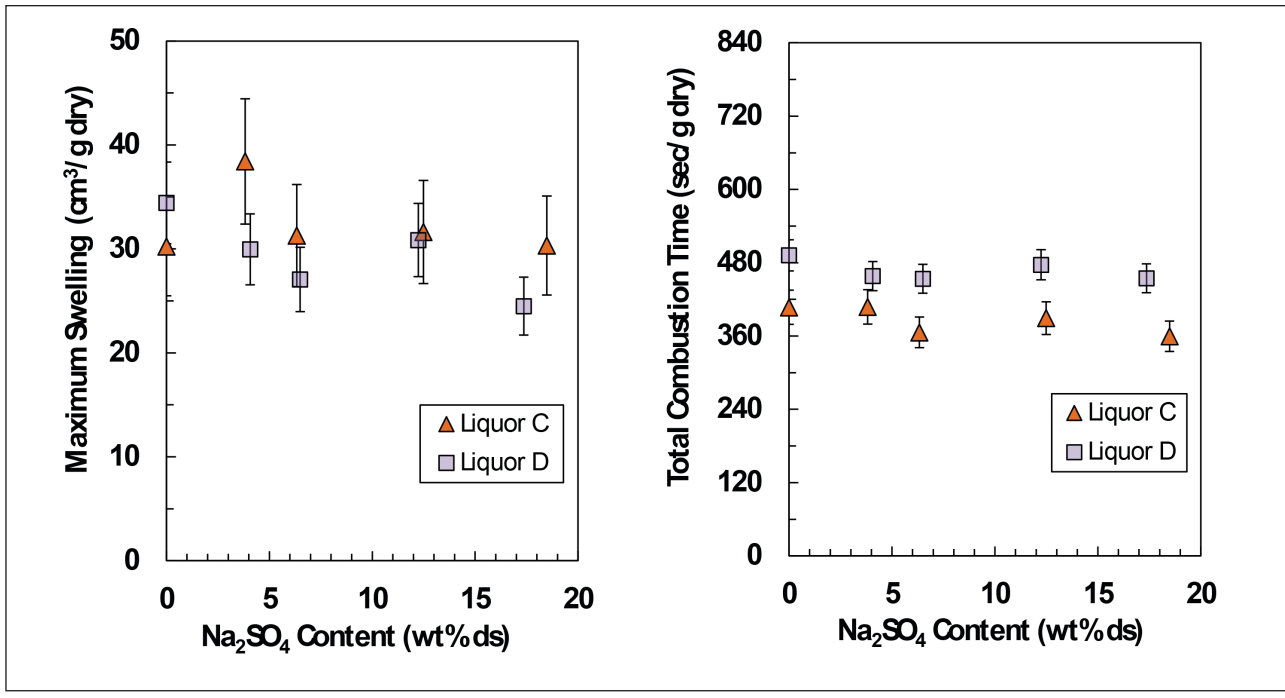
Figure 2 also shows the effect of soap on the total combustion time. For both liquors, as the soap content increased, the total combustion time increased and then levelled off as the soap content reached about 20 wt% ds. The results were consistent with those shown for liquor A, suggesting that up to about 20 wt% ds, adding soap to black liquor makes the liquor swell less during the volatile burning and the resulting char becomes denser and more difficult to burn.

In practice, however, the soap content in black liquor is relatively small and the adverse effect of tall oil soap on liquor swelling and combustion time might not be as pronounced as that found in the laboratory, as concluded by Niemi et al. [13]. Hardwood black liquor is known to contain little soap. Softwood black liquor, on the other hand, has a soap content of about 1.2 wt% ds, varying from 0.5–7 wt% ds depending mainly on wood species, digester pulping conditions, and soap skimming efficiency [7,17]. Milanova [7], for example, reported unskimmed softwood black liquors from two kraft mills in Canada containing 4.4 wt% ds and 6.2 wt% ds soap, whereas well-skimmed liquors from the same mills contained only 0.53 wt% ds and 0.63 wt% ds soap, respectively.

Effect of residual effective alkali

For this series of experiments, black liquors B, D, and F were used. The test procedure was the same as that used in the soap addition experiment, except that instead of soap, various amounts of NaOH and white liquor were used as a source of caustic. They were added to the liquor to produce mixtures with various REA content. Because black liquor always contains some REA, the REA content of each liquor before and after caustic addition was analyzed using the calibrated titration method proposed by Radiotis et al. [18].

Figure 3 plots the maximum swollen volume and the total combustion time as a function of REA content (expressed as wt% ds as Na_2O) in the liquors. All the black liquors used in this study already contained some REA before caustic addition (Table I), so there are no data points at 0 wt% REA content in Fig. 3. The results clearly show that as for soap addition, increasing the REA content in the liquor decreased the maximum swelling and increased the total combustion time. The adverse effect of caustic addition, however, appears to level off at an REA content higher than 12 wt% ds as Na_2O.



4. Effect of sodium sulfate (Na_2SO_4) content on maximum swollen volume (left) and total combustion time (right) of black liquors C and D. Furnace temperature = 830°C; liquor dry solids content before burning = 70 wt%.

Effects of sodium sulfate and precipitator ash

Sodium sulfate is one of the main makeup chemicals for sodium and sulfur losses in the kraft recovery operation. It is also the largest component (typically over 85 wt%) of the recovery boiler precipitator ash. Makeup Na_2SO_4 and precipitator ash are mixed with strong black liquor in the mix tank. The resulting liquor, known as as-fired black liquor, typically contains 5–6 wt% Na_2SO_4 on a dry basis. Depending on the boiler operation, reduction efficiency, and liquor sulfidity, however, the Na_2SO_4 content in the as-fired black liquor may range from 4–15 wt% ds.

In this series of experiments, black liquors C and D were used. The liquors were mixed with various amounts of Na_2SO_4 and their solids contents were adjusted to 70 wt% ds before testing. **Figure 4** shows the effect of Na_2SO_4 addition (expressed as wt% ds) on the maximum swelling and the total combustion time. No significant change with Na_2SO_4 addition was found for either liquor.

Six additional tests were performed to examine the effect of precipitator ash on the combustion behavior of black liquor C. One was black liquor C alone without precipitator ash addition, and the other five were black liquor C mixed respectively with 5 wt% ds of precipitator ash from three different kraft mills, pure Na_2SO_4, and pure Na_2CO_3. These pure chemicals were used for comparison purposes because they are the two main components of the precipitator ash. In all cases, no significant difference in maximum swelling and total combustion time was found between black liquor C with and without 5 wt% ds of added materials. These results suggest that under normal recovery operations, makeup Na_2SO_4 and precipitator ash have little effect on the black liquor burning behavior.

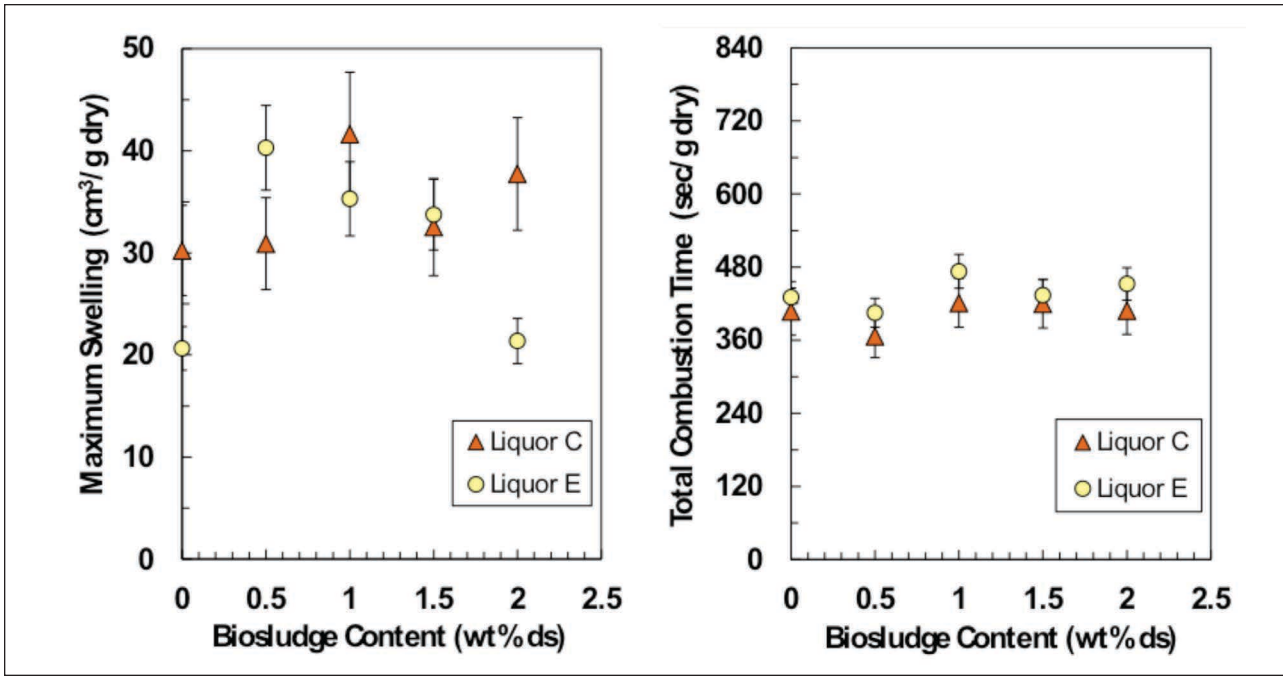
Effect of biosludge

In this series of experiments, a biosludge sample from an NH_4-based sulfite mill was used because kraft mill biosludge was not available in our laboratory at the time of the study. The biosludge had a composition and thermal properties similar to those of kraft mill biosludge and had an initial solids content of 4.7 wt%.

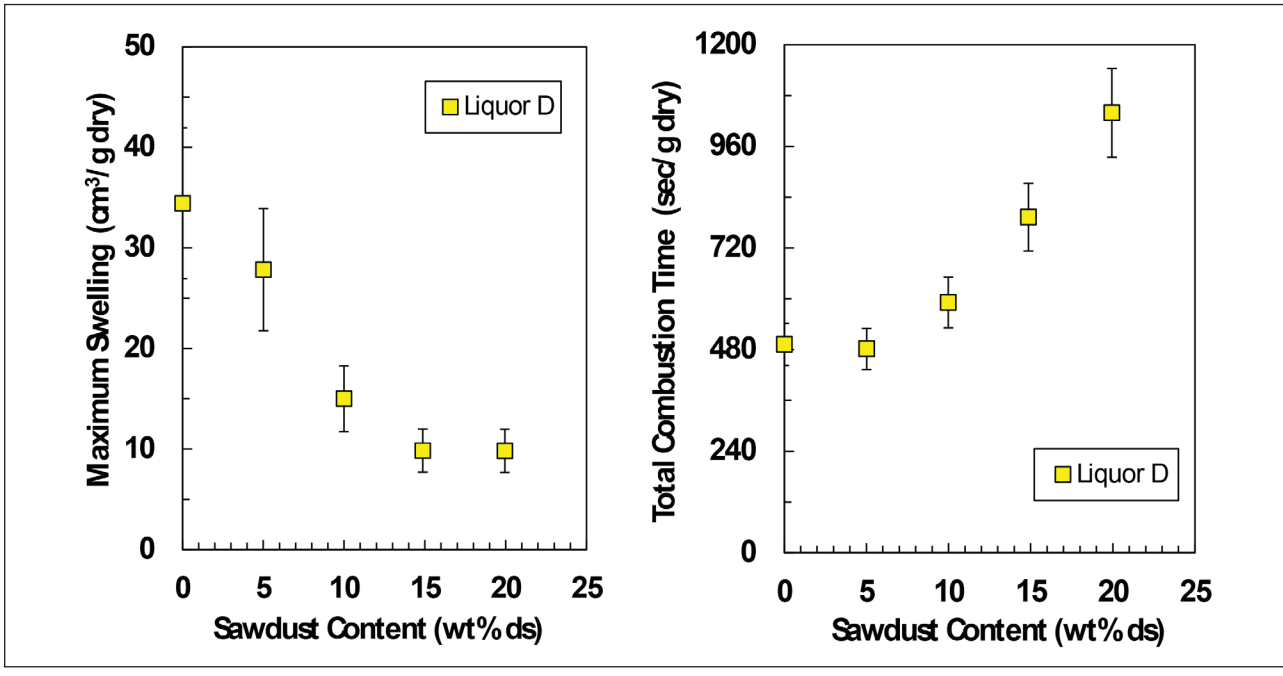
The dilute sludge was first mixed with black liquors C and E. The resulting mixtures were concentrated by drying slowly in an oven controlled at 105°C to 70 wt% ds before testing. **Figure 5** shows the maximum swelling and total combustion time of liquors C and E as a function of biosludge content. The data were scattering, due probably to the much smaller amount of sludge used (0–2 wt% ds) compared with other experiments. Nonetheless, the maximum swelling was somewhat greater, particularly for liquor E, while the total combustion time was slightly shorter at a biosludge content of about 0.5 wt% ds for both liquors.

DeMartini et al. [14] also reported an inclusive effect of biosludge addition on black liquor combustion. They showed that adding 0.8 wt% biosludge to a black liquor made the liquor swell 2.3 times more, while adding 1.8 wt% biosludge made the liquor swell slightly less compared to that without biosludge addition. The devolatilization and char burning times of these black liquors with biosludge addition, however, were about the same as those without biosludge addition.

The results of this research and work by DeMartini et al. [14] suggest that up to 2 wt% ds, biosludge addition has an insignificant effect on black liquor combustion.



5. Effect of biosludge content on maximum swollen volume (left) and total combustion time (right) of black liquors C and E. Furnace temperature = 830°C; liquor dry solids content before burning = 70 wt%.



6. Effect of sawdust content on maximum swollen volume (left) and total combustion time (right) of black liquor D. Furnace temperature = 830°C; liquor dry solids content before burning = 70 wt%.

Effect of sawdust

In this series of experiments, black liquor D was used. The sawdust was pulverized dry pine that had been sieved to a uniform particle size of <0.8 mm. Because of the dryness of the sawdust, the solids content of the resulting sawdust/black liquor mixtures was adjusted to 70 wt% by adding an appropriate amount of water before testing. As shown in **Fig. 6**, adding sawdust to black liquor significantly decreased the maximum swelling and increased the total combustion time.

The adverse effect of sawdust addition is understandable. Sawdust is essentially wood that does not swell during combustion [19]. Furthermore, sawdust contains much less ash (<2 wt% ds) compared with black liquor, which has a high ash content (inorganic residue) of about 50 wt% ds. Therefore,

adding sawdust to black liquor would proportionally decrease the amount of the swelling organic matter in the sawdust/black liquor mixture and, at the same time, increase the amount of nonswelling organic matter in the mixture. This, in turn, makes the mixture swell less and produces more and denser char that requires a longer time to burn completely.

SUMMARY

A systematic study was performed to investigate the effects of added materials on black liquor combustibility using a TG combustor. Added materials included tall oil soap, caustic or white liquor, saltcake, biosludge, and sawdust. The results show that adding tall oil soap, caustic or white liquor, and sawdust to black liquor significantly decreases the swelling of the mixed liquor and increases the total time needed for the liquor to completely burn. The adverse effect of soap addition, however, levelled off at about 20 wt% ds of soap while the adverse effect of caustic addition maxed out at an REA content of about 12 wt% ds as Na_2O. Under normal recovery operations, adding makeup saltcake (Na_2SO_4) and precipitator ash to black liquor does not affect the black liquor burning behavior. Finally, adding biosludge up to 2 wt% ds has an insignificant effect on the black liquor combustion. **TJ**

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ABOUT THE AUTHORS

Black liquor is often mixed with various materials before being burned in the recovery boiler. We chose this topic to research to help mills understand how each added material might affect the black liquor combustion characteristics so that they can improve their boiler operation.

This research compliments previous work by us, as well as other groups. Our focus, however, is on the effects of various types of added materials.

The most difficult part of this research was the high variability of the test results. We addressed the problem by carrying out a large number of tests for each added material and test condition to make sure that the results are statistically meaningful. The most interesting finding was that some added materials make black liquor more difficult to burn, while others have no effect.

Mills can use this information to determine the appropriate amount of materials to be added without altering the black liquor burning behavior. The next step is to study why some added materials reduce the liquor swelling tendency while others do not.


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