Reconciling material balances with laboratory test results: The case of the inorganic-to-organic ratio in black liquor

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ABSTRACT: When evaluating the composition of black liquor using material balance techniques that estimate the organics from the wood and the inorganics from the cooking liquor, the solids content of the black liquor is determined to be roughly 1/3 inorganic matter and 2/3 organic matter. When actual laboratory testing using simplified ashing methodologies are performed, the results typically suggest that black liquor solids contain roughly 43%-49% organics and 51%-57% inorganics. We determined that the applied hydroxide and sulfide mineralize carbon and oxygen from the organic portion of the black liquor and convert it to carbonate and sulfate during the cooking and ashing process, thus increasing the apparent inorganic content of the black liquor. This becomes problematic when attempting to estimate total black liquor production using the organics removed during cooking and the inorganic content using results from the ashed black liquor sample. We used Microsoft Excel material balances to develop a conversion factor to correct the laboratory test results. Multiplying the percent ash in the laboratory test by 0.65 to 0.70 provided a more realistic estimate of the initial inorganics to be used along with organics removed in the digester to estimate black liquor production. This conversion factor was determined to be independent of pulp yield and white liquor charge in the digester. The initial white liquor composition, as reported by the ABC test, does have a slight effect on this value.

Application: The results from this work may be used to reconcile laboratory testing results with actual material and energy balances. Using the new factor developed in this work will allow simplified laboratory methods to be used to obtain real world results.

In general, one of the largest and most expensive pieces of equipment within a pulp mill complex is the recovery boiler. As such, many mills attempt to maximize the throughput and performance of the recovery boiler to fully use the largest process asset. The purpose of the recovery boiler is twofold. It generates high pressure steam to turn turbines and supply heat to the processes, and it converts inorganic material into smelt as part of the chemical recovery cycle.

It is often important to know the inorganic-to-organic ratio of the black liquor feeding the recovery boiler. Several different methods of measuring that ratio in black liquor have been developed over the years. Some of these methods involve potentiometric, gravimetric, and conductimetric methods that require several days to complete a single analysis [1]. Other methods estimate the inorganic content of the black liquor by correlating it with the sulfated ash content of the liquor [2]. Still others require specialized equipment, such as an ion chromatograph, for performing the analysis [3]. Sodium and sulfide determination using ion selective electrodes has been determined to be a more precise method [4] than the atomic absorption/ion chromatography methodology [3]. McDonald reports an analysis method that uses a titrimetric method employing combustion and titration [5].

Considering that these methods are 17-35 years old, discussions were held with three commercial analytical laboratories and five different universities to determine if improvements in instrumental methods have altered the validity of these findings. X-ray fluorescence and X-ray diffraction techniques can be used to determine inorganic content. Ion chromatography and inductively coupled plasma analysis is sometimes used to quantify specific ions and elements. A flame photometer may be used to measure sodium and a Leco sulfur analyzer (St. Joseph, MI, USA) can be used for sulfur content determination. Headspace gas chromatography and gas chromatography-mass spectroscopy may be used to determine methanol concentration or other volatile organic carbon sources. In general, the current TAPPI Standard Test Method T-625 cm 85 "Analysis of soda and sulfate black liquor," developed from the previous references [1-5], appears to be the only standardized methodology used for inorganic content determination at this time.

Unfortunately, all of these methods are relatively time-consuming or require specialized equipment that is typically not available in an operating pulp and paper mill. Several of

these methods also require a well-trained technical staff to perform the analysis, something few mills still have. To simplify the analysis, Green and Grace [5] developed detailed spreadsheets in Microsoft Excel to estimate the composition and heating value of black liquor using process data [6]. Specific mill data, including the pulp production rate, unbleached pulp yield, bleaching yield, kappa number, applied active alkali as a percent sodium oxide on ovendry wood, and the sulfidity are required to use these spreadsheets. Improved estimates of the black liquor heating value and composition can be obtained from these spreadsheets if more process data are obtained for a specific set of operating conditions. Those data include volatiles lost in the digester and evaporator relief gases, lignin content of the wood, resin and fatty acids in the wood, tall oil recovery, active alkali concentration in white liquor, white liquor density, white liquor solids, brownstock washing efficiency, black liquor solids in the black liquor to the boiler, and the black liquor density [6]. If these extra data are not available, rough estimates can be found in the published literature [6]. However, use of rough estimates might increase the error in these predicted values.

Many mills still have difficulty routinely collecting and estimating the inorganic-to-organic ratio of their black liquor using the spreadsheet technique. Several mills have developed simple, repeatable ashing tests that can be easily performed with a muffle furnace and a balance in about 1½ to 2 hours. Details of this testing procedure will be reviewed later.

The organic material in the black liquor is the main source of energy supplied to the boiler. The inorganic material is converted to smelt, which is dissolved into water or weak wash to form green liquor. The inorganic sulfur (sulfide and thiosulfate) that is supplied to the boiler from the black liquor also adds some amount of heat to the reaction. Thus, when the heating value of black liquor is estimated from the cooking liquor composition and the dissolved wood organics, the calculated heating value of the liquor is usually lower than experimentally obtained results. The use of polysulfide liquors results in even greater heating value discrepancies because of the increased sodium hydroxide in the resulting polysulfide black liquors [7].

While performing WinGEMS material and energy balance calculations for the back end of a high yield kraft pine mill (pulp mill, evaporation, recovery, and recausticization islands), it became apparent that the black liquor being generated by the mill should contain roughly 1/3 inorganic material and 2/3 organic material by mass. The WinGEMS model tracked sodium, carbonate, hydroxide, hydrosulfide, and sulfate throughout the liquor streams. The reaction block used to simulate the digesters passes all the inorganic ions in the incoming white liquor through to the exiting pulp and liquor stream, except for the hydroxide ion. An input parameter in the block specifies the percentage of the incoming hydroxide that is converted to water. The model used a value of 80%. Another input parameter sets the percentage of the incoming wood that is converted to dissolved wood solids (dissolved organics).

Routinely performed laboratory tests supplied long-term process data suggesting that the ratio of inorganic-to-organic material values was far closer to 1-to-1 by mass than the predicted 1-to-2 ratio. Predictions of the black liquor production based on the organics removed in the digester from the pulp yield and the inorganic content based on results from ashed samples were consistently above the black liquor production estimated from the WinGEMS models. The current work attempts to reconcile the differences between the laboratory generated test results using modified mill procedures and the material balance predictions.

MILL-SCALE BALANCES ON BLACK LIQUOR CONTENT

We initially tried to better understand the apparent difference between the WinGEMS material balance values and laboratory testing. The WinGEMS balance was based on mill process data and laboratory cooks to determine black liquor production and pulp production requirements (e.g., pulp yield and metric tons of pulp produced). Mass balances were prepared using Excel material balances adapted from Frederick's Table 3.6 [8]. The manual calculations with the spreadsheet started at the digester. We assumed that 633 metric tons of ovendry pine pulp was required from the batch digesters. An effective alkali charge of 11.5% on ovendry wood was also added to the process. Recycled weak black liquor was added as padding liquor, but, because the padding liquor is simply an internal recycle stream, it may be ignored in the current calculation. We assumed a pulp yield of 54% on ovendry wood. This number was obtained from long-term estimates of mill performance and verified with laboratory cooks performed using mill chips and liquor in a 1 kg ovendry wood digester. The total titratable alkali of the white liquor was measured as 122 gal/L. Nonprocess inorganic deadload in the liquor was assumed to be about 12%. The white liquor specific gravity was measured as 1.17.

We assumed that all of the inorganic species in the black liquor originated from the applied white liquor and all of the organic material originated as dissolved wood material with a correction for water produced from neutralization of organic acids in the digester. Using these assumptions, we determined that the organic content of the black liquor should represent about 69% of the total black liquor mass and the inorganic content of the black liquor should be about 31% of the total mass. The manual spreadsheet calculation verified the WinGEMS balance values.

LABORATORY TESTING OF INORGANIC-TO-ORGANIC CONTENT

After the material balance calculations were verified, attention turned to the actual laboratory tests being performed. The mill did not have the expertise or the specialized equipment to perform the standard TAPPI T-625

cm 85 test method or the modified and improved ion selective electrode testing method suggested by Fricke [4]. Therefore, the mill had developed a modified testing method loosely based on the sulfated ash testing procedure described in TAPPI T-625 cm 85 test method. (Similar modified testing procedures have been used in multiple mills within North America and South America.) Routinely collected samples of virgin and as-fired heavy black liquor samples were collected and the organic and inorganic portions were determined with a muffle furnace and balance. The procedure determined the weight percent dry solids in the liquor. Then, a small amount of heavy liquor was placed inside a tarred crucible and ashed in a muffle furnace at 550°C for 1.5 h. The total weight of residue was determined to represent the inorganic content of the liquor. This value was determined gravimetrically and subtracted from the initial dry mass of liquor placed into the crucible.

The difference was reported as the organic content of the liquor. As sodium and potassium carbonate reduction is minimal below 700°C, performing ashing tests at 550°C for only 1.5-4 h should result in minimal loss of sodium or potassium via fume formation. Thus, these inorganic elements should form sulfates or carbonates and not be lost via volatilization [9,10] during this low-temperature ashing technique. When this test was questioned, samples were sent to an outside laboratory and to two different universities (Guia Páctica – Universidad de Guadalajara, Mexico, and Universidade Federal do Paraná, Brazil) for testing. The outside laboratories used three different testing methods [11,12]. The universities used two slightly different, in-house test methods for determining organic and inorganic material in black liquor. (The university testing methods may be obtained on request directly from the universities.) The mill test method was repeated with the sample being kept in the muffle furnace for 4 h instead of 1.5 h to bring the testing procedure closer in line with the TAPPI procedure on which the mill test was loosely based. All of the laboratory tests returned results with an inorganic to organic ratio of roughly 1-to-1.

RECONCILIATION OF MATERIAL BALANCE WITH LABORATORY RESULTS

When all of the laboratory tests returned similar results, significant effort was expended to reconcile the laboratory and the computed mass balance results. It is well understood that residual sulfide is converted to sulfate during the ashing process. The applied sodium hydroxide is either converted into sodium salts of organic acids and water, or to sodium carbonate by the degradation of lignin and carbohydrates during the pulping process [8]. In either case, after the black liquor has been ashed, carbon and oxygen have been removed from the organic fraction during the mineralization reaction. Any residual hydroxide reacts with organic carbon from the black liquor and mineralizes it while being converted into carbonate via the following reaction:

$$\text{C (from black liquor organics)} + O_2 \longrightarrow CO_2$$
$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

Provisions were made to the Excel balance to perform these chemical conversions on the generated black liquor (**Table I**). After these chemical reactions were successfully modeled, the inorganic-to-organic content was determined to be about 58%-75% organics and 25%-42% inorganics. These values agreed well with the laboratory testing results.

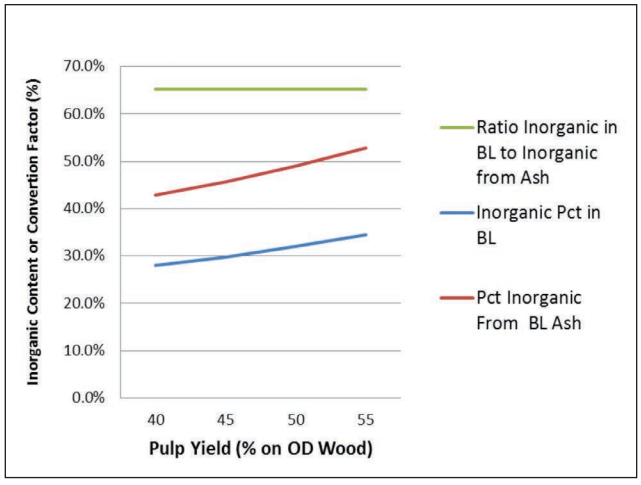
EFFECTS OF YIELD AND WHITE LIQUOR TEST VALUES

When the effect of ashing was understood and modeled, we wanted to develop a factor to convert the ash test results back to the actual inorganic and organic percentages in the original black liquor. Using the Excel spreadsheet to convert the white liquor caustic and sulfide into sulfate and carbonate, it was possible to develop this factor and to determine the effects of

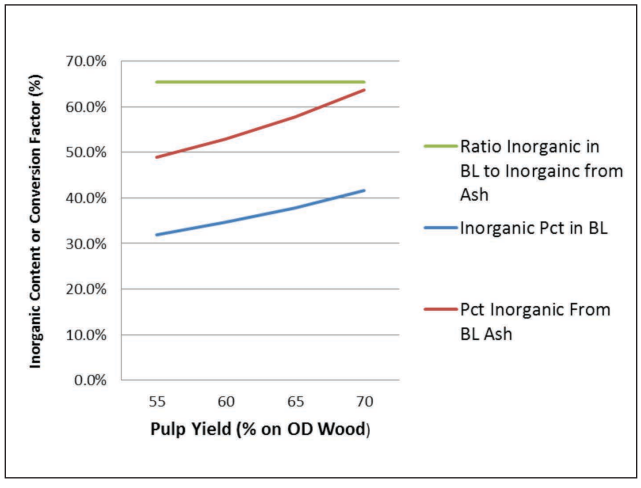
		White Liquor Charge		Ashed Black Liquor	
Na_2SO_4 in white liquor	o.d. lb/ metric ton pulp	23.7		296	
Na_2S	o.d. lb/ metric ton pulp	149.6			
NaOH	o.d. lb/ metric ton pulp	472.6			
$NaCO_3$	o.d. lb/ metric ton pulp	162.6		789	
Total inorganic solids	o.d. lb/ metric ton pulp	809		1085	
Water formed	lb/ metric ton pulp	98.0		-	
Remaining inorganic solids	o.d. lb/ metric ton pulp	716	31%*	1085	47%*
Organics from wood	o.d. lb/ metric ton pulp	1589	69%	1220**	53%
Total black liquor solids	lb/ metric ton pulp	2305		2305	

* 31% mass balance inorganic / 47% ash inorganic = 66% factor
** By difference

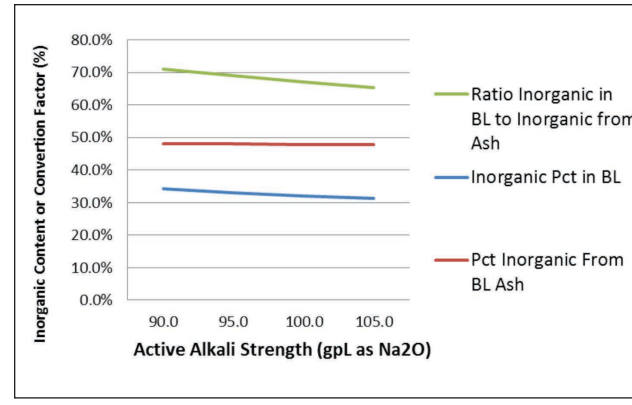
I. Details of how inorganics from white liquor are converted into inorganics in ashed black liquor samples in the Excel spreadsheet balances.



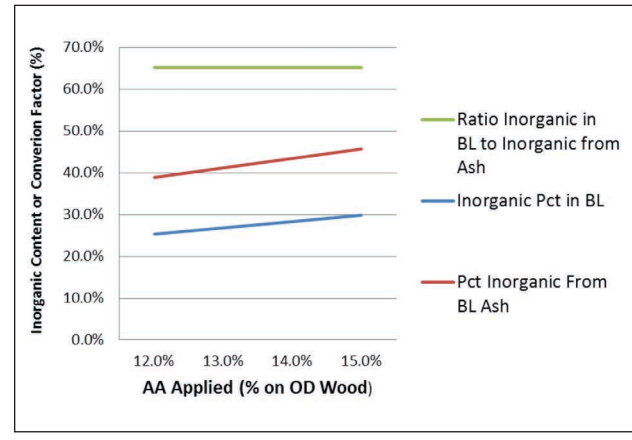
1. Comparison of inorganic content in black liquor and from black liquor ash samples at constant white liquor charge and compostion for various softwood yields.



2. Comparison of inorganic content in black liquor and from black liquor ash samples at constant white liquor charge and compostion for various hardwood yields.



3. Comparison of inorganic content in black liquor and from black liquor ash samples at various white liquor compostions for constant white liquor charge and yields.



4. Comparison of inorganic content in black liquor and from black liquor ash samples at various white liquor charges for constant white liquor active alkali and yields.

pulp yield, liquor charge, and white liquor chemical composition on this conversion factor. Pulp yields were altered from about 40% on wood to about 70% on wood to represent the typical range between bleachable grade and high yield kraft pulping for pine and hardwood pulps. We determined that pulp yield has almost no effect on the conversion factor for converting the percentage of inorganics in ash into percentage of inorganics in black liquor (**Figs. 1** and **2**). What did affect the inorganic content of the black liquor was the initial ABC test [13] values of the white liquor entering the digester (**Fig. 3**). As it turns out, the factor to convert laboratory testing results into the actual inorganic-to-organic ratio is independent of yield or liquor charge (**Fig. 4**) but varies by the ABC test. Certainly the organic-to-inorganic ratio changes with yield and effective alkali charge, but the correction factor to get back to the percentage of inorganics in the black liquor is only a factor of the cooking liquor properties. The material balance results were used to develop a factor to convert the percent inorganics from the ashed sample (laboratory test) to the original inorganics in the black liquor.

The factor is around 65% to 70%. (% inorganics in ash x factor = % inorganics in black liquor). This factor is most useful when attempting to estimate the total black liquor solids produced using the inorganic ratio from black liquor ashed samples and pulp yield. If the formula below is used, then the estimated black liquor solids will be overstated.

Black liquor solids per o.d. ton pulp = [(1 / pulp yield -1) / (1 - % inorganic in ash)] * 2000

The percentage of inorganics in ash would need to be corrected by the factor described to result in the proper estimate.

CONCLUSIONS

Material balances looking at the source of carbon and various inorganics in black liquor will predict that about 2/3 of the black liquor solids should contain organic material derived from dissolved wood components. However, when laboratory

testing is performed, organic values closer to half of the total black liquor solids are measured. The apparent discrepancy results from the mineralization of organic carbon from the wood into carbonate and the conversion of residual sulfide into sulfate during the ashing process. We determined that the ratio of inorganics in black liquor to the inorganic fraction in the ash was 0.734. This ratio was constant over a wide range of pulp yield data. The only properties that affected this ratio were the initial ABC test values of the white liquor entering the digester. **TJ**

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ABOUT THE AUTHORS

While attempting to reconcile engineering estimated material and energy balances from a pulp mill expansion project with startup and laboratory data, it became apparent that the estimated and experimentally obtained inorganic-to-organic ratios of the black liquor were vastly different. The current work attempts to reconcile these differences.

Previous work, mainly performed 15-35 years ago, attempted to develop fairly complex but highly accurate experimental methods to determine the inorganic-to-organic ratio in black liquor. The current work attempted to develop a fundamentally based factor that could be applied to the "quick and dirty" low tech experiments routinely performed in a mill to obtain reasonable results.

The current work had to develop an understanding of the reactions occurring between organic carbon and inorganic sodium and sulfide compounds to develop a reasonable factor. Fume formation and the temperatures likely to result in fume losses also had to be understood.

The most interesting finding was that the pulp yield and the amount of applied active or effective alkali did not significantly affect the value of the developed factor. Only the ABC test of the applied white liquor affected the value of the factor.

The use of this reconciliation factor will allow a mill to use a quick, in-house ashing method to determine the actual inorganic-to-organic ratio of their black liquor. Mills will no longer have to send samples to outside laboratories and wait several weeks for results to be returned.

The next step is to disseminate this information to other mills.

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