Reductive burning of high-yield spent pulping liquors by the addition of pulverized coal

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ABSTRACT: The reductive burning of high-yield spent pulping liquors can be accomplished by the addition of pulverized coal to increase the heat content and generate the proper reducing conditions. Samples from a 78%-yield sodium bisulfite pulping process employing a hardwood furnish were mixed with 10–50% pulverized coal and burned at 950° C under reducing conditions in a box furnace. Even in these uncontrolled combustion conditions, 76.5% of the sulfur found in the soluble portion of the smelt was converted from lignosulfonates to useful sulfide ion. For the remainder of the sulfur, analyses determined it to be 19.5% as sulfite ion, 3.1% as thiosulfate ion, and 0.9% as sulfate ion.

KEYWORDS: Coal, combustion, high-yield pulping, reduction, sodium bisulfite, spent liquor, sulfur compounds.

A current trend in pulping operations in the United States is that mills are switching to processes that produce higher yields. There are two general reasons for this shift. First, yields of 80–85%, compared to the typical 50–55% achieved with kraft processes, are much more economical in terms of raw materials usage. Second, the capital investment is much less than for kraft facilities.

One of the major advantages of kraft operations, however, is the possibility of chemical recovery. For most high-yield processes, a suitable recovery system has not yet been developed, and the spent liquors are simply sewered to secondary treatment.

One of the major limitations to inorganic chemical recovery is the lack of carbon-containing chemicals sufficient to sustain combustion of the liquors. The higher-yield processes simply do not dissolve sufficient lignin and hemicelluloses to attain the approximately 5500 Btu/o.d. lb (12.8 kJ/g) needed. With all current recovery processes, it is necessary to oxidize the organic materials prior to recovering the inorganic pulping chemicals.

Our purpose in this study was to look at the first step in a proposed chemicals recovery process, that of "reductive burning." Reductive burning is actually the conversion of only the sulfur species to their reduced forms—mainly sulfide, or S^{2-}. The organic carbon, oxygen, and hydrogen are actually oxidized, or "combusted," to CO_2 and H_2O, for example.

Reductive burning

Reductive burning of spent liquors not only generates heat for steam production, but it also converts the sulfur from either sulfate or lignosulfonates (depending on the type of high-yield process employed) to useful sulfide. Sulfide ions can be recycled directly as a pulping chemical in sulfide-based (e.g., green liquor) processes. Alternatively, the sulfide can be partially oxidized and then converted to sulfite (SO_3^{2-}) ions for use in sulfite-based processes such as neutral sulfite semichemical (NSSC) or sodium bisulfite pulping.

Recovery systems based on reductive burning of spent liquors are common and include the kraft recovery process as well as many sulfite liquor recovery processes (*1–5*).

Oxidative burning is generally not suitable for recycling sodium sulfide or sodium sulfite spent liquors. Though some mills do burn their spent sodium sulfite-based liquors oxidatively in, for example, a fluidized bed boiler, the primary product in that case is Na_2SO_4 (salt cake). This salt cake is used as a kraft makeup chemical, but it must be mixed with the kraft black liquor and then reductively burned to form S^{2-} before it can be used again for pulping.

The technique studied here entailed the introduction of pulverized coal into the spent liquor at a rate sufficient to

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sustain combustion and reduce the various sulfur species, particularly the lignosulfonates, to sulfide. Pulverized coal potentially can be used to duplicate the conditions in common kraft liquors. If perfected for high-yield liquors, the reductive burning phase can become the first step in a recovery process for the inorganic chemicals.

Oil and heavy residues of low-quality petroleum have been co-fired with spent liquor to increase the organic content during recovery. Previous experience with the SCA Billerud recovery process at an 80%-yield sodium sulfite semichemical mill reinforces the belief that a pulverized coal might also be used successfully (*6*). At this mill, an excess of fine carbon particles was building up in the system. This carbonaceous material could be disposed of by landfilling, but doing so would result in a loss of chemicals, primarily sulfur as sulfates. So, this excess carbon was instead recycled back to the weak liquor. Rather than creating operational problems, this fine carbon served to scour the evaporators, eliminating any necessary maintenance cleaning. If pulverized coal could be used similarly for liquors with insufficient organic content, it may provide a more available, more convenient, and, in the case of oil, more economical way of obtaining the same advantages.

There are two potential problems, however, that should be mentioned in conjunction with the proposed reductive burning process. First, the coal used in this study was low in sulfur but relatively high in ash. To minimize scaling, a coal lower in ash would be preferred for commercial use. The amount of organic sulfur is not a problem, however, because the sulfur can add to that recovered as S^{2-}. Second, any high-yield spent liquor contains a heavy water-removal load. The liquors will have to be concentrated substantially prior to burning.

On the positive side, however, for higher-yield liquors, it is not necessary to use a kraft-type furnace that is fully equipped with superheater and economizer sections (*7*). A simple Broby smelter, such as used for "intermediate yield" liquors, would probably be sufficient and would be much less costly.

Experimental methods

Spent liquor samples were obtained from a 78%-yield sodium bisulfite pulping process employing a hardwood furnish. In the past, the mill had used a lower yield process, and the plant had burned the liquor and sold the resulting salt cake in solid form to a kraft mill. However, the liquor from the higher yield process has less organic content and cannot be successfully burned. Currently this liquor is sewered to secondary treatment.

The heating value of the weak liquor was measured by a Parr Adiabatic Bomb Calorimeter. Solids measurements were determined by weighing the filtered solids after evaporating.

Samples of 5 L, at about 11% solids, were treated with KOH to increase the pH and thus to decrease potential sulfur losses during our preliminary analyses. The concentrations of the various sulfur species were determined as described below. The results are in **Table I.**

For the reductive burning tests, the weak liquor samples were evaporated to approximately 1 L, or about 50% solids, and were mixed with pulverized coal from the Wisconsin Public Service Corp. Pulliam Plant in quantities thought sufficient to reduce all the oxysulfur salts to Na_2S (10–50% coal). The chemical composition of the coal is given in **Table II.**

Ten-gram samples of the various concentrated liquor–coal mixes were heated in a reducing atmosphere in a Blue M Rad-O-Glow carbon-element box furnace, modified with a small inlet tube for the introduction of argon. A porcelain crucible was used to hold each sample mixture. The furnace was brought to temperature (950°C) with argon flowing in sufficient volumes to exclude oxygen. The samples were placed in the furnace. Initially, the argon flowed for the entire reaction period. However, better reduction was

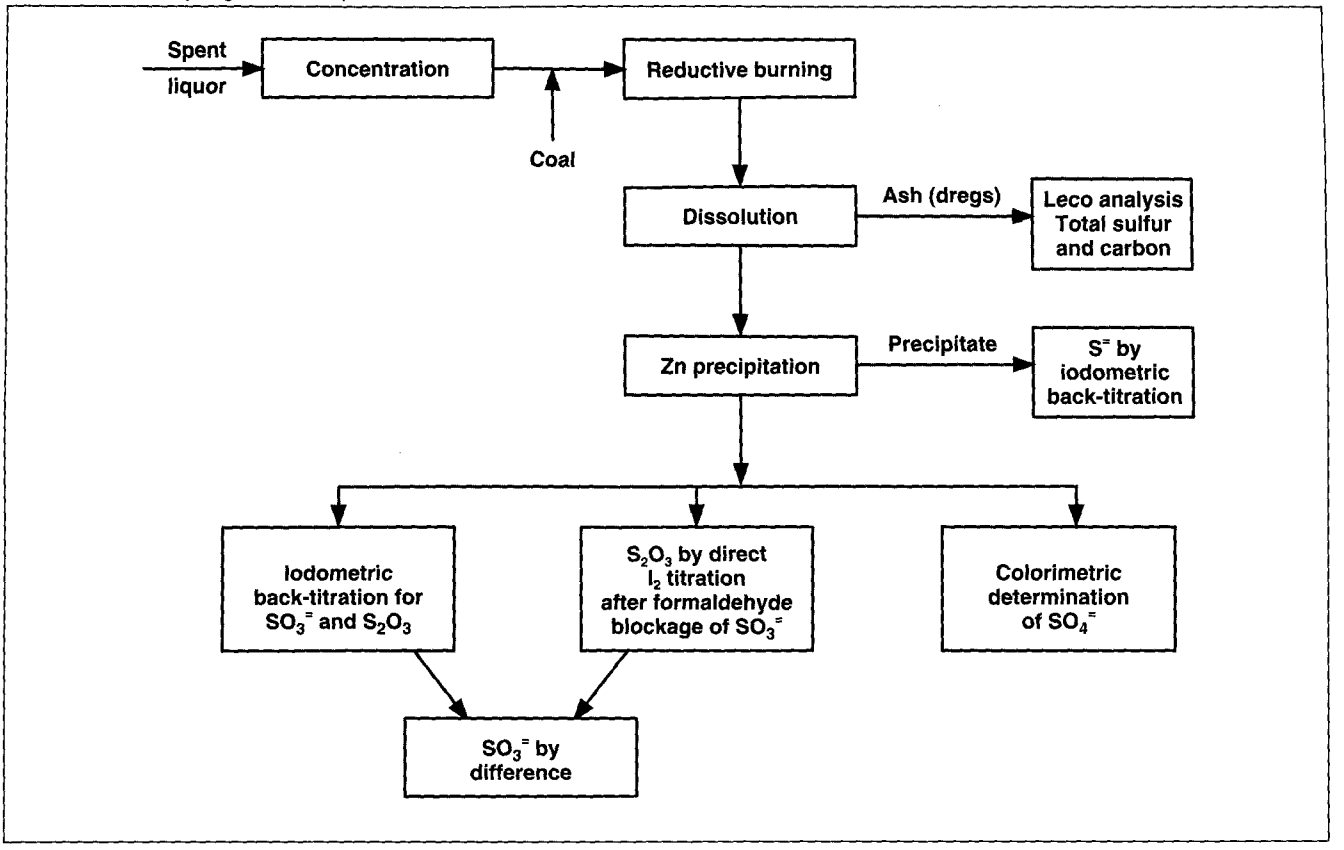
I. Properties of the spent liquor

pH	5.25 ± 0.01
Solids, %	11.0
Density, g/mL	1.12 ± 0.03
Heating value	
BTU/lb o.d. solids	2700
kJ/g o.d. solids	6.29
Total sulfur	
mmol/mL	0.424 ± 0.005
g/mL	0.0136 ± 0.002
Sulfite, mmol/mL	0.152 ± 0.001
Thiosulfite, mmol/mL	0.027 ± 0.002
Sulfide, mmol/mL	0.030 ± 0.001
Sulfate, mmol/mL	0.014 ± 0.001

II. Analysis of coal from Wisconsin Public Service (dry basis)

Moisture, %	...
Carbon, %	74.68
Hydrogen, %	4.95
Nitrogen, %	1.23
Sulfur, %	
Organic	0.78
Pyritic	0.03
Total	0.81
Ash, %	9.93
Oxygen, %	8.40
Heat content	
BTU/lb	13,265
kJ/g	30.87

1. Scheme for analyzing the sulfur species



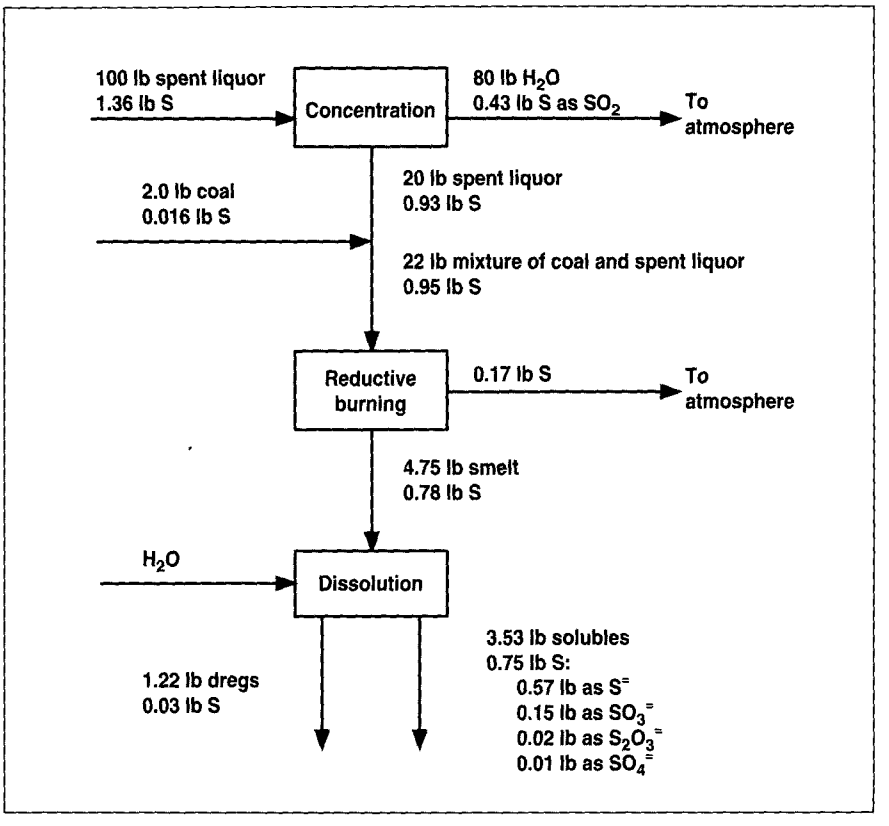
observed if the argon was used only prior to sample introduction (5 min at about 2–3 L/min) and then again immediately prior to sample removal (5 min at about 1 L/min). The samples were removed and cooled under the argon atmosphere. Reaction times of 15, 30, 45, 60, and 120 min were used to test the effect of the time variable.

After combustion, the remaining ash (or the cooled "smelt") was dissolved in water. The solution was analyzed for the various oxidation states of sulfur (**Fig. 1**); the residual, the water-insoluble ash, was analyzed for total sulfur.

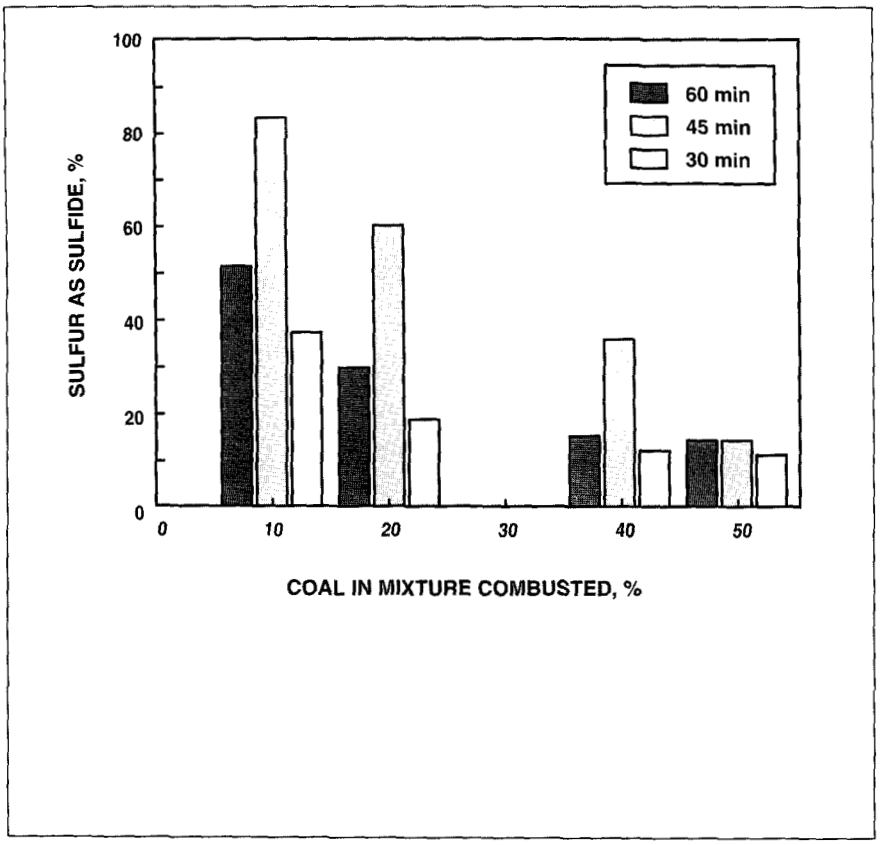
The sulfide was determined by standard iodometric titration (*8*), consisting of back titration of excess I_2 with thiosulfate after separation by the formation of a zinc sulfide precipitate (*9*).

Sulfite and thiosulfate are jointly determined from the zinc sulfide filtrate by a similar $I_2/S_2O_3^{-2}$ titration. The thiosulfate alone was measured by a direct I_2 titration after the sulfite had

3. Sulfur balance



2. Sulfide in the soluble portion of char after reductive burning



been reacted with formaldehyde to form inert hydroxysulfonate. The sulfite quantity was calculated by difference (*10*).

The sulfate, determined also for the zinc sulfide filtrate, was measured colorimetrically after reaction with barium chloranilate, $BaC_6Cl_2O_4$ (*11*).

Total sulfur was measured by a Leco Carbon/Sulfur Analyzer.

Two types of experiments were performed. Initially the burning times and ratios of coal to spent liquor were varied to optimize the formation of sulfide. In these experiments, only the S^{2-} species was determined. With those optimum times and coal percentage parameters, additional tests were performed. In these experiments, all of the sulfur species were measured. In both sets of experiments, the carbon content also was monitored using the Leco Carbon/Sulfur Analyzer.

Results and discussion

Since the furnace supplied heat to the system, it was impossible to determine the amount of coal needed to maintain self-sustained combustion. We assumed that the combined spent liquor and coal heating value must approach the generally assumed minimum of 5500 Btu/o.d. lb. On that basis, the *minimum coal requirement*, assuming heating values of 13,265 Btu/o.d. lb and 2700 Btu/o.d. lb for the coal and liquor, respectively, would be about 25% by weight. The coal requirement for these tests, however, was based on the sulfur reduction, not the minimum required energy content.

Figure 2 summarizes the results of the burning tests in terms of the percentage of sulfide produced. Apparently, the preferred conditions in these tests correspond to a 45-min burn time and a coal–spent liquor ratio of 1:9. It is possible an even smaller coal addition might be better; however, since the percentage of sulfur as either sulfide or sulfite is already 96% of the total, the increase could not be sizable.

Figure 3 is an overall sulfur balance under these preferred conditions. The 0.43 lb of sulfur per 100 lb of spent liquor which is emitted into the atmosphere in the concentration stage may appear high, but it is realistic for these liquors. Subsequent studies of high-yield sulfite liquors, in contrast to kraft and normal-yield sulfite liquors, verified the large SO_2 emissions under acid conditions.

Table III provides more detailed information as to the chemical characteristics of the resulting product. Under these conditions, 76.5% of the dissolved sulfur was converted to S^{2-}. Analyses found 19.5% of the dissolved sulfur as SO_3^{2-}, 3.1% as thiosulfate ($S_2O_3^{2-}$), and 0.9% as sulfate (SO_4^{2-}).

The liquor used in these tests was from a sodium bisulfite high-yield process. In this case, the sulfide can be recovered by a method such as that marketed by a number of vendors—that is, converted to H_2S, burned to form SO_2, and then dissolved to regenerate sulfite ions, SO_3^{2-}. The sulfite can be converted to bisulfite directly in the solution by acidification. In this manner, "fresh" white liquor can be produced.

If the spent liquor were from a kraft or green liquor high-yield process, the S^{2-} could be reused in much the same way it is reused in the normal kraft recovery process. We surmise that the SO_3^{2-} yield would be substantially lower in these situations, because the spent liquor would not have relatively large amounts of the unreacted bisulfite from the pulping operation.

In all of the burning tests, approximately 70% of the carbon was "lost" in the combustion. This situation is very similar to that for kraft liquor.

About 30% of the carbon remains in the smelt. Of this 30%, two thirds is water-soluble, probably as carbonates. The remaining one third is likely a mixture of insoluble carbonates (i.e., $CaCO_3$, $FeCO_3$) and unreacted coal.

Overall, about 5–6% of the coal–

III. Weights of materials in reductive burning trials*

Material	*Weight, g*	*Percentage of initial mixture, %*
	Before reductive burning	
Mixture of coal and spent liquor, g	10.2066 ± 0.0040	100.00
Spent liquor	9.1627 ± 0.0040	88.61
Coal, g	1.0439 ± 0.0080	
	After reductive burning	
Smelt, g	2.204 ± 0.170	21.59
	Dissolution of smelt in 250 mL of boiled water	
Dregs, g	0.5651 ± 0.0225	5.454

* Averages of four trials.

IV. Total sulfur, sulfur species dissolved, and total carbon

	Total sulfur	
In:	*Sulfur, mmol*	*% of total*
Mixture	13.559 ± 0.023	100.0
Smelt	11.072 ± 1.915	81.66 ± 7.51
Dregs	0.4991 ± 0.0196	3.68 ± 1.34
	Sulfur species dissolved	
Species	*Sulfur, mmol*	*% of total*
$S^=$	8.089 ± 1.383	76.5
$S_2O_3^=$	0.328 ± 0.157	3.1
$SO_3^=$	2.058 ± 0.370	19.5
$SO_4^=$	0.099 ± 0.005	0.9
		100.0
	Total carbon	
In:	*Weight, g*	*% of initial*
Mixture	1.584 ± 0.052	100.0
Smelt	0.448 ± 0.064	38.3
Dregs	0.145 ± 0.008	9.2
Lost in combustion	1.136 ± 0.124	71.7

Averages of four trials.

spent liquor mixture results in a water-insoluble residue, or "dregs." This 5–6% is a larger percentage than normally experienced in kraft recovery operations, but it could be due to either an excess of coal, coal ash, or incomplete combustion. This circumstance is not totally unexpected, since the burning conditions are less favorable than those in commercial recovery furnaces and since the coal used was almost 10% ash.

It is not clear why the process was more efficient when the argon flowed only at the beginning and the end of the heating periods. Since the nonsulfur species require oxygen for conversion to the final combustion products, it is possible that small amounts of atmospheric oxygen, from unintentional leaks, enhance the overall process. No attempt was made to thoroughly seal the furnace chamber. The supposition that small amounts of atmospheric oxygen are available is also supported by the fact that the 45-min processing time always produced the highest sulfide value. Longer times could have allowed some of the sulfide to be oxidized after the volatiles had escaped from the organics.

The processing conditions identified as providing these results are not expected to be directly transferable to a commercial installation. The gas phase conditions during the tests could not be monitored; hence, it is possible that reduction did not occur during the entire heating period.

Similarly, it is not clear whether the organics in the liquor are gasified or pyrolyzed during the processing. The intent was simply to determine whether or not the process would work. From these results, it appears that the added coal could be used to combust the organics in the spent liquor under sulfur-reducing conditions.

Conclusions

Even under such relatively crude reductive burning conditions as those used in these tests, a large percentage of the sulfur in the spent liquor can be reduced to sulfide or maintained as sulfite. Thus, the process appears to be feasible, though further studies are needed to investigate potential scaling problems and to more thoroughly monitor the sulfur conversion. TJ

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