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CARBONATE ANALYSIS IN BLACK LIQUORS FROM PULPING AND EVAPORATION PROCESS

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ABSTRACT

Carbonate in black liquor is one of the main causes related to fouling in the evaporator. Due to the lack of accurate methods for carbonate analysis in black liquors, it is misconceptually believed that the only source of carbonate in black liquor is due to incomplete conversion in the causticizing process in mill practice. In this paper, we present a simple and rapid headspace gas chromatographic method for accurate determination of carbonate in black liquor. We determined the carbonate in black liquors from lab pulping and mill evaporators. We found that a certain amount of carbonate was formed in the pulping process.

Keywords: Headspace; GC; carbonate; black liquor; pulping; evaporation.

INTRODUCTION

Carbonate in black liquor is one of the major species that is responsible for the fouling and scaling in kraft mill evaporators in the chemical recovery cycle. The solubility of carbonate is strongly dependent on the total solids content in the black liquor. It has been well understood that two types of carbonate precipitates will be formed during black liquor evaporation. Burkeite, a double salt ($2\text{Na}_2\text{SO}_4\cdot\text{Na}_2\text{CO}_3$), is first precipitated and then burkeite plus sodium carbonate (Na_2CO_3) will be precipitated. Therefore, the quantification of carbonate and its solubility in black liquor is very important to control evaporator fouling to reduce mill downtime caused by fouling.

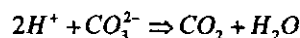
The major source of carbonate is the recausticizing process where due to limitation in the mass transfer process, the carbonate in green liquor cannot be completely converted to hydroxide. Thus, a certain amount of carbonate remains in the white liquor and is recycled to the pulping process to become dead load. The carbonate in white liquor can be determined by the traditional ABC titration method [1]. In mill practice, it is believed that the carbonate in the black liquor is simply due to the incomplete conversion in the causticizing process. Unfortunately, carbonate can also be formed in the pulping process as we found in this study, which increases the carbonate in black liquor and makes the quantitative analysis of carbonate in black liquor necessary.

However, accurate carbonate analysis in black liquors is very difficult. The ABC titration method cannot be used for analysis of carbonate in black liquor primarily due to a significant amount of organic acid salts. The application of capillary ion electrophoresis [2] and ion chromatography [3-5] for carbonate analysis in black liquors requires complicated sample pretreatment and procedures. Furthermore, the sensitivity and repeatability of these methods are very poor. The time-consuming coulometric technique [6], though used in commercial analytical laboratories for carbonate analysis in black liquors, presents difficulties and measurement uncertainties due to the interference of other volatile species released during black liquor acidification pretreatment.

In the present study, we first briefly present a method for accurately quantifying carbonate in black liquor using a phase reaction conversion (PRC) headspace gas chromatographic (HSGC) method that we developed [7]. We then investigate the effects of the pulping process and wood species on carbonate formation. Carbonate analysis in concentrated black liquors collected in a kraft mill was also conducted.

METHODOLOGY

HSGC is only suitable for the analysis of volatile species and cannot be directly applied to quantify nonvolatile species such as inorganic ions. However, if the nonvolatile species can easily be converted into a volatile species, the HSGC method can be applied. Based on this approach, we developed a phase reaction conversion (PRC) HSGC method for analysis of carbonate in solutions [7]. Carbonate is converted to carbon dioxide by acidification, i.e.,



The carbon dioxide can be easily measured by thermal conductivity detector (TCD) in GC. In the PRC method, it is very important to have a constant (or complete) conversion of the carbonate in the sample solution into CO_2 . Excess amount of acid was used in acidification to achieve complete (constant) conversion. The constant conversion rate of the nonvolatile species (carbonate) was verified through two sets of experiments using an aqueous 0.1 mol/L sodium carbonate solution and a kraft black liquor, respectively. The sample size was varied in each set of experiments. As shown in Fig. 1, it was found that the TCD signal peak area varies linearly with black liquor sample size, indicating that the conversion of carbonate to carbon dioxide is a constant. External standard was used for calibration. A detailed description of the method can be found in our previous study [7].

We also conducted a repeatability test of the PRC-HSGC method; the relative standard deviation in 5 measurements is only 3.7%. In addition, we also demonstrated simultaneous carbonate and sulfide measurements in black, white, and green liquors using the PRC-HSGC method. Excellent agreement of the measured carbonate and sulfide in white and green liquors between the PRC-HSGC and ABC titration method was obtained. The PRC-HSGC method is simple, rapid, and automated.

EXPERIMENTAL

Pulping

To study carbonate formation in pulping, batch pulping experiments were carried out using eight rotating bomb digesters in an oil bath. Fifty grams (ODW) of wood chips in each bomb were subjected to a conventional digestion. For the pulping of loblolly pine, the active alkali charge varied from 15 to 18% and sulfidities of 0, 15, and 30% were employed with a liquor-to-wood ratio of 4:1. For the other wood species, an active alkali charge of 17%, a sulfidity of 31%, and a liquor-to-wood ratio of 3.7:1 were chosen. The initial heat-up was controlled at a rate of 2.14°C per minute. Detailed descriptions of the experiments can be found in our previous publications [8,9].

Analytical apparatus and operation

All measurements were carried out using an HP-7694 Automatic Headspace Sampler and Model HP-6890 capillary gas chromatograph equipped with a thermal conductivity detector (Hewlett-Packard, now Agilent Technologies, Palo Alto, CA, USA). GC conditions were: capillary column with an ID = 0.53 mm and a length of 30 m (model GS-Q, J&W Scientific Inc., Folsom, CA, USA) at 30°C, carrier gas helium flow rate of 3.1 mL/min. Headspace Sampler operating conditions were: oven temperature of 60°C; 0.5 min strong shaking of the sample; vial pressurized by nitrogen and pressurization time of 0.2 min; sample-loop fill time of 0.2 min; loop equilibration time of 0.05 min; vial equilibration time of 0.5 min; and loop fill time of 1.0 min.

The sample preparation and measurement procedures were as follows: A sample vial of 21.6 mL was first sealed with a PTFE/butyl-molded septum (Cat No. 73822A-20 Kimble Kontes, Vineland, NJ, USA). The sample vial was then purged by nitrogen gas at a flow rate of 130 mL/s for 2 min to eliminate the carbon dioxide present in the air in the vial headspace before adding 0.5 mL of 2 mol/L sulfuric acid. The sealed and nitrogen-purged vial was injected with 10-1000 µL of black liquor sample solution using a microsyringe and placed in the headspace sampler tray for automatic HSGC measurements. Most industrial liquid samples, such as weak and concentrated black liquors, white liquors, and green liquors, can be directly injected into the sample vial for analysis without pretreatment. Concentrated black liquors were diluted to a solids content of about 20% before analysis.

RESULTS AND DISCUSSION

Carbonate formation during conventional pulping process

To study the formation of carbonate in pulping, all white liquors used in experiments were prepared using analytical-grade chemicals, i.e., there is no carbonate in the original cooking liquor. Information on time-dependent carbonate formation was obtained by analyzing the black liquors that were collected from pulping experiments terminated at different pulping times. Figure 2 shows the time-dependent carbonate formation during conventional alkaline pulping of loblolly pine. It can be seen that the carbonate in the cooking

liquor increases with time as the pulping process proceeds. The rapid increase in carbonate occurs at the initial phase of the cook while EA was rapidly decreasing. When compared to the EA consumption, the amount of carbonate formed during the entire pulping process is small. This is because EA is mainly consumed by the neutralization of organic acids, and to form organic sodium salts. Figure 2 indicates that carbonate formation is dependent on EA. However, the time-dependent profile for carbonate formation is not affected by the presence of AQ. The carbonate concentration in the spent liquor was found to be 1.8 g/L as sodium oxide.

Effect of cooking conditions on carbonate formation

As discussed previously, carbonate formation is dependent on EA. We plotted the relationship between carbonate and consumed EA. As shown in Fig. 3, carbonate formation correlates well to the amount of consumed EA. The carbonate data from different pulping processes fall onto a universal curve, independent of sulfidity, AQ, and active alkali charge. Linear regression analysis of the data indicates that the correlation between carbonate formation and consumed EA fits to a straight line very well within the EA range of the samples collected. This correlation is important because it can be used for the prediction of carbonate formation during pulping.

Effect of wood species on carbonate formation

We also investigated carbonate formation using different wood species. The results are listed in Table I. The target kappa number of the final pulp was set at 30 for softwood, and 15 for hardwood. Table I indicates that there is no significant variation of carbonate formation among various softwood species. The small variation is due to the slight variation of the final kappa number. Similar conclusions can be drawn for the hardwood species except for aspen and oak.

In kraft mills, the carbonate concentration in the make-up of white liquor is about 10 g/L (as Na₂O). From the data reported in this study, we can conclude that about 18% of the carbonate in the black liquor was formed in the pulping process for bleachable grade softwood pulp. From the controlling of evaporator fouling standpoint, 18% is significant and should be controlled and minimized.

Formation of carbonate during black liquor evaporation?

The black liquor samples were collected from various stages of a multiple-effect evaporator in two kraft mills. Figure 4 shows a schematic process flow diagram of the evaporator in kraft mill A. The sample bottles were filled with black liquor without headspace and shipped to our laboratory for analysis.

The carbonate in these samples was analyzed using the PRC-HSGC method. In the black liquor evaporation process, water in the liquor is lost due to vaporization that increases the total solids content of the liquor. Therefore, we represent the carbonate data in terms of weight by weight of dissolved solids. The results are listed in Table II. The results were inconclusive about whether or not there is carbonate formation. The liquor samples were collected more or less the same time; however, the retention time of liquor in each stage

of the evaporator can be relatively longer than the time delay in sample collection, which means that the samples are not from the same liquor source. Therefore, the small variation in the carbonate data listed in Table II could well be due to the variations in the sources. The data in Table II also shows that the variations of carbonate in the liquor were small, indicating that even if there is carbonate formation in evaporation, the amount of formation is not significant.

CONCLUSIONS

A PRC-HSGC method has been developed for the determination of carbonate in black liquor. The present method is rapid, simple, accurate, and repeatable.

The study showed that carbonate formation during alkaline pulping linearly correlates to the consumed EA very well. A high EA consumption leads to more carbonate formation.

The study also showed that formation of carbonate during black liquor evaporation is not significant.

ACKNOWLEDGEMENTS

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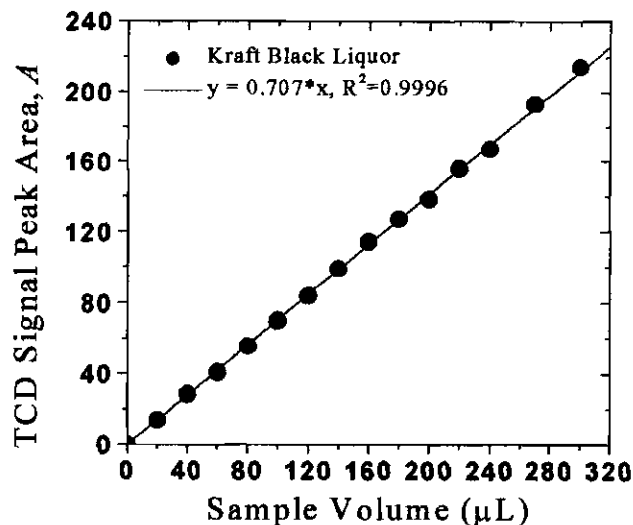


Fig. 1 Verification of constant conversion of carbonate to carbon dioxide using different sample sizes.

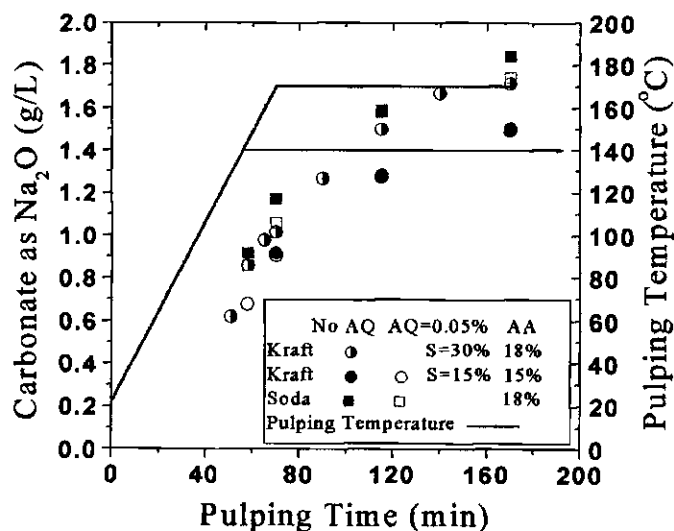


Fig. 2 Time-dependent carbonate in conventional alkaline pulping of loblolly pine.

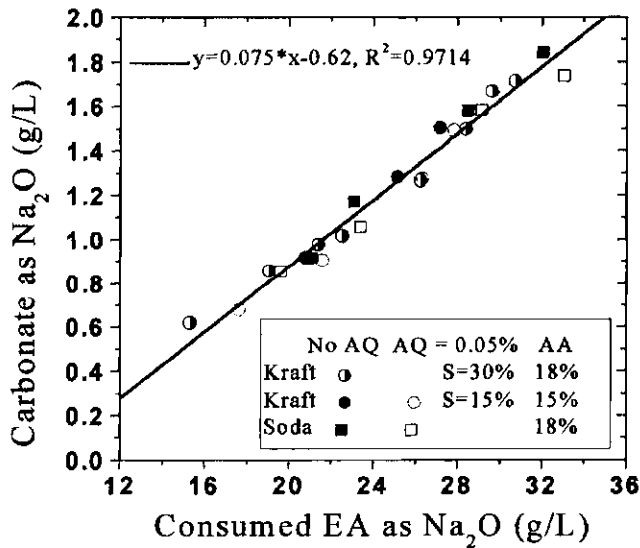


Fig. 3 Correlation of carbonate formation with consumed EA in alkaline pulping of loblolly pine.

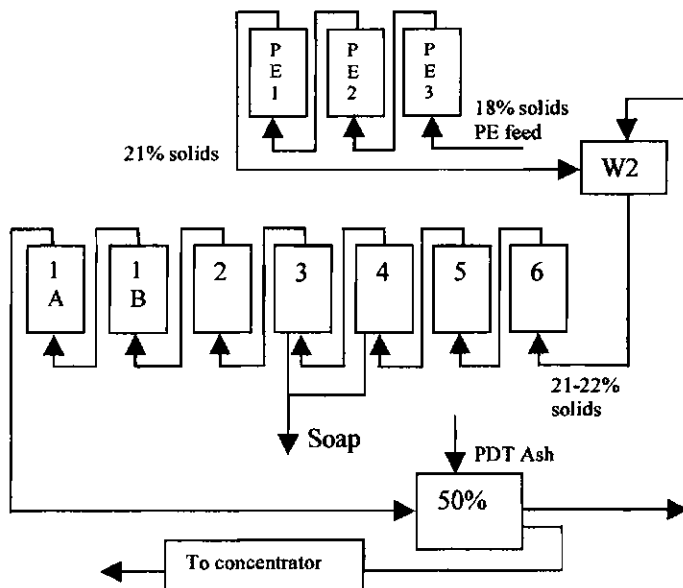


Fig. 4 A schematic diagram of the multiple-effect evaporator.

Table I. Carbonate contents in black liquor from conventional kraft pulping*.

Wood Species	Kappa No.	Na ₂ CO ₃ as of Na ₂ O (g/L)
Softwood		
Loblolly pine	32.4	1.81
Douglas-fir	28.7	2.10
White spruce	31.4	1.62
Western hemlock	32.9	1.72
Hardwood		
Aspen	11.7	1.31
Basswood	12.5	2.16
Birch	12.2	1.81
Maple	14.2	1.92
Sweetgum	15.1	2.25
Oak	17.1	4.62

* AA = 17%, sulfidity = 31%.

Table II. Carbonate contents in black liquor at different evaporating stages*.

Evaporator ID	TDS (%)	Na ₂ CO ₃ (%)
Mill A		
Evaporator feed	18.32	6.03
1	20.42	5.95
2	23.48	6.03
3	26.58	6.13
4	31.01	6.27
5	36.68	6.15
6	42.84	6.40
7	47.52	6.21
Mill B		
Evaporator feed	16.49	9.87
1	22.14	10.74
2	27.41	10.44
3	32.66	9.88
4	43.44	10.58
5	52.11	11.09

* w/w based