

White Liquor Sodium Carbonate Effects on the Pulping of Southeastern Softwood

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Abstract

Laboratory kraft pulping has long been used to break out the noise and production constraints found in mill production pulping. It has been used to help our understanding of the fundamentals and to understand the “noise.” The kraft process dominates the industry in its adaptation for both batch and continuous cooking of wood to fiber. When laboratories do not have access to mill liquors often a synthetic mixture of sodium hydroxide and sodium sulfide are prepared. It works and effective results are gained in pulping studies while usable fiber for strength studies can be gained. However, the reality of production and kraft chemical recovery is that other minor amounts of material intentional or not come along for the ride, predominately sodium carbonate and sulfated salts that make their way through the recovery cycle and become part of the cooking liquor once again. This study aims specifically to investigate the impact of sodium carbonates as typically the third highest compositional ingredient behind primary cooking chemistries sodium hydroxide and sodium sulfide. Sodium carbonate is mostly introduced as carryover from the incomplete causticizing reactions for mill white liquor preparations. Carbonate impacts other than those related to evaporative scaling or other mill problems are often dismissed as “inactive” in the kraft pulping process. Specifically, this work will focus on influence on unbleached southern yellow pine softwood for the purposes of higher yield containerboard, kraft bag paper, solid unbleached sulfate (SUS) board and lower yield bleachable softwood production examining the strength impacts prior to bleaching. It was found for a high yield kappa target (96 kappa) that carbonate content can influence the delignification rate and fiber refining development influence with statistical significance. At traditional bleachable grade softwood delignification targets (30 to 32 kappa), statistical differences were not evident in the much longer cooking times. Strength and refining properties were found to be heavily dependent on the kappa target with little impacts over the carbonate dosage studied. It is believed that the sodium carbonate has influence in the alkali profile available during the cook and contributes as an active pulping ingredient during shorter high yield unbleached cooks. Future work will consider the influence of the sulfate materials and calcium ions. This paper remains focused on the influence provided specifically by sodium carbonate of the total titratable alkali (TTA) equation.

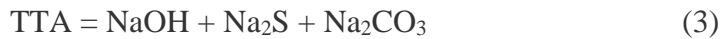
Keywords

kraft pulping, sodium carbonate, white liquor, ionic effects, total titratable alkali

Introduction

When wood is digested the reaction with alkali has been summed up in the literature as five key mechanisms to include neutralization of different organic acids (original wood acids or produced by hydrolysis); reaction with resins in the wood; dissolution of carbohydrates; reactions with lignin; and lastly adsorption by the fibers. [1]

Alkali is formed from the following species and included in the calculations of AA (active alkali), EA (effective alkali), TTA (total titratable alkali), and TA (total alkali) represented in the equations below. These terms are well described in several publications [2,3,4] Some authors have included a $\frac{1}{2} \text{Na}_2\text{SO}_3$ term in the TTA calculation and others have not, we have left it off here with current focus on the sodium carbonate influences.



Typically normalized by units of Na_2O

Sodium hydroxide (NaOH) and sodium sulfide (Na_2S) dominate the kraft process and are the key control variables or “actives” to specifying delignification levels through addition of these components on an oven dried wood basis. Often the contribution of alkali from Na_2CO_3 sodium carbonate from the carryover of insufficient causticizing efficiency is overlooked in the pulping reactions and digester control. It is however, acknowledged in the total titratable alkali (TTA) measurements from chemical recovery liquor testing. Its contribution is typically not included in the cooking alkali calculations on an oven dried wood basis.

This work seeks to evaluate the assumption of cooking parameters based on typical AA and EA charges and the influence of an elevated carbonate content from a mill running poor causticizing reactions as can be represented by TTA for the pulping of southern yellow pine softwood species. Examination of both lower delignification cooks to produce softwood suitable for linerboard and SUS unbleached grades (89 to 98 kappa) as well as softwood pulp cooked to bleachable grade kappa (28 to 32 kappa) is investigated. Additionally, the influence of the carbonate load on cooked pulp’s refining results are also presented with Valley beater trials and strength from resulting handsheets discussed.

Experimental Design

A slotted chip thickness screen ensured use of optimum chip sizes between 2 and 8 millimeters of recently chipped southern yellow pine softwood. The removal of other outlier items (knots, bark, etc.) by hand was incorporated to minimize contamination. Cooking was performed on an M&K batch digester with external liquor recirculation with electric heating. Synthetic cooking liquors were prepared from NaOH, Na₂S, and Na₂CO₃ solutions with bulking water to a 4:1 liquor to wood ratio which included the moisture in the wood chips. A digester temperature set point of 165°C was used with an initial ramp time of all cooks averaging ~50 minutes to cook temperature. These values remained constant.

Cooking charges of 18% AA on oven dried wood by equation (2) were used with an approximate 25% sulfidity calculated on a TTA basis from the equation (3) above. Experimental design made comparisons between two carbonate loads, 0 and 7.5% Na₂CO₃ on oven dried wood on a Na₂O basis, at a high and low kappa target. Literature shows that typical sodium carbonate loading in commercial white liquors are about in the range of 11 to 44 grams per liter on a Na₂O basis for mill produced cooking white liquor, NaOH loading 81 to 120 grams per liter on a Na₂O basis, and Na₂S loading 30 to 40 grams per liter on a Na₂O basis [5]. These levels can be determined utilizing the “ABC titration method” derived from the traditional TAPPI standard T 624. Carbonate concentrations were confirmed by the traditional C – B calculation shown in Table 1 below along with definitions of “A” and “B”. The high end of carbonate loading simulating poor causticizing efficiency in the mill was chosen for study.

$\text{NaOH} = [2A - B]$	$\text{EA} = A$
$\text{Na}_2\text{S} = [2(B - A)]$	$\text{AA} = B$
$\text{Na}_2\text{CO}_3 = [C - B]$	$\text{TTA} = C$

Table 1. “ABC” titration definitions derived from TAPPI standard T 624 Titrations. All values expressed on a Na₂O g/L basis. EA, AA, and TTA defined by equations (1), (2), and (3).

Washing and deshiving was performed using the same procedures for all conditions, using a KRK refiner with “C” plates to hot stock refine the pulps. Pulps were washed of residual cooking liquor using fresh water. The resulting stock was prepared for TAPPI standard Valley beating and sampled at five equal points between the starting freeness of each stock (~770 mL on average) to 300 mL. Valley beater refined stock was tested for freeness and fiber morphology before being made into TAPPI standard handsheets for strength evaluations.

Experimental conditions

Chips: Prepared cook charge batches of 800 OD gram lab screened chips for entire study

- Softwood mostly southern yellow pine with other hard pine species– mill screened prior to collection
- Lab Chip Screening
 - Domtar slotted 2-8 mm accepts chips used for cooking study
 - Hand removal of knots, bark, and debris
 - Moisture content measured as 52.3%

Cook: M&K Pilot Plant Digester

- Batch size: 800 oven dried grams wood
- Cooking Liquor: Synthetic white liquor prepared from NaOH, Na₂S, Na₂CO₃ and bulking water to hit consistent L/W ratio.
- L/W Ratio: 4 represented as total weight pulping liquor over the dry weight of the wood. Our definition of L/W ratio does include the moisture in the wood chips.
- 18% AA on OD wood held constant for all cooks; AA defined by eq. (2) no carbonate influence is added to the actives
- 25% sulfidity target on TTA basis $\text{Na}_2\text{S}/(\text{NaOH} + \text{Na}_2\text{S} + \text{Na}_2\text{CO}_3)$ as Na₂O
- Cook Temperature: 165°C
- Heat up ramp rate ~50 minutes
- Kappa Target: 96 +/- 5 for high kappa, 32 +/- 5 for low kappa
 - Adjust h-factor to find the targets in desired kappa targets, adjust on time
 - h-Factor targets: 1145 for low kappa, 345 for high kappa; 327 adjusted h-factor for high kappa w carbonate for constant delignification
 - Main – Adjust to find a kappa target and complete a total of 5 cooks at this value for further refining/strength study and cooking statistics

Experimental conditions – 5 cooks at each condition to target kappa at two different carbonate loads; Levels were adjusted to maintain the sulfidity level to 25% on a TTA basis.

- no sodium carbonate white liquor additions on wood:
 - 107.8 g Na₂O [NaOH]; 36.1 g Na₂O [Na₂S]
- Sodium carbonate white liquor additions on wood:
 - 91.0 g Na₂O [NaOH]; 53.1 g Na₂O [Na₂S]; 60 g Na₂O [Na₂CO₃]

Brown Stock Washing: Mixing and pressing digester contents – the first 3 washing steps are repeated 3 times

- Dilute fiber in 7-gallon bucket
- Mix 5 minutes on overhead lighting mixer
- Dewater in muslin bag by pressing to ~25% solids in hydraulic press
- Final washed fiber homogenized in Hobart mixer at medium consistency

- Total yield values determined by amount of oven dried material recovered at this point

KRK Refining: <5% shives target simulating hot stock refiner operations on washed fiber with no or little CSF drop.

- Plates – “C”
- Refiner plate Gap – 0.2 mm
- Consistency – 4%
- Passes – 3

Valley beating following TAPPI standards T 200 from starting freeness of each pulp to 300 mL

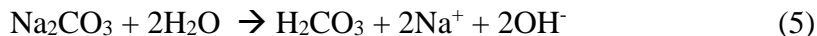
- Approximate targets 770 mL, 650 mL, 530 mL, 415 mL, 300 mL

Handsheets:

- Preparation
 - o Style – TAPPI 6”
 - o Basis weight target –120 gsm
- Testing:
 - o STFI
 - o Burst
 - o Tensile
 - o Tear

Results and Discussions

When dissolved in liquid water, Na_2CO_3 is a salt that, when taken up, will raise the pH (lower the quantity of free H^+ ions that have been dissolved in the water). This is because of the salt's relatively powerful base CO_3^{2-} . As a result, we can conclude that Na_2CO_3 has a pH of eleven by itself. This is summarized by the following reaction:



Water molecules combine to form OH^- and HCO_3^- ions to give a slightly basic solution. However, literature reports that the causticization of sodium carbonate is typically suppressed under high hydroxyl OH^- content from hydrolyzed sodium sulfide [6]. Although not to the level of alkalinity of the NaOH and Na_2S contribution it is demonstrated particularly for shorter high yield softwood cooks for containerboard, that indeed sodium carbonate content studied can indeed influence the cooking results. This effect is further diluted with extended cooking time and further neutralization of wood acids and dissolution of carbohydrates and lignin as the cook progresses past the traditional bulk delignification phase for bleachable grade kappa softwood pulp.

The liquor to wood ratio (L/W) was kept constant at a 4 to 1 ratio for all cooks. Water from chip moisture was included in the L/W calculation. Deionized water was utilized as the bulking liquor to maintain L/W ratio for all cooks.

It was important that % sulfidity was maintained constant on a TTA basis between the sodium carbonate loading so that this property could be maintained between cooks. Sulfidity has been shown to be an important variable to drive the delignification reaction rates [4]. A 25% sulfidity target on a TTA basis was used for this study adjusting the NaOH and Na₂S contributions when Na₂CO₃ was added to remain constant.

Each cooking target was repeated with five independent cooks of the laboratory digester, results are taken from the average of the five cooks after locking down the cooking conditions. Table 2 lists the cooking result averages.

Condition	% Na ₂ CO ₃ on OD Wood (Na ₂ O basis)	h-factor	Average kappa	Average % total yield	Average Residual Effective Alkali (g Na ₂ O/L)
High kappa no carbonate	0	345	95.7 [1.8]	55.7 [0.5]	12.2
High kappa carbonate	7.5	345	90.9 [2.9]	55.3 [0.4]	9.8
High kappa carbonate kappa adjusted h factor to similar delignification	7.5	327	95.8 [2.3]	56.3 [0.5]	9.5
Low Kappa no carbonate	0	1145	32.4 [1.6]	45.4 [0.9]	9.2
Low Kappa carbonate	7.5	1145	30.0 [2.6]	45.1 [0.6]	8.6

Table 2. “Kraft Cooking summary with and without carbonate loading of laboratory synthetic kraft white liquors. All cooks utilized 18.0% AA on oven dried wood basis, at about 25% sulfidity calculated on a TTA Na₂O basis; cook temperature 165 deg C; time to temperature 50 minutes; 4:1 liquor to wood ratio which included chip moisture. Table value represents the average of five independent cooks, the standard deviation where appropriate represented in brackets [std dev] *note: EA as describe by equation (1); there is no alkali compensation given to sodium carbonate content; kept %AA constant, % EA varied to maintain % sulfidity on TTA basis

The influence of the high carbonate content white liquor cooks on kappa and yield are shown in Figures 1 and 2, respectively. The addition of the carbonate demonstrated a clear statistical difference in the delignification rate with all other cooking variables held constant. It was imperative the white liquor charge was balanced when adding the carbonate to give the same sulfidity calculated on a TTA basis with the denominator represented in equation 3. This was

kept close to twenty-five percent. It is very well known that sulfidity has a strong response to the delignification response in kraft cooking [4]. It was imperative to keep this constant to study only the influence of the carbonate content. At the level of carbonate studied the high yield softwood delignification response was accelerated. If carbonate content becomes appreciable in the white cooking kraft liquor, the contributions of equation (5) may become relevant in high yield cooking. Sodium carbonate contribution to the alkali profile in the initial phases of the delignification can no longer be considered as inactive in the liquor charge. In response to the accelerated delignification, the same liquor charge was made, and the h factor based on time was reduced while maintaining the same cooking temperature. As a net result the kappa result was increased as seen in Figure 2 where the delignification result was no longer statistically significant with or without the carbonate. As a result of this cooking change Figure 2 shows an increase in total cook yield by as much as one yield percentage point with the presence of carbonate compared at a constant delignification level. Elevated carbonate in a kraft cook may pose some advantage to yield preservation. A true carbohydrate measurement was not conducted to identify which carbohydrates were preserved but suggested for future study. Inspection of the residual alkali after these cooks in the generated black liquor confirmed adequate alkali charge was being made; however, since the calculation is represented only by equation (1) this may be an under representation of total alkali remaining if the carbonate does contribute to the cooking alkali. A TTA of the residual cooking black liquor was not made.

The cooking reaction was then allowed to continue to higher h factor targets, same temperature but increasing time to push the reactions through bulk delignification phase to produce bleachable softwood kappa. Cooking results for kappa and total yield are shown in Figures 3 and 4, respectively. In this case, identical cooking conditions produced delignification that was not shown to be statistically different for the five independent cooks made for each carbonate loading of Table 2. A reduction of about 2.4 kappa points was noted for the carbonate addition cooks but, over five separate repeat cooks, was not found to be statistically significant. The total yield determinations at the lower kappa softwood cooking were also found not to be statistically different in Figure 4. This aligns with traditional thought that carbonate content in white liquor from poor causticizing for traditional low yield cooks are not statistically different. Figure 5 shows the residual effective alkali measured from the residual black liquor after cooking for each condition. Plenty of alkali was utilized for these cooks to achieve the desired delignification with good residual alkali levels remaining. The low kappa target conditions consumed more alkali as expected.

After cooking select batches at each repeated identical cooking conditions, cooks were combined to form a batch composite to provide enough furnish to accomplish a traditional valley beater run for both the low and high kappa pulps. Figure 6 represents a typical beater curve showing measured pulp freeness CSF (ml) versus beating time of the pulp. As expected, the biggest difference in beating was due to the delignification with lower lignin containing softwood providing for a faster freeness development curve. The low kappa furnish containing carbonate or not showed little freeness development difference. The larger influence on beating time was

seen on the ability of the carbonate containing high yield cooks to beat much faster than their control. For a development to 500 ml CSF, it took twenty-five minutes longer to develop pulps cooked without carbonates to the same level of freeness. This suggests that carbonates through the additional alkali content in the liquor from the ionic disassociation may be influencing the lignin removal rate from the primary cell wall. It has been explained in the literature that an extremely high percentage of lignin resides within the primary cell wall and the middle lamella layers of the wood fiber [7]. Improved alkali profiles early in the delignification phases may be facilitating lignin removal at an accelerated rate earlier in the delignification at the cell wall which allows for improved refining response. Data is only preliminary and the influence needs to be scaled to disk refining with calculated energy per ton refining inputs at a given intensity. Earlier reports have suggested calcium ionic influences from the wood as a mechanism [8] but remains beyond the scope of this work.

Select strength properties were examined from these pulps with relevance to grades produced with these kappa numbers. It does not represent a complete list but enough of the fundamental properties to scan for the influence of carbonates at the applied levels. Bleaching was not conducted in this study but would remain a next step to final bleachable grade softwood.

Containerboard remains a staple product utilizing the high yield southern yellow pine with its dominance in the Southeastern United States. Figures 7 and 8 plot two familiar containerboard properties for short span compression (SCT) and Mullen burst, respectively. Strength testing included the lower kappa unbleached softwood as well for demonstrating the influence of the lignin content on strength developments but traditional linerboard is typically not made at this kappa. The obvious strength improvement with reduced lignin content was evident with good differentiation of the error bars. Within similar delignification though, any strength differences were not as evident with overlapping error bars. Although the difference in beating times were different for the higher kappa pulps. For the same freeness development similar SCT and burst behavior was demonstrated.

Further strength developments including tear versus tensile performance more relevant to kraft bag properties are shown in Figures 9. Again, the strong dependence on lignin content of these kraft cooked softwood fibers was highly evident with good error bar separation of the curves. Lower kappa or higher delignification levels led to higher strength characteristics. Tear goes through its traditional peak with some refining followed by a reduction as tensile continues to build. No significantly different measurable strength differences were observed for the changes in carbonate studied at each specific delignification level; however, the lignin content remained the dominant factor.

Conclusions

Influence of levels of sodium carbonate in the range studied in traditional laboratory kraft cooks demonstrated a decreased refining response to a given freeness level at the higher kappa numbers. If valid, it has large implications on the energy demands of ever-increasing lignin content fibers in the pursuit of higher total yields for the purposes of containerboard production. Interaction of the specific ionic components or the alkali profile induced from sodium carbonate with the primary cell wall delignification of softwoods prior to and entering the bulk delignification phase may have a key role influencing the refining response of high kappa pulps. This effect is diminished as bleachable grade kappa is produced. The response of strength characteristics versus delignification levels was expected and was the dominate influencer on both refining development and several strength characteristics. For the recommendation whether to include carbonates in laboratory made down white liquors, from a strength to specific freeness values there did not appear to be much influence at the carbonate level studied. The general conclusion for any pulping yield delignification h factor study and even studies involving later refining operations at defined energy inputs, it is highly encouraged to include carbonates in the make down of laboratory kraft cooking liquors.

Acknowledgment

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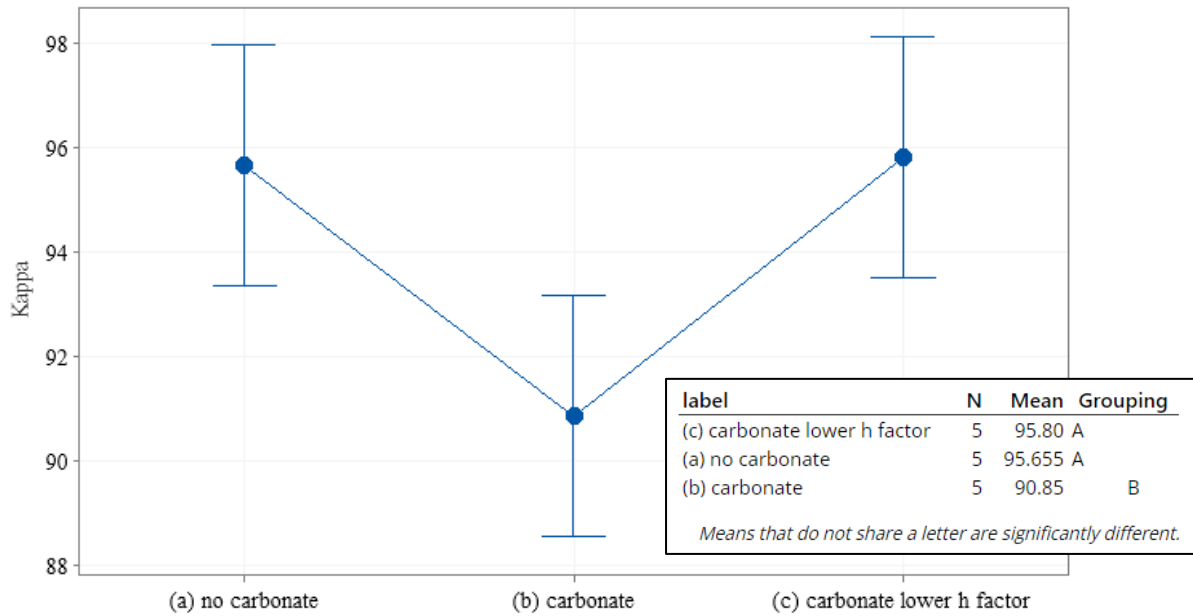


Figure 1. High kappa number response to carbonate loading for containerboard softwood pulp. 18% AA on wood; 25% sulfidity on TTA basis, 4:1 Liquor to Wood Ratio. Each data point an average of five independent cooks. (a) no carbonate; 0% Na₂CO₃ on OD Wood; h-factor 345; (b) carbonate; 7.5% Na₂CO₃ on OD Wood; h-factor 345; (c) carbonate lower h-factor; 7.50% Na₂CO₃ on OD Wood; h-factor 327.

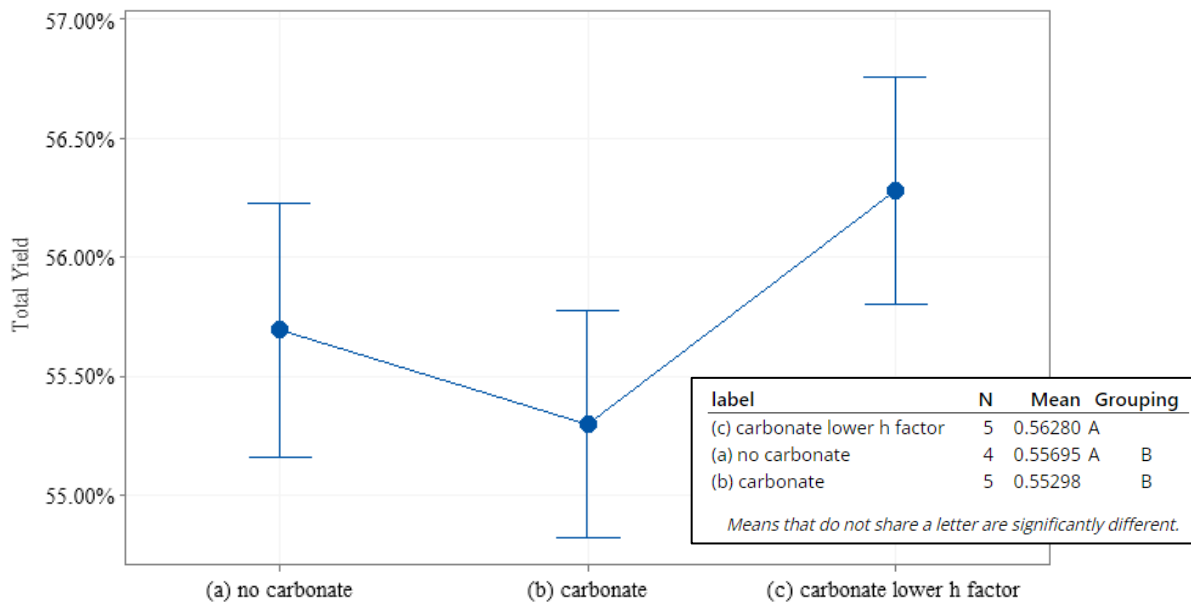


Figure 2. Total yield response to carbonate loading for containerboard pulp. high kappa. 18% AA on wood; 25% sulfidity on TTA basis, 4:1 Liquor to Wood Ratio. Each data point an average of five independent cooks. (a) high kappa 95.7; no carbonate; 0% Na₂CO₃ on OD Wood; h-factor 345; (b) high kappa 90.9; carbonate; 7.5% Na₂CO₃ on OD Wood; h-factor 345; (c) high kappa 95.8; carbonate lower h-factor; 7.5% Na₂CO₃ on OD Wood; h-factor 327.

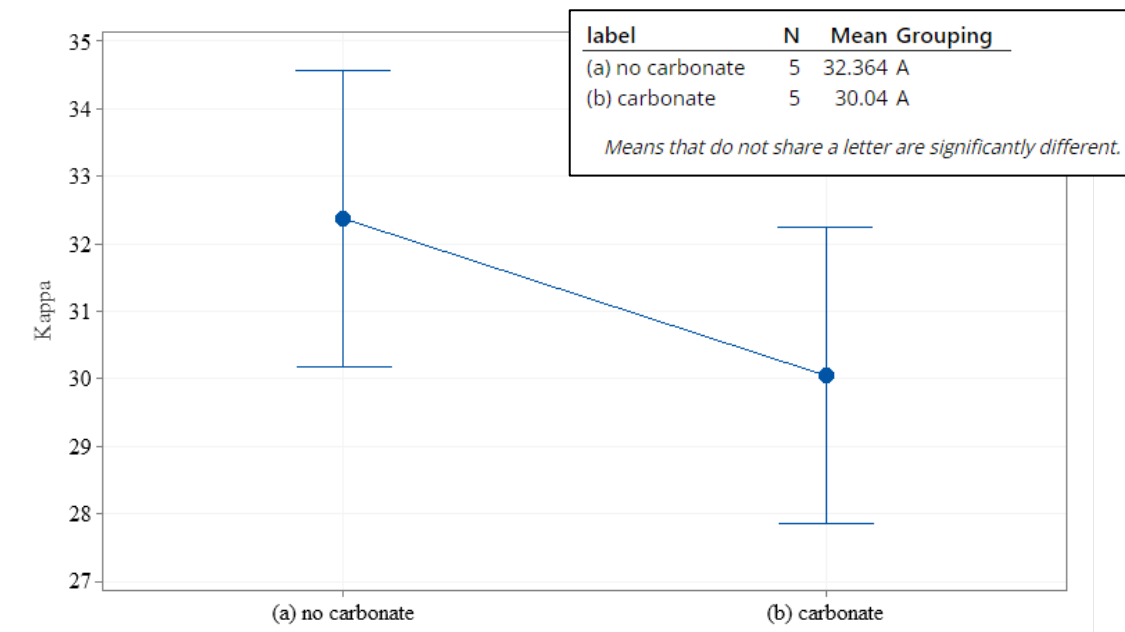


Figure 3. Low kappa number response to carbonate loading for bleachable grade softwood. 18% AA on wood; 25% sulfidity on TTA basis, 4:1 Liquor to Wood Ratio. Each data point an average of five independent cooks. (a) no carbonate; 0% Na₂CO₃ on OD Wood; h-factor 1145; (b) carbonate; 7.5% Na₂CO₃ on OD Wood; h-factor 1145.

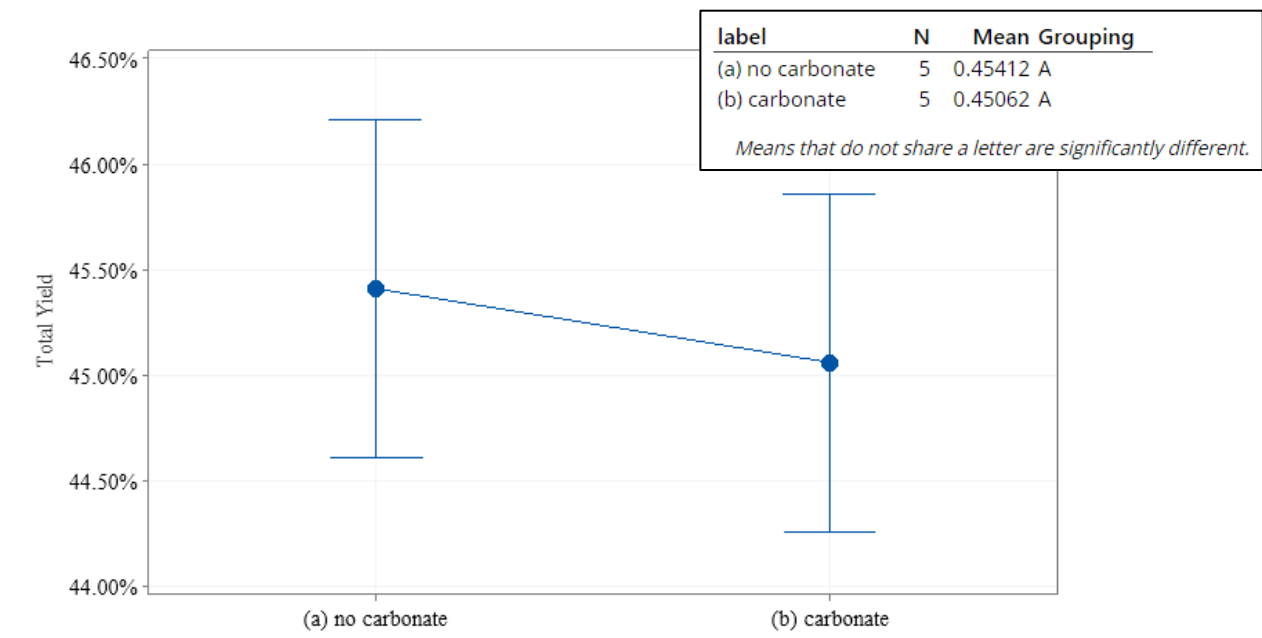


Figure 4. Total yield response to carbonate loading for bleachable grade softwood pulp. 18% AA on wood; 25% sulfidity on TTA basis, 4:1 Liquor to Wood Ratio. Each data point an average of five independent cooks. (a) low kappa 32.4; no carbonate; 0% Na₂CO₃ on OD Wood; h-factor 1145; (b) low kappa 30.0; carbonate; 7.5% Na₂CO₃ on OD Wood; h-factor 1145.

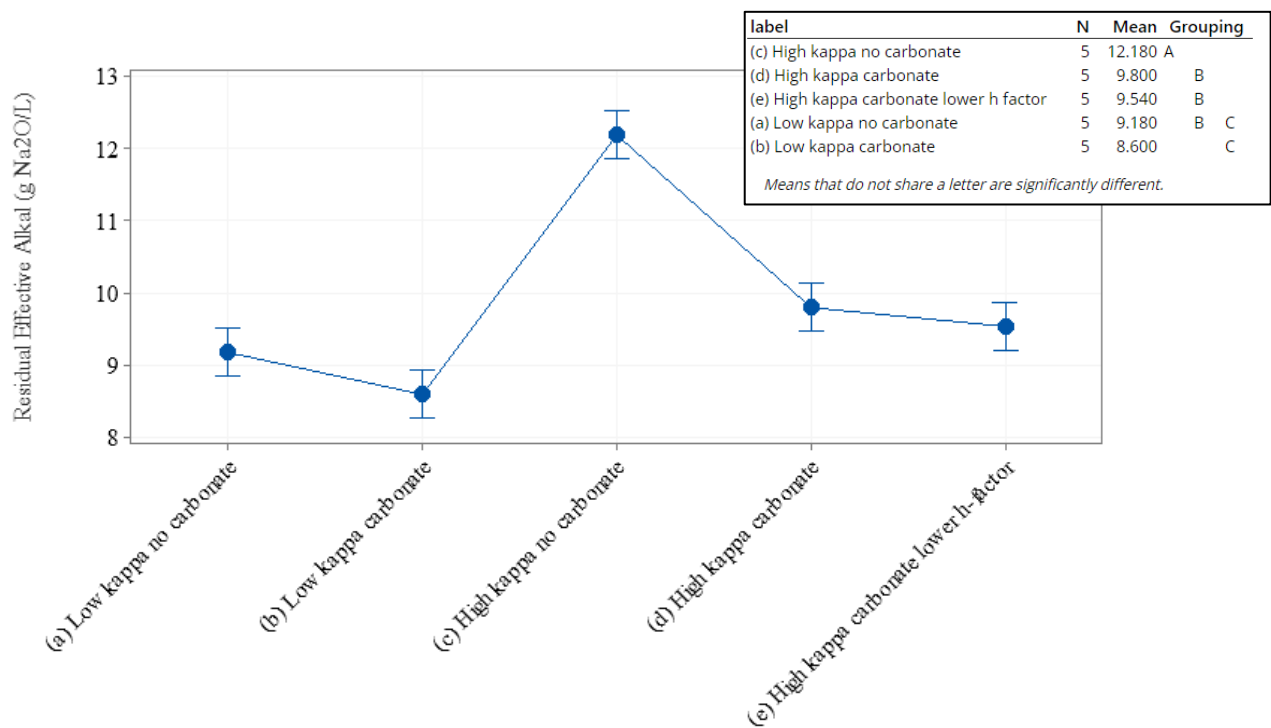


Figure 5. Residual effective alkali levels all pulping conditions. 18% AA on wood; 25% sulfidity on TTA basis, 4:1 Liquor to Wood Ratio. Each data point an average of five independent cooks. (a) low kappa 32.4; no carbonate; 0% Na_2CO_3 on OD Wood; h-factor 1145; (b) low kappa 30.0; carbonate; 7.5% Na_2CO_3 on OD Wood; h-factor 1145. (c) high kappa 95.7; no carbonate; 0% Na_2CO_3 on OD Wood; h-factor 345; (d) high kappa 90.9; carbonate; 7.5% Na_2CO_3 on OD Wood; h-factor 345; (e) high kappa 95.8; h-factor 327.

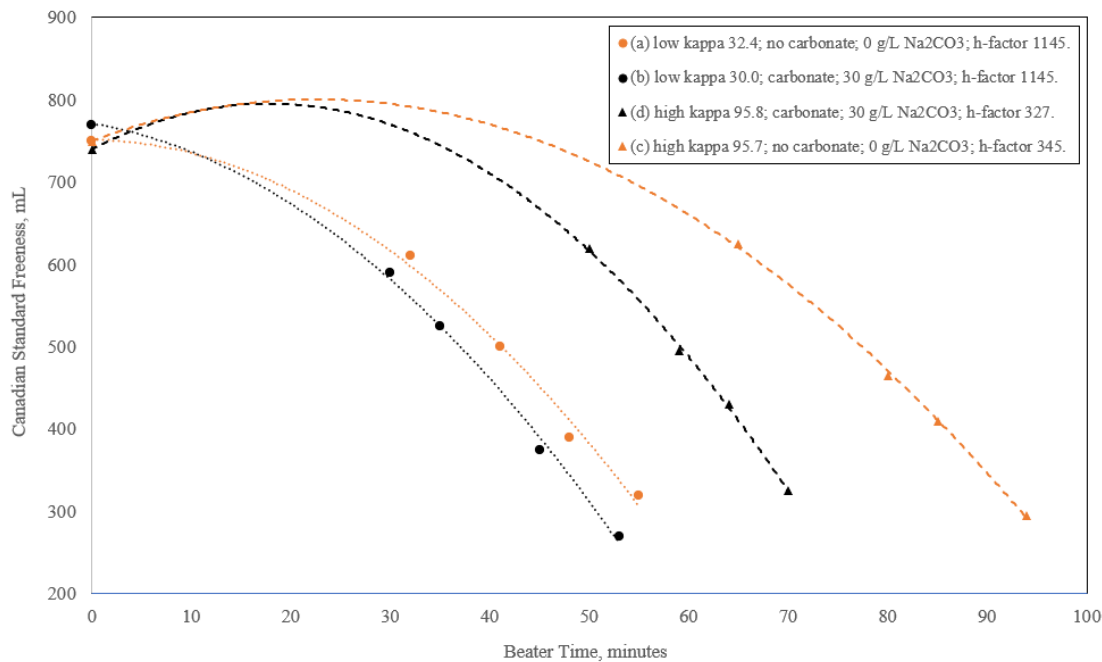


Figure 6. Valley beater refining response for softwood pulp cooked with and without sodium carbonate for two kappa targets. (a) low kappa 32.4; no carbonate; 0% Na_2CO_3 on OD Wood; h-factor 1145; (b) low kappa 30.0; carbonate; 7.5% Na_2CO_3 on OD Wood; h-factor 1145. (c) high kappa 95.7; no carbonate; 0% Na_2CO_3 on OD Wood; h-factor 345; (d) high kappa 95.8; carbonate; 7.5% Na_2CO_3 on OD Wood; h-factor 327.

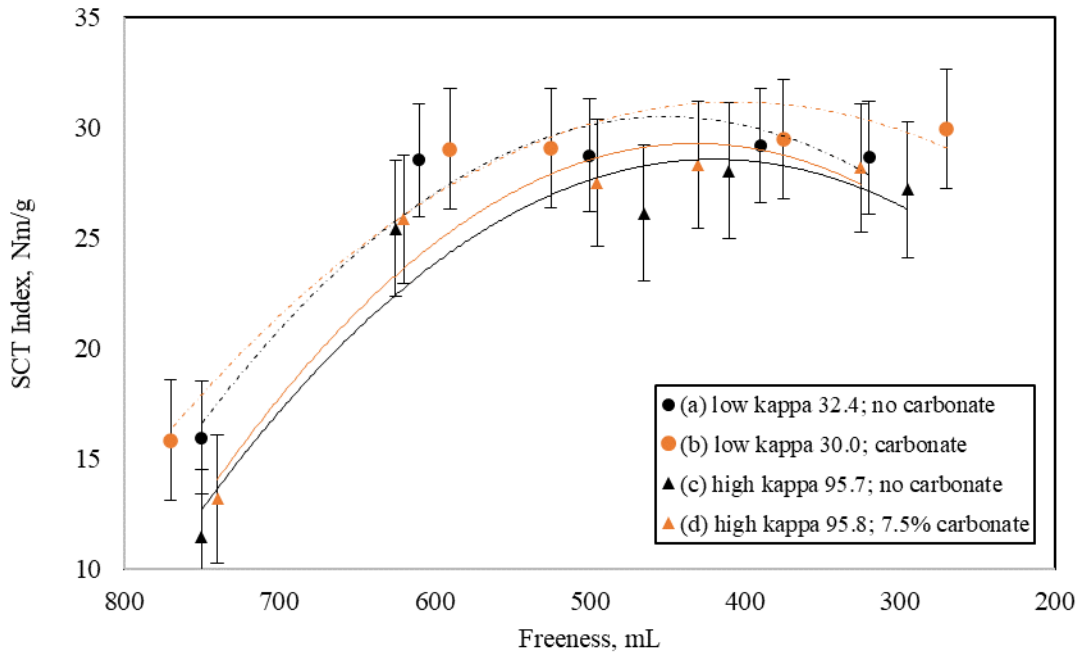


Figure 7. Short span compression response for the refining of softwood pulps cooked with and without sodium carbonate for two kappa targets. (a) low kappa 32.4; no carbonate; 0% Na_2CO_3 on OD Wood; h-factor 1145; (b) low kappa 30.0; carbonate; 7.5% Na_2CO_3 on OD Wood; h-factor 1145. (c) high kappa 95.7; no carbonate; 0% Na_2CO_3 on OD Wood; h-factor 345; (d) high kappa 95.8; carbonate; 7.5% Na_2CO_3 on OD Wood; h-factor 327.

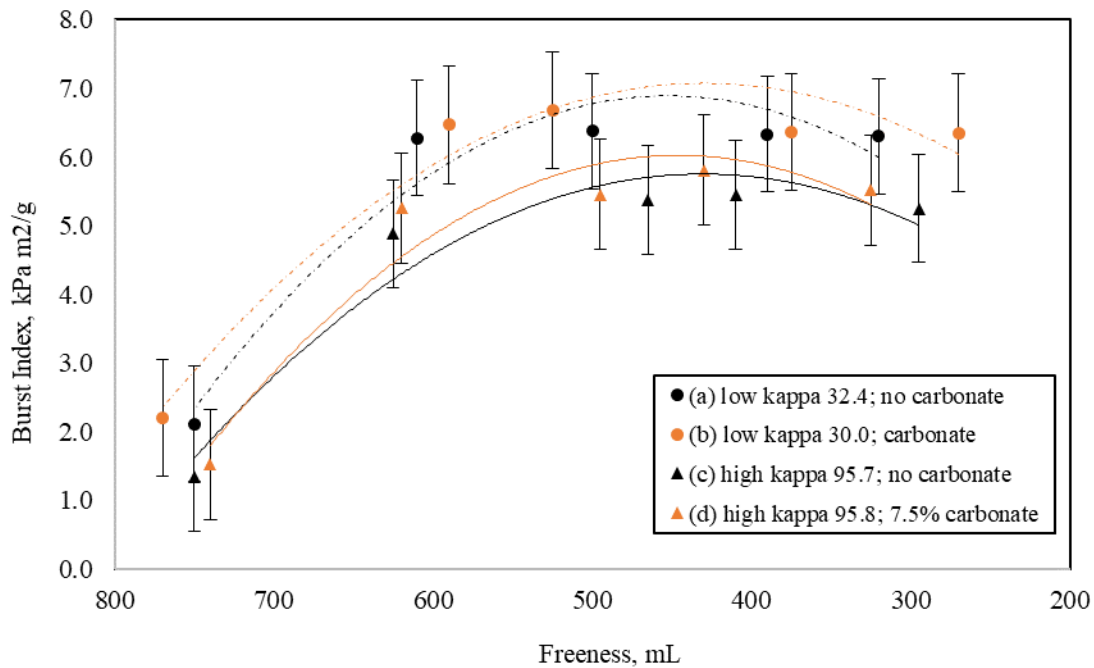


Figure 8. Bursting strength response for the refining of softwood pulps cooked with and without sodium carbonate for two kappa targets. (a) low kappa 32.4; no carbonate; 0% Na_2CO_3 on OD Wood; h-factor 1145; (b) low kappa 30.0; carbonate; 7.5% Na_2CO_3 on OD Wood; h-factor 1145. (c) high kappa 95.7; no carbonate; 0% Na_2CO_3 on OD Wood; h-factor 345; (d) high kappa 95.8; carbonate; 7.5% Na_2CO_3 on OD Wood; h-factor 327.

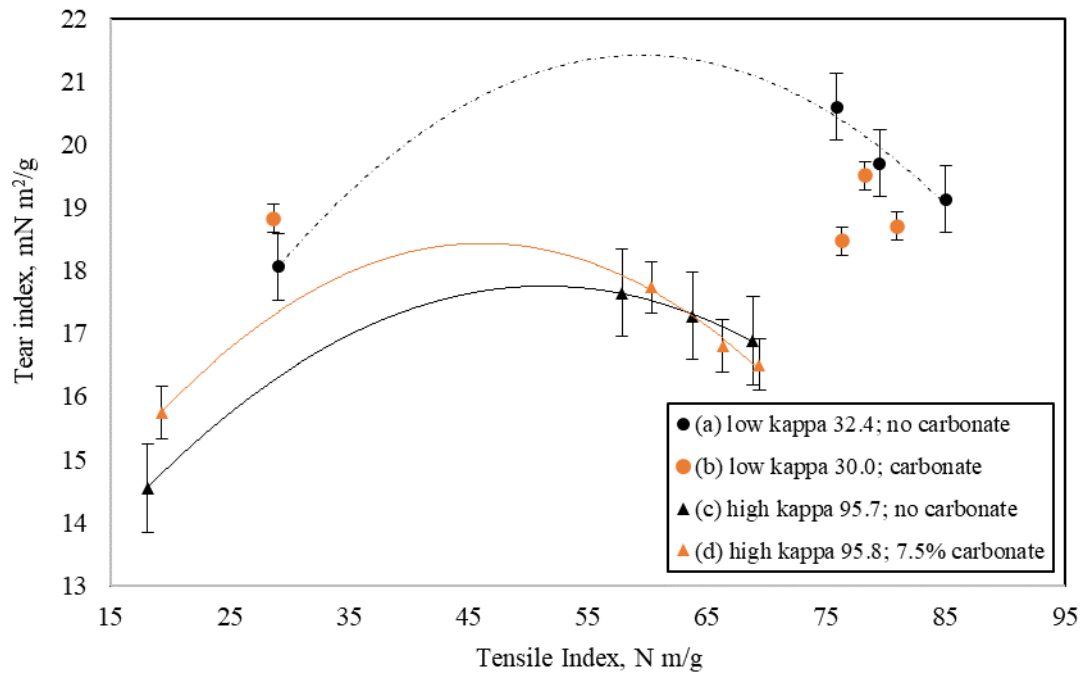


Figure 9. Tear versus tensile response for the refining of softwood pulps cooked with and without sodium carbonate for two kappa targets. (a) low kappa 32.4; no carbonate; 0% Na₂CO₃ on OD Wood; h-factor 1145; (b) low kappa 30.0; carbonate; 7.5% Na₂CO₃ on OD Wood; h-factor 1145. (c) high kappa 95.7; no carbonate; 0% Na₂CO₃ on OD Wood; h-factor 345; (d) high kappa 95.8; carbonate; 7.5% Na₂CO₃ on OD Wood; h-factor 327.