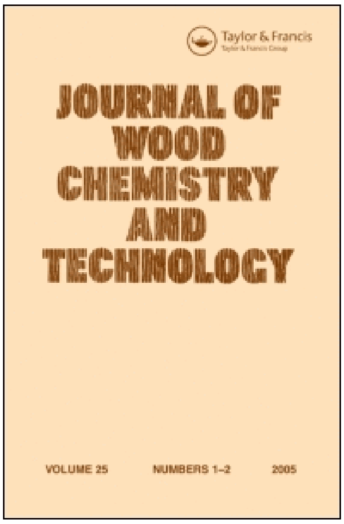

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EXTENDED DELIGNIFICATION KRAFT PULPING OF SOFTWOODS - EFFECT OF TREATMENTS ON CHIPS AND PULP WITH SULFIDE-CONTAINING LIQUORS*

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ABSTRACT

Pretreatment of softwood chips with Na_2S liquors at moderately-elevated temperatures prior to a kraft stage delignification resulted in higher pulp viscosity at a given kappa number as compared to that of a conventionally-cooked reference kraft pulp. Final pulp yields were equivalent to, or slightly better than for conventional kraft pulps. The high viscosity is due to the lower alkali requirement during the kraft stage as a result of the pretreatment. The decreased alkali requirement is due to the extraction and removal of hemicelluloses during pretreatment which normally produce sugar acids via peeling reactions. The presence of sulfide in the pretreatment promotes lignin degradation and also enhances polysaccharide stability during the subsequent kraft stage. When kraft pulps, pretreated with sulfide-containing liquors, were further delignified in an oxygen stage, lower kappa numbers at equivalent viscosity were obtained versus conventional kraft-O_2 treatment. This enhanced polysaccharide stability toward an oxygen stage can also be achieved by treating a conventional kraft pulp with sulfide-containing liquors, including green liquor and black liquor, but a lesser effect is achieved compared with chip pretreatment.

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INTRODUCTION

Extending kraft pulp delignification by means of an oxygen prebleaching stage results in decreasing bleach plant effluent and pollutant loads since the oxygen-stage effluent may be recycled to the conventional kraft recovery systems. However, only about 50% of the residual kraft pulp lignin may be removed in an oxygen stage before severe carbohydrate degradation occurs. The remaining lignin must still be removed with expensive and corrosive chlorine-based chemicals. If the existing pulping process could be modified to improve delignification selectivity beyond current practice (~30-35 kappa number for softwoods), then the feasibility of eliminating the conventional chlorine and extraction stages may be expected. This would allow the use of mainly chlorine dioxide in subsequent bleaching stages and significantly decrease bleach plant effluent load and toxicity. The effluents would then be treatable in existing wastewater treatment facilities and allow the mill to meet present or future regulations at greatly reduced risk of having to purchase and install advanced treatment technology.

Clearly, opportunity for significant savings in capital and operational costs would be possible if either, or both, the kraft and oxygen delignification stages were improved to allow extended delignification without severe losses of pulp yield and strength. For this reason, extended delignification has been dealt with in recent research by several groups. Hartler (1-2), Teder (3-4) and their coworkers have demonstrated the feasibility of extended delignification at lab-scale by optimal control of alkali, hydrosulfide ion and dissolved lignin during the various stages of a kraft cook. These approaches are relatively complicated and retrofit to existing digesters, especially batch, may be difficult. McDonough and Van Drunen (5-7) pulped southern pine to low lignin contents by applying anthraquinone (AQ) at 0.2-0.3% and also by applying high effective alkali (18-22%) and liquor sulfidities (38-40%). The AQ dosage is currently outside legal limits and although the high chemical costs may be offset by lower associated bleaching and waste treatment costs, the increased inorganic load to the chemical recovery system may be a critical problem for retrofit into an existing kraft mill.

Our approach (19) to extending delignification is to search for simple modifications that are fully compatible with currently-existing technology. Our aim is to provide techniques that would allow retrofit at minimum disturbance into an existing mill. This paper reports the preliminary results of research efforts toward this goal. Results of material balances and computer simulation based on these data have already been published (20).

RESULTS AND DISCUSION

Effect of Post-Kraft Pulp Treatment with Sulfide-Containing Liquors Prior to Oxygen Delignification

Preliminary experiments were aimed at testing a variety of post-kraft treatments prior to oxygen delignification. From these screening results we generally found that various reducing agents gave significant improvements in subsequent oxygen stage selectivity (i.e., viscosity at a given kappa number). The two reagents of greatest interest were sodium borohydride and sodium sulfide.

As a base case, kraft pulp (34.4 kappa number - 29.8 mPa•s viscosity) was treated with the proven reducing agent, sodium borohydride, under ambient conditions for 48 hours. A modest decrease in kappa number was observed coupled with an increase in viscosity from the initial value. The latter is due to apparent stabilization of polysaccharides towards degradation in the cuene reagent used in the TAPPI T-230 viscosity measurement. Some degradation is known to occur during this analytical technique (8). However, when the borohydride-stabilized pulp was subjected to a conventional oxygen stage treatment, the viscosity of the resultant pulp at any given kappa number was about 4 mPa•s higher than comparable kraft-O_2 without borohydride. Thus, reduction of the carbonyl group- in the pulp apparently decreases polysaccharide degradation during both cuene viscosity measurement and oxygen bleaching. However, borohydride is too expensive for commercial practice and a cheaper reagent was sought.

The same kraft pulp was treated with an aqueous Na_2S solution at three temperatures (105°C, 135°C and 165°C). Figure 1 illustrates that this treatment results in some considerable delignification (24-45% of initial kappa), especially at high temperatures, with minimal loss of viscosity. The low temperature (105°C) sulfide treatment resulted in a higher-than-initial viscosity indicating a stabilization of carbohydrates toward the cuene reagent as was observed for borohydride. When these pulps were subjected to oxygen delignification, the resulting pulps were about 5 mPa•s higher in viscosity than their conventional kraft-O_2 counterparts at any given kappa number. This result was even better than the experience with the borohydride-stabilized pulps treated similarly. This sulfide treatment then permits pulps of 10-12 kappa number after a conventional oxygen stage while maintaining the same viscosity as for conventional kraft-oxygen pulps at 15-17 kappa number. Thus, the sulfide treatment plus oxygen delignification removes 65-70% of the residual kraft pulp lignin as compared to 50-55% removal with only oxygen treatment.

The Na_2S treatments, although cheaper than borohydride, were still considered to be too expensive for commercial practice. However, similar results were obtained when conventional green liquor (1.2% Na_2S on O.D. pulp) was applied at 135°C. In this case, a combined green liquor-oxygen delignification treatment resulted in obtaining 10-11 kappa number while still maintaining a 4 mPa•s increase in viscosity versus conventional treatment. These results are particularly interesting since green liquor is a readily available source of sulfide-containing liquor in a kraft mill. Such a treatment at commercial scale could be carried out in the high-heat washing zone of a continuous digester or in the recently-developed pressurized diffuser washer (9).

Although sulfide ion has been proposed to act as a reducing agent in kraft pulping, there is no reason to believe that it can reduce the carbonyl groups in polysaccharides as does borohydride. It therefore remains to be determined what role the sulfide ion plays in stabilizing polysaccharides during cuene viscosity analysis and oxygen delignification. As encouraging as these

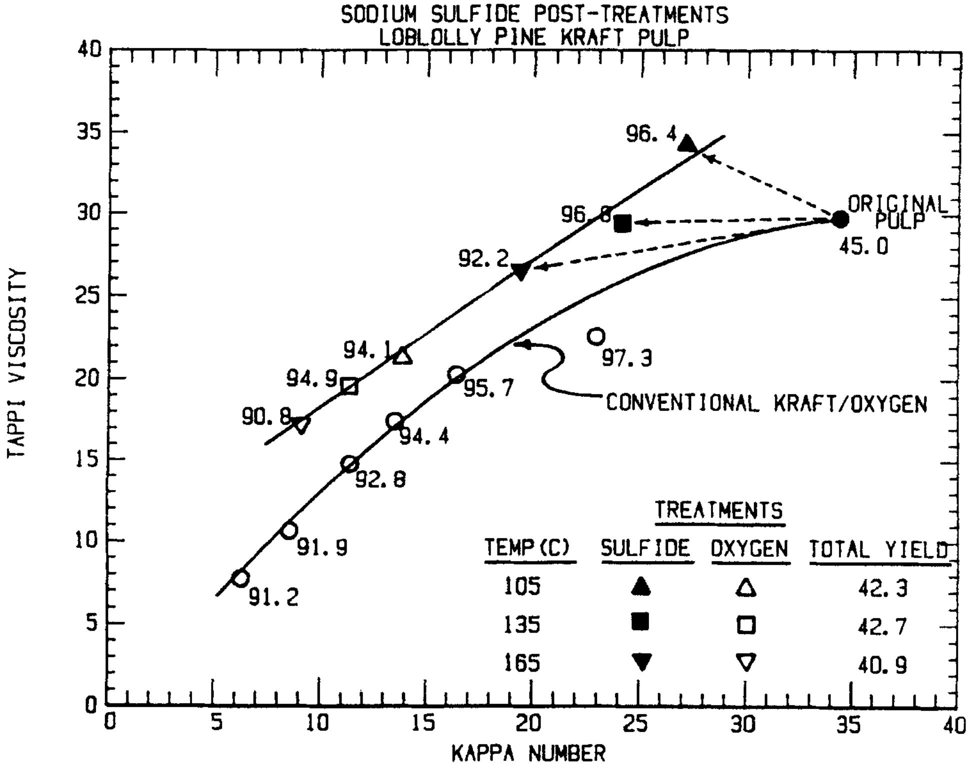

Figure 1: Effect of sodium sulfide treatments of kraft pulp on the viscosity and kappa number of oxygen-delignified pulp. Sulfide charges were 8.7 wt-% as Na_2O based on O.D. pulp. Numbers are yields based on original pulp. Total yields refer to the original wood chip basis.

current results are, the overall process and treatment conditions have not yet been optimized. These are the subjects of current study.

Pretreatment of Chips with Sulfide-Containing Liquors

Our discovery that pretreatment of pulp with sulfide-containing liquors improved carbohydrate stability prompted us to examine the possibility that similar treatment, applied to wood chips prior to kraft stage cooking, would have similar benefits. Various ways of wood chip pretreatment with sulfide-containing liquors to improve yield and kraft pulp properties have been examined (10-12). Figure 2 shows that pretreatment of loblolly pine chips with sulfide-containing liquors prior to a kraft stage delignification results in higher pulp viscosity than that of the conventionally-cooked kraft pulp at equivalent kappa number. It is therefore possible to cook to lower kappa numbers while maintaining the same viscosity as conventional kraft. Furthermore, these results imply that incremental viscosity improvements are possible by increasing the Na_2S concentration of the pretreatment liquor.

Those pulps in Figure 2 having bleachable-grade kappa numbers (30-35) were delignified in a follow-up oxygen stage and compared against a reference kraft-O_2 pulp under the same conditions (Figure 3). Pretreatment of chips with conventional green liquor (CGL) prior to kraft stage delignification resulted in a pulp having nearly identical kappa number and viscosity versus its conventional kraft counterpart. However, treatment through identical oxygen stages resulted in the CGL-pulp having higher final viscosity than the reference kraft pulp at any given level of delignification. Therefore, CGL-pretreatment of wood chips, like CGL-pretreatment of kraft pulp, leads to enhanced stability of polysaccharides in an alkaline-oxygen delignification stage.

Pretreatment with fortified green liquor (HSGL) or pure sodium sulfide solution (Na_2S) resulted in kraft pulps of higher initial viscosity at similar kappa number to that of the reference kraft pulp. In these cases, further delignification through an oxygen stage resulted in both pulps experiencing viscosity decreases much faster than the CGL-pretreated pulp. Only for final kappa numbers greater than 10 do these higher sulfide-containing liquors offer any advantages over CGL-pretreatment. However, all three of the pretreated pulps gave higher final viscosity than the reference kraft pulp when all were treated by an identical oxygen stage to a given kappa number.

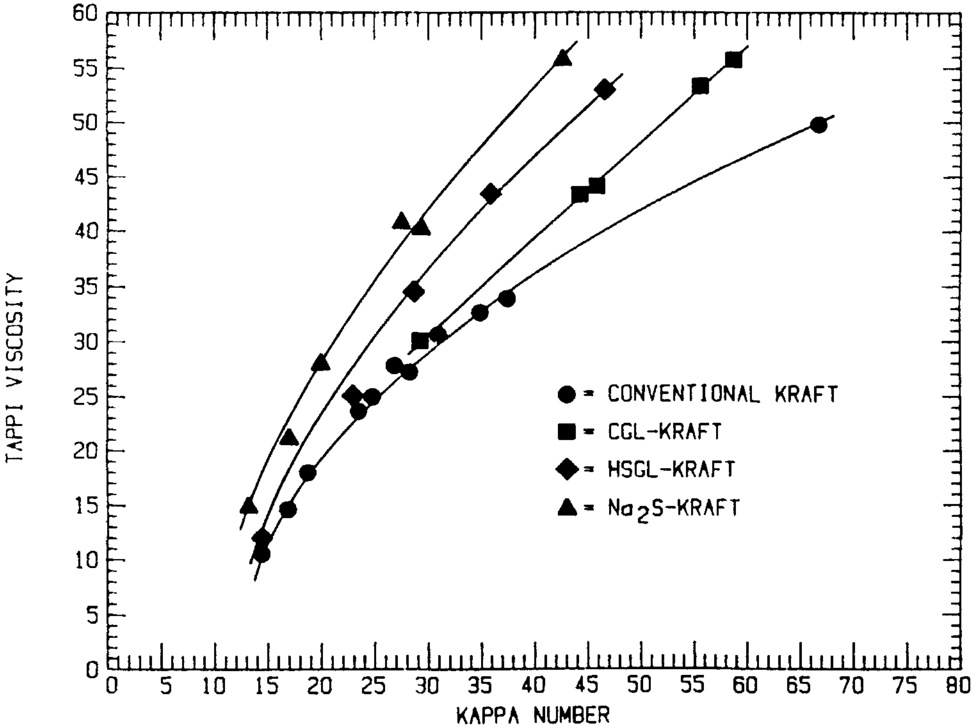

Figure 2: Effect of sulfide-containing liquor pretreatments of loblolly pine chips on pulp viscosity as a function of the kappa number after the kraft stage.

CGL = conventional green liquor
HSGL = high sulfidity (fortified) green liquor

When the Na_2S pretreated chips of Figure 3 were delignified in a kraft cook to a viscosity similar to that of the reference kraft pulp, a kappa number of 20 was obtained representing a 33% residual lignin reduction compared to the 30 kappa number reference kraft pulp (Figure 4). When this pulp was subjected to a subsequent oxygen stage, the final pulp viscosities were significantly better than those obtained from all of the higher kappa number pulps. In this case, oxygen-stage delignification to well below 10 kappa number was obtained while still maintaining acceptable viscosities. It is also pointed out that final oxygen stage pulp yields for the sulfide-liquor pretreatments in Figures 3 and 4 were at least

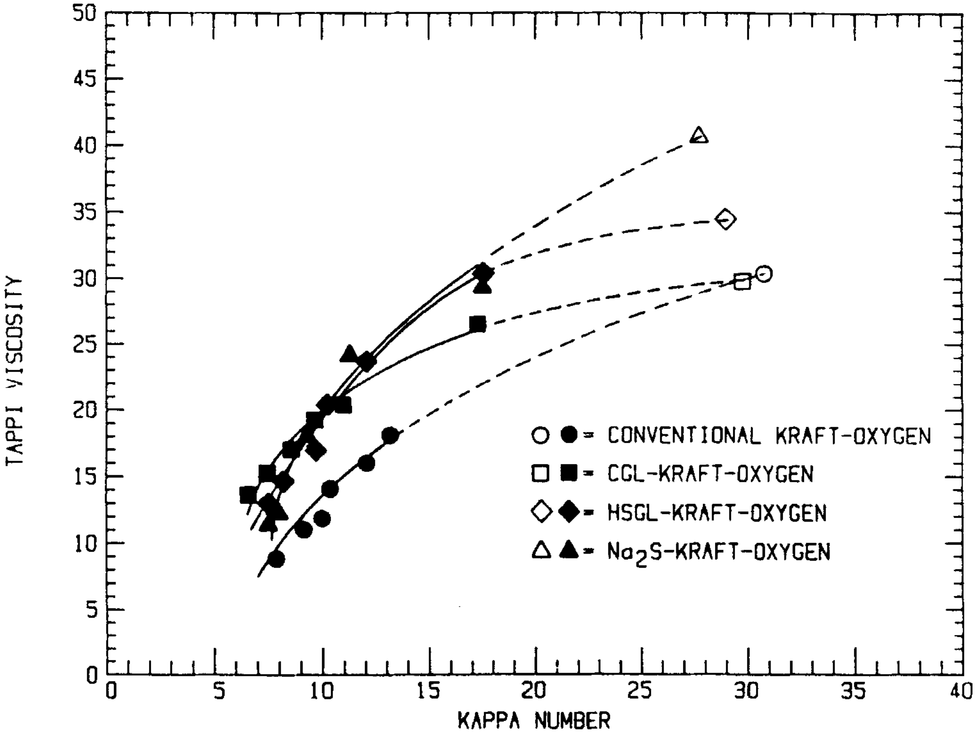

Figure 3: Effect of oxygen delignification on viscosity for loblolly pine chip-pretreated pulps.

equivalent to, or slightly better than those of the reference kraft-O_2.

Effect of Chip Pretreatment on the Alkali Requirement During Kraft-Stage Delignification

In addition to the benefits of extended delignification, chip pretreatment with sulfide-containing liquors results in a considerable decrease (25-50%) in the required effective alkali for the kraft stage as illustrated by the examples in Figures 5 and 6.

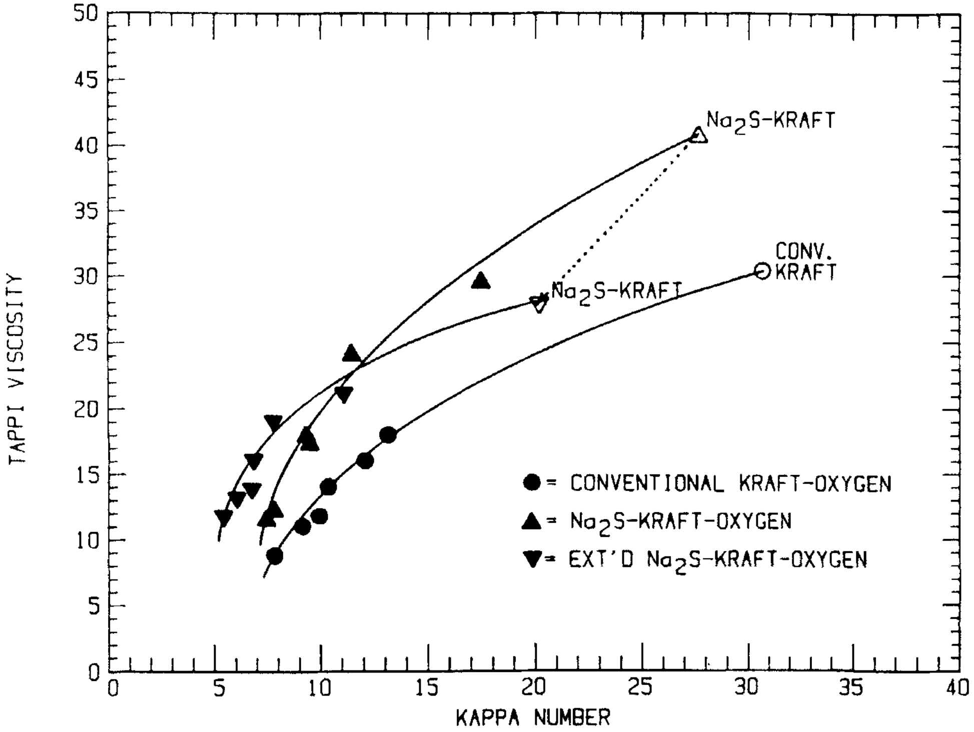

Figure 4: Effect of extended kraft-stage delignification on the final oxygen stage pulp viscosity for sodium sulfide-pretreated chips from mature loblolly pine.

The higher the sulfide dosage on chips during pretreatment, the further the reduction in effective alkali to reach bleachable-grade kappa numbers. Similar results were observed by Briggs et al (11) on pretreatment of Eucalyptus chips with sodium hydrosulfide or black liquor.

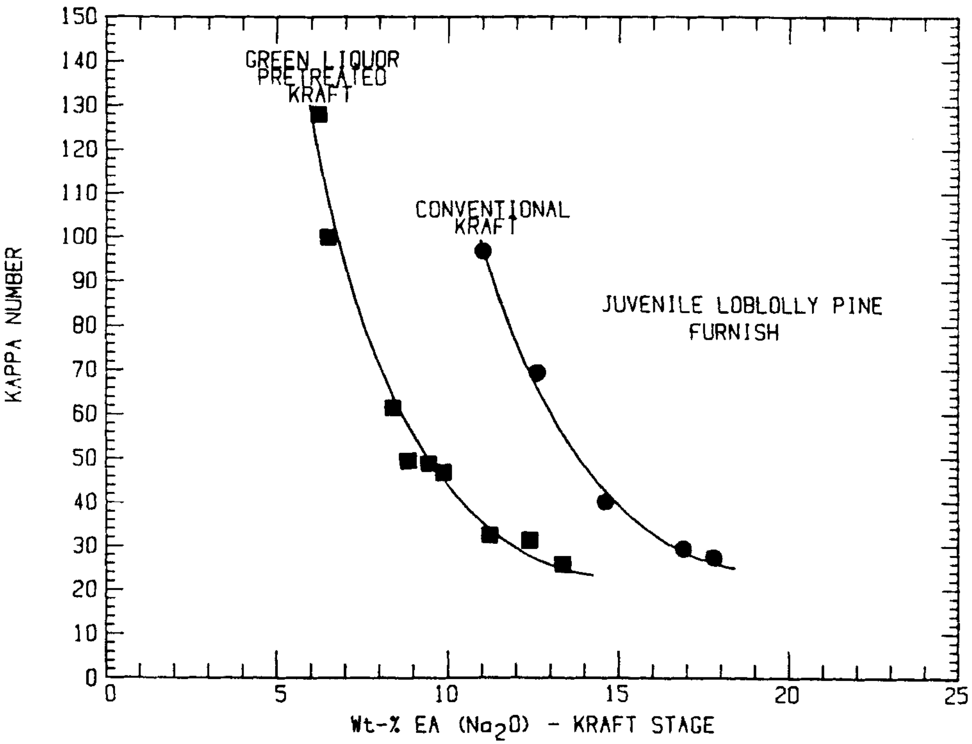

Figure 5: Effect of green liquor pretreatment on the effective alkali (EA) requirements of the kraft stage - juvenile loblolly pine chip furnish.

The Separate Effects of Sulfidity and Alkalinity During the Pretreatment Stage

The fact that pretreatment of chips with sulfide-containing liquors results in decreased alkali requirement, equivalent or better yield and improved pulp viscosity in the subsequent kraft stage is very intriguing. It is generally believed that with the exception of polysulfide, sulfide has little effect on carbohydrates in alkaline pulping (8,13-14). In order to gain a better understanding of the effect of this approach to pretreatment, the influences of sulfidity and alkalinity were

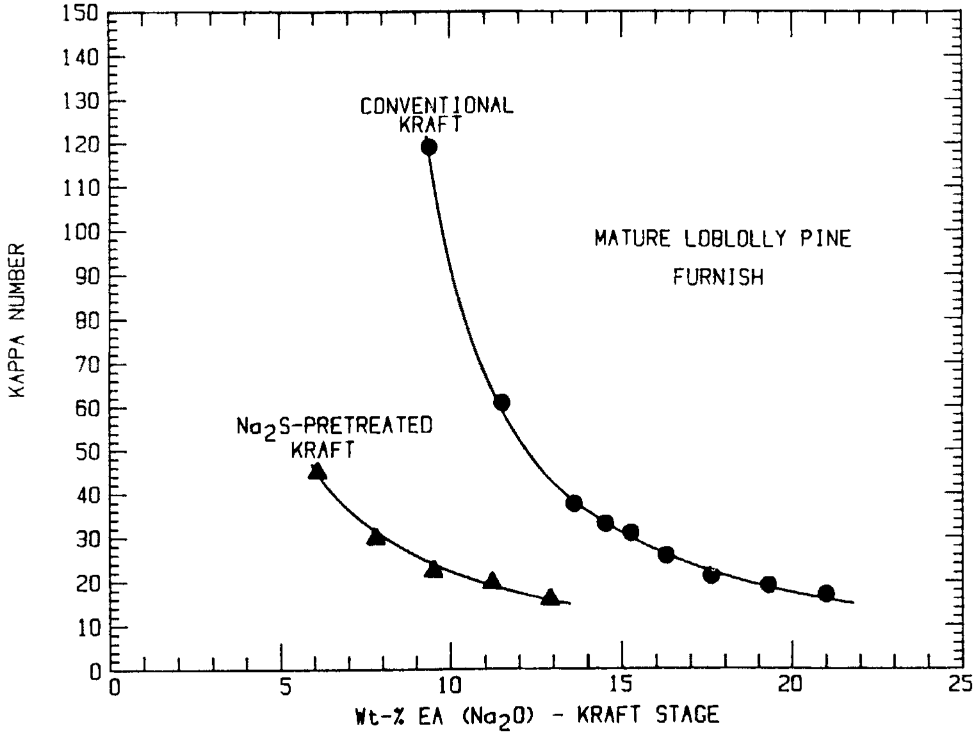

Figure 6: **Effect of sodium sulfide pretreatment on the effective alkali (EA) requirements of the kraft stage - mature loblolly pine chip furnish.**

investigated for this stage using either sodium hydroxide or sodium sulfide as the effective alkali (EA) source. A constant pretreatment stage total titratable alkali (TTA = Na_2S + NaOH + Na_2CO_3) dosage was maintained at 10.5 wt-% (as Na_2O on chips) using sodium carbonate as the make-up alkali. Yield, kappa number and viscosity were measured following a conventional kraft stage in which the conditions of treatment were held constant. As shown in Figure 7, without chip pretreatment, the mild kraft delignification conditions (9.6% EA, 30.8% liquor sulfidity and 1600 H-factor) gave a reference kraft pulp of 117 kappa number (58.9% total yield). If

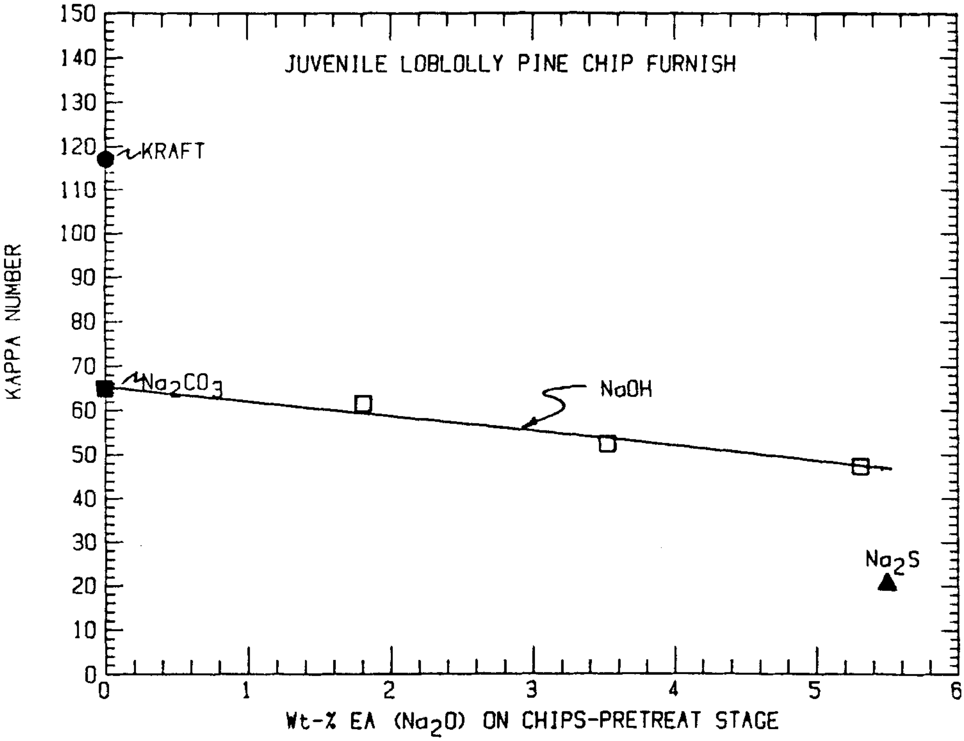

Figure 7: Effect of effective alkali source and dosage during pretreatment on delignification carried through a kraft stage at constant conditions - juvenile loblolly pine chip furnish.

pretreatment is carried out using only Na_2CO_3, a 65 kappa pulp is obtained (47.7% total yield), indicating the significant effect of a weak alkali extraction during pretreatment. Increasing the effective alkali from 0 to 5.3% (on chips) by replacing half of the carbonate with hydroxide results in a further reduction to 47 kappa number (44.4% total yield). Thus, the effect of increased alkalinity (Na_2CO_3 versus NaOH) is relatively small compared to that of Na_2CO_3 only. If hydroxide is replaced by Na_2S at the same 5.3% EA level, a pulp of about 20 kappa number (43.6% total yield) is obtained. Identical results were also obtained on a different batch of chips under a slightly different set of constant kraft cooking conditions as seen in Figure 8. The large incremental effect of carbonate is repeated as well as the smaller hydroxide and sulfide effects. It is also obvious that only a very small amount of sulfide (1-2% as Na_2O on chips) is required to achieve maximum incremental benefit; the effect of additional sulfide being primarily an increase in alkalinity.

These results imply that the reduction in effective alkali required for the kraft stage as a consequence of pretreatment is due largely to the mild alkaline extraction of hemicelluloses, among other substances, and the subsequent removal of most of the dissolved organics between stages. These soluble hemicelluloses would otherwise consume alkali as a consequence of the peeling reaction during a normal kraft cook. This conclusion is supported by the following three experimental results:

1. At a given total effective alkali charge, including that of pretreatment, the final black liquor pH was higher for the kraft cook following pretreatment than for the reference kraft cook.

2. Pretreatment with green liquor at 10.5% TTA resulted in about 20% wood weight loss (80% yield), of which only 8% was attributed to lignin. The remaining 12% was mainly hemicelluloses, galactoglucomonnan being the major component.

This is consistent with the fact that during the early stage of kraft cooking, considerable amounts of hemicelluloses are dissolved (15,16). Since most of the alkali is consumed by the carbohydrate degradation products (17), removal of a part of these carbohydrates should result in a decreased alkali requirement.

3. In a typical procedure used in this study (19), about 70% of the pretreatment liquor is removed prior to addition of white liquor and subsequent kraft cooking. When the pretreatment

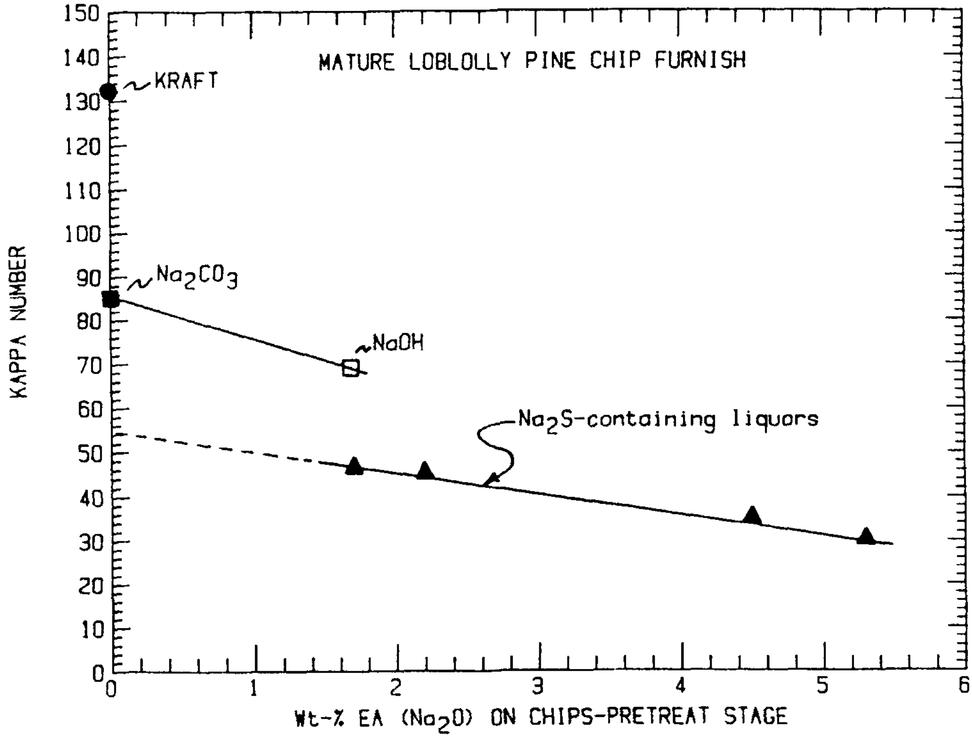

Figure 8: Effect of effective alkali source and dosage during pretreatment on delignification carried through a kraft stage at constant conditions - mature loblolly pine chip furnish.

liquor was not removed, and white liquor was added directly to the pretreatment liquor, the resulting kraft pulp kappa number (64.4) was much higher than in the typical procedure (34.5). Furthermore, the pH of the black liquor was lower for the modified procedure.

While the effect of pretreatment on the subsequent kraft delignification is mainly due to the alkaline extraction of hemicelluloses, the significance of sulfidity during pretreatment on pulp viscosity has been established in Figure 2. This is further confirmed by the results in Figure 9. The absence of sulfide during

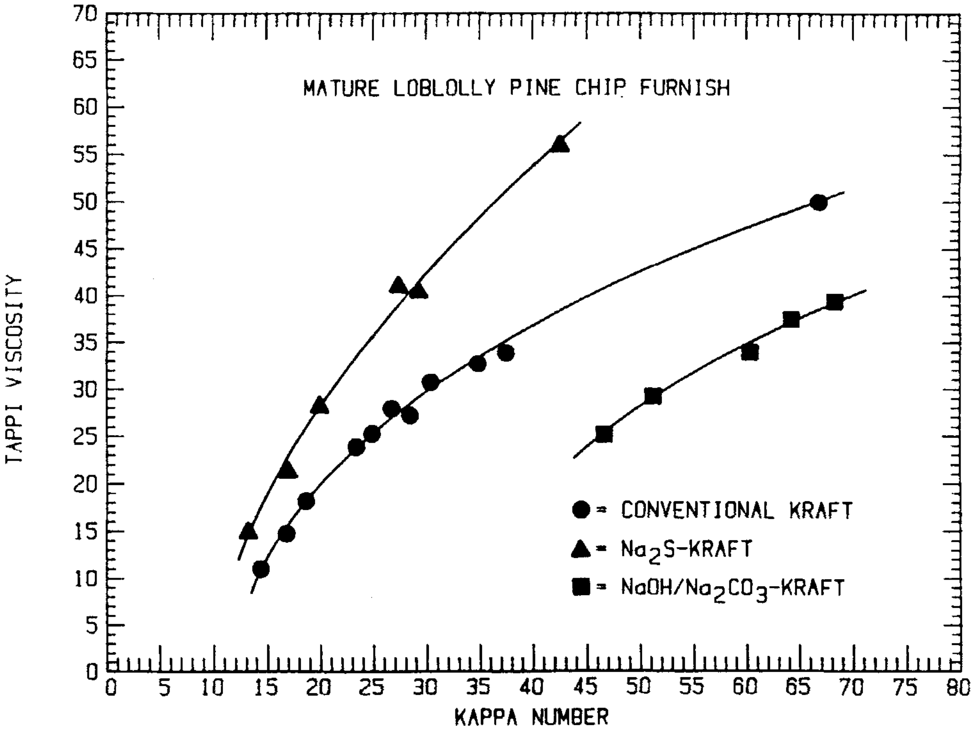

Figure 9: **Effect of the presence and absence of liquor sulfidity during the pretreatment stage on pulp viscosity after a kraft cook on loblolly pine chips.**

pretreatment leads to a final overall pulp viscosity which is very inferior, even when compared to conventional kraft. The effect of pretreatment sulfidity is understandable for delignification since sulfide is known to react with lignin at the pretreatment temperature (135°C). On the other hand, the inferior viscosity resulting from pretreatment without sulfide was unexpected since the effective alkali dosage in the subsequent kraft stage was much lower than in comparable reference kraft cooks.

A recent study (18) suggested that additives such as sulfide and anthraquinone have little effect on pulp viscosity. Instead, viscosity was shown to be a function of effective alkali dosage. In

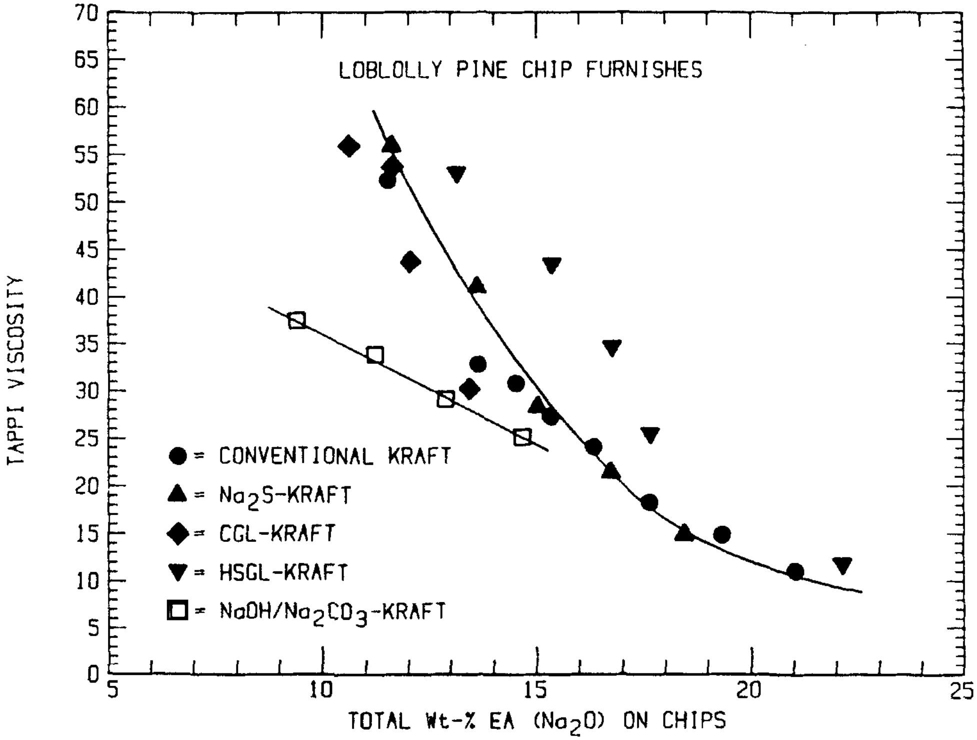

Figure 10: **Effect of total applied effective alkali on brownstock pulp viscosity after the kraft stage for conventional and pretreated loblolly pine chips.**

such a case, the role of an additive is to promote delignification at any given alkali dosage. In Figure 10, pulp viscosity values are plotted against total effective alkali charge including the pretreatment stage. While sulfide liquor pretreatments and conventional kraft pulp viscosities generally follow a similar curve, the viscosities of carbonate/hydroxide-pretreated pulps are lower at a given effective alkali level. These results, and the fact that pretreatment of chips and post-treatment of pulp with Na_2S solution enhances polysaccharide stability during oxygen delignification, clearly demonstrates the need to pursue an investigation of the reactions between sodium sulfide and carbohydrates.

EXPERIMENTAL

Two batches of loblolly pine chips were used in this investigation. One was obtained from the chip pile at the Weyerhaeuser mill in New Bern, North Carolina, and the other from a single tree, 17 years old, from the Hill forest in North Carolina - cut into bolts and chipped by a laboratory chipper. Both batches were air-dried and screened to obtain the 10 to 22 mm mesh size for cooking studies.

Pretreatments and kraft cooks were carried out in 2.8 liter stainless steel pipe bombs suitably valved and instrumented for liquor introduction and removal and temperature monitoring with thermocouples. Bombs containing liquor at a 4:1 liquor:wood (vol:wt) ratio (usually 450 g O.D. basis) were charged to a previously-heated, rotating forced-air convection oven for the desired treatment time. In the case of pretreatment (135°C), liquor was discharged from the chips at temperature, evacuated, and white liquor drawn into the bomb containing hot chips. At the end of kraft cooking, bombs were submerged into a cold water bath, vented and the cooked chips removed. Cooked chips were passed twice through a laboratory refiner set to a clearance of 0.50-0.80 mm, collected on a fine mesh screen box and transferred to a laboratory flat screen (0.30 mm) to effect separation of rejects and accepts. Rejects were oven-dried directly. Accepts were further centrifuged to $\sim$33% consistency, fluffed to effect separation of the pulp mat into fibers and stored in polyethylene bags at 34-36°F until needed for analysis and/or further processing. Yields were measured by oven-drying aliquots (4) of the fluffed pulp at 105°C in an air-circulation oven overnight ($\geq$4 hours).

Oxygenation treatments were carried out using 2-8 grams of pulp (O.D. basis) in 45 cc stainless steel reactor bombs (Parr Apparatus Co.). All oxygen treatments were conducted at 105°C, 20% pulp consistency with 1% $MgSO_4$ on O.D. pulp as stabilizer, 40 minutes total treatment time and 600-1400 kPa oxygen partial pressure. Wt-% NaOH on O.D. pulp was varied (1-10%) to effect various degrees of delignification.

Pulp pretreatments with borohydride and sulfide-containing liquors were also carried out in the 45 cc bombs. Temperature (105-165°C) and liquor dosages on O.D. pulp were varied to effect treatment. All treatments were carried out at 12.5% consistency and a total treatment time of 60 minutes.

All white liquors and sulfide-containing green liquors were prepared in the laboratory from technical- or reagent-grade chemicals to simulate typical mill practice. These were routinely titrated for composition during the course of this investigation.

Kappa numbers and viscosities were measured using TAPPI UM-246 (Micro Kappa Number) and T-230 os-76, respectively. Pooled standard deviations for the mean observations (at 95% confidence level) were as follows: Yield at $\pm$1.6%, Kappa Number at $\pm$0.5 and Viscosity at $\pm$1.0 mPa•s.

CONCLUSIONS

Using Na_2S and green liquors as examples of sulfide-containing liquors to post-treat a conventional kraft pulp followed by conventional oxygen technology resulted in significantly improved delignification selectivity. Sulfide-containing liquor pretreatments of wood chips followed by conventional kraft pulping at reduced alkali dosage and oxygen delignification resulted in kappa numbers in the 8-10 range while preserving equivalent conventional viscosity (~18 mPa·s) at equivalent or slightly improved pulp yield. As a consequence of pretreatment, the kraft stage may be used to extend delignification from 35 down to 20 kappa number. The role of alkali during pretreatment is to act as a mild extractant of the peelable hemicelluloses and their subsequent removal from the system. On the other hand, the presence of small amounts of sulfide (1-2% as Na_2O on chips) is necessary to enhance subsequent delignification and to provide carbohydrate stabilization to the pulp entering an oxygen delignification stage.

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