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GREEN LIQUOR CHIP PRETREATMENT AS A FEASIBLE METHOD FOR THE ENHANCEMENT OF SOFTWOOD PULP CHEMICAL PROPERTIES

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The influence of green liquor pretreatment of softwood (SW) chips on the efficiency of extended kraft delignification processes has been studied. The pretreatment of SW chips with hydrosulfide ion-rich industrial green liquor (GL) increases delignification selectivity, giving a statistically significant, higher pulp yield and lower lignin level (kappa number). It has also been observed that the kappa number drop is a direct function of pretreatment temperatures. In addition, an increase in pretreatment time from 40 minutes to 120 minutes does not significantly impact the yield. In general, one of the most interesting results of this work is that the GL pretreated chips tend to have a lower active alkali requirement in post kraft cooking and provide approximately 5% yield increase over conventional kraft. The neutralization of sodium hydroxide in green liquor does not give any improvement in delignification or yield compared to a conventional kraft cook. In an attempt to improve yield gain through lower pretreatment temperatures, it was found that pretreatment at room temperature does not provide any benefit in yield. The optimum concentration of green liquor for pretreatment is approximately $1 m^3$/adt of wood.

Key words: delignification, pulping, green liquor

INTRODUCTION

The cost effectiveness of US kraft pulping operations is largely controlled by fiber costs and pulp yield and consequently demands significant research attention. A practical way to successfully develop cost -effective operations is to improve the kraft pulping process without incurring significant capital costs. The core chemical engineering principles underlying the industrial kraft pulping process were mostly unchanged until the concepts of *modified kraft cooking* were introduced (1-3). The essential elements of the process as elaborated by Hartler include: (1) a consistent concentration profile of the hydroxyl ion which , should be low at the onset of cooking; (2) high concentration of the hydrosulfide ion during the initial phase; and (3) low concentrations of dissolved matter, particularly at the end of cooking.

High concentration of the hydrosulfide ion has been successfully identified as a key criterion for improving the strength, viscosity, bleachability, and potentially the yield of kraft pulp (6-11). The hydrosulfide ion attacks phenyl propanoid β-aryl ether lignin structures, which undergo hydrolysis with increased solubility. Moreover, the hydrosulfide ion has been found to increase pulp carbohydrate stability. It is well known that the dearth of hydrosulfide ions during the transition from initial to bulk phase delignification (1-4) of the kraft cook leads to the formation of stable enol ether structures in the residual fiber lignin. These types of compounds are formed from β-aryl ether linkages under alkaline conditions. This undesirable reaction therefore interferes with the ability of the cooking process to delignify pulp to a low kappa number and also compromises subsequent pulp bleachability. The use of two separate (split) white liquor

additions at different sulfidities has been suggested to address the issue of obtaining the optimal sulfide and hydroxide profiles according to the modified kraft pulping themes described above. Although the split sulfidity technique has received considerable research attention (5), it nonetheless suffers from the serious drawbacks, since it requires significant modifications of pulping operations and additional capital..

The objective of this research is to reap the benefits of hydrosulfide pulp chemistry with the lowest capital additions by fulfilling the first two (1-2) principles of Hartler's modified pulping process (*vide infra*). Green liquor, an easily accessible and rich hydrosulfide and low hydroxide source in kraft mills, has been used as a means to initiate the cook through chip impregnation/pretreatment. The present report demonstrates the effect of green liquor pretreatment on SW chips by measuring changes in yield, viscosity, and kappa number over conventional kraft pulping. Different charges of green liquor have been used in our studies to optimize the pulping process. In one set of experiments, adjusting the pH before the cook changed the ratio of hydrosulfide/hydroxide ions.

EXPERIMENTAL

Wood chips: US southern pine chips were obtained from an industrial member of the Institute of Paper Science and Technology. A pilot- scale screener was used to screen the chips. The accepts passed through 2–8 mm screens and were collected for all experiments. The screened chips were thoroughly washed and air-dried for several days under a hood to provide homogeneous moisture content.

Green Liquor: Our industrial sponsors generously provided the mill green liquor to us. It was analyzed by standard TAPPI titration methods (TM 624 cm-85) and found to contain 25.4 g/l Na_2S, 16.4 g/L NaOH, and 72.2 g/L Na_2CO3 (all quantities are expressed in g/L relative to Na_2O).

Pulping Equipment: The pulping experiments were conducted using a multi-unit stainless steel bomb digestive system designed in the pulping and bleaching labs of IPST. Eight different cooks could be performed simultaneously ; temperature ramps were adjusted using a computer-controlled oil bath (temperature ramps were on the order of 1.2°C/minute). Each bomb could accommodate a total volume of 500 mL Approximately 50 mL headspace was allowed in each bomb that contained a total mass of 50 g of o.d. wood chips.

Cooking Procedure: The bomb cooks were carried out in two distinct stages: (1) A pretreatment stage was characterized by combining 50 g of o.d. wood and mill green liquor in a liquor:wood ratio of 4:1. The liquor and wood were charged into a bomb digester and brought to the desired pretreatment temperatures in about 30 minutes; temperatures were maintained for various times. Afterwards the free pulping liquor was drained. (2) Post kraft cooking stage: a new liquor of particular caustic charge and sulfidity was added to the digester in order to perform the final cooking stage. This stage is referred to as the *post kraft cook* and was done for 2.5 additional hours. At the end of the cook, the liquor was drained and the cooked chips were refined and thoroughly washed. The resulting pulps were analyzed for yield, kappa number, and viscosity. All green liquor pretreatment runs were done in parallel with at least one conventional kraft cook (no green liquor charge) as a control. The chemical variability between the kraft control and the green liquor pretreatment runs was maintained as low as possible.

RESULTS AND DISCUSSION

Effect of pretreatment conditions on yield, kappa number, and viscosity

The pine chips were pretreated with undiluted mill green liquor for varying time intervals at the following temperatures: 95°C, 128°C , and 150°C. After pretreatment, the liquor was drained and a post kraft cook was done at 18% active alkali and 30% sulfidity. The results shown in Fig. # 1 indicate that the kappa numbers drop significantly for all three pretreatment temperatures while the yield is preserved at approximately 5% higher than conventional kraft at equivalent kappa numbers. The drop of kappa numbers is of course more pronounced at higher temperatures, but without a significant yield loss. In general, the increase of pretreatment time from 40 to 120 minutes does not correlate with any remarkable difference in pulp yields or kappa number. Thus, since the gains in yield and drops in kappa numbers appear to level off at about 60 minutes, this pretreatment time was selected for all subsequent work in this study. Similar studies employing green liquor and its derivatives have shown that yield increases of 2% are possible, but longer times and higher temperatures were used to obtain these yields (11). Indeed, other studies by Lopez *et al.* have reported similar yield increases for pretreatment (13). Figure 2 gives the plots of viscosity vs. the kappa number. As the figure illustrates, the viscosities naturally drop at higher temperatures in conjunction with the drop in kappa numbers. However, the viscosities for the runs treated with green liquor are much higher (approximately 30%) than conventional kraft pulp trials for every level of kappa number obtained. This observation tends to confirm the contention that the absorption of sulfide

ions during the pretreatment stage protects the cellulose from severe depolymerization reactions during the bulk delignification phase.

Effect of green liquor pretreatment on active alkali requirement in post kraft cooking

Figures 3 and 4 illustrate the relationship between green liquor pretreatment and the active alkali requirement in post kraft cooking. It is apparent from the figures that to achieve a particular yield or kappa number, the pulps pretreated with green liquor need **~37-41% less active alkali** as compared to conventional kraft pulps. This latter fact accounts for a great saving in terms of expensive chemicals. Indeed, work by Svedman et al. has conclusively supported this latter finding, demonstrating white liquor savings of up to 20% for pretreatment work with *P. sylvestris* (10). The results are also summarized in Table 1. It is observed that at a given kappa number, the yield of pretreated pulp is 4-5% higher than the corresponding conventional kraft pulps. The decreased alkali requirement in the post kraft stage is probably due to the extraction and liberation of pulp hemicelluloses during green liquor pretreatment that normally tend to produce sugar acids via peeling reactions (4, 12). Typically, these sugar acids are the main culprit outside of lignin for consuming fairly large amounts of active alkali during conventional kraft cooking. The native alkali content of the green liquor instead acts to consume the sugar acids before they react with normal white liquor.

Effect of pH adjustment on green liquor pretreatment

It has been mentioned previously and in the literature (1,2) that in the early stage of kraft cooking a high hydrosulfide and low hydroxide ion concentration should be maintained to achieve increasingly more selective delignification. In fact, Chang *et al.*(13), in the study of the effect of sodium sulfide on kraft pulping have, demonstrated that a high hydrosulfide/hydroxide value favors the sulfur adsorption in the wood and gives better delignification. Other work, however, indicates that the issue of high initial hydrosulfide concentrations is complicated by the fact that the interior of wood tends to preferentially sequester hydroxide ions more rapidly than hydrosulfide (11, 14). In order to verify the conceptually appealing basis for green liquor pretreatment and address concerns of hydroxide concentration, some of the hydroxide ions in the green liquor were neutralized to lower the pH to 12.5. The results shown in Table 2 indicate that despite using a high (15%) active alkali in post kraft cooking to compensate for the diminished hydroxide capacity in the pretreatment stage, the kappa number of pulps remains higher than anticipated. This result indicates that the green liquor should have a hydrosulfide:hydroxide ion equivalent ratio of at least 2:1 in order to represent an excellent hydrosulfide source to ensure high pulping performance throughout the process (10). Although the carbonate concentrations are presumed to be a dead load arising from the pretreatment process, we believe that the carbonate represents a rich alkali-buffering source to impede viscosity losses during the pulping. In fact, the use of crystallized green liquor (green liquor without the lime mud) may help us determine the precise role of carbonate in pulping reactions.

Optimization of green liquor concentration for pretreatments

Green liquor is the main component produced in the recovery system, and therefore there is a practical limit as to how much of it can be directly spared to the pulping operations without compromising the recovery system. In order to address this issue, variations in the green liquor charges for pretreatments of a series of pulps were introduced by employing different dilutions of green liquor in the pretreatment and by conducting post kraft cooking at a fixed active alkali (15%) and sulfidity (30%). The pretreatments were done at 20°C and 135°C. The results are shown in Table 3 and plotted in Figs. 5 and 6. It is apparent from the figures that the pretreatment at the lower temperature does not give any significant improvement in yields or any reduction in kappa number. However, at the higher temperature pretreatments, it can be observed that the green liquor concentration can be decreased to 25% while the improvement in yield and reduction in kappa number are maintained. Thus, a proposed practical green liquor application concentration is about $1 m^3$/adt of wood.

CONCLUSIONS

In this study the wood chips were pretreated with industrial green liquor at different concentrations, pH values, temperatures, and time intervals. The post kraft cooks were carried out at varying active alkali and a fixed sulfidity of 30%. Our results indicate that the pretreatment temperatures of 95°C, 128°C, and 150°C provide a significant drop in

kappa number while preserving the yield at a level of ~5% higher than the conventional kraft cook control pulp. The increase in viscosities is also substantially higher (approximately 30%) for the green liquor treated pulps as compared to the kraft control pulps. In general, the increase of pretreatment time from 40 minutes to 120 minutes does not show any remarkable difference in pulp yield or drop in kappa number. In addition, the green liquor pretreatments at 20°C are not as effective as at 135°C. Remarkably, in order to achieve a particular yield or kappa number in these studies, the green liquor pretreated pulps need almost 40% less active alkali in the post kraft stage as compared to conventional kraft pulps. It was also observed that the decrease in pH to optimize the hydrosulfide:hydroxide concentration during the pretreatment has a negative effect on delignification, perhaps due to lack of buffering action of sodium carbonate at the lower alkali levels. Finally, the optimum application concentration of green liquor for pretreatments in these studies to address total charge of green liquor and pulp properties has been found to be about $1 m^3$/adt of wood.

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Table 1. Active alkali requirement in post kraft cook

Active Alkali	GL Pretreated Pulps		Conventional Kraft Pulps	
(% wood)	Yield %	Kappa Number	Yield %	Kappa Number
8.0	52.2	43.4	-	-
12.0	47.9	29.7	-	-
15.0	45.3	20.9	-	-
18.0	45.3	19.0	48.7	42.1
21.0	-	-	45.4	28.5

Table 2. Effect of pH on green liquor pretreatment of chips.

pH	% Active Alkali	Yield %	Kappa Number
12.5	12.0	57.8	77.3
12.5	15.0	51.2	56.6

Table 3. Effect of green liquor concentration on kappa number, viscosity, and yield of softwood pulp

Green Liquor Concentration	Pretreatment at 20°C			Pretreatment at 135°C		
(% as received)	Yield %	Kappa Number	Viscosity, cP	Yield %	Kappa Number	Viscosity, cP
22.2	51.6	54.6	39.2	49.4	33.1	31.2
44.3	49.9	42.1	31.7	48.4	34.9	32.0
66.4	48.4	38.2	34.9	45.6	23.3	26.6
88.5	48.7	37.6	32.3	45.3	20.9	22.9
Original	45.4	28.5	25.8	-	-	-

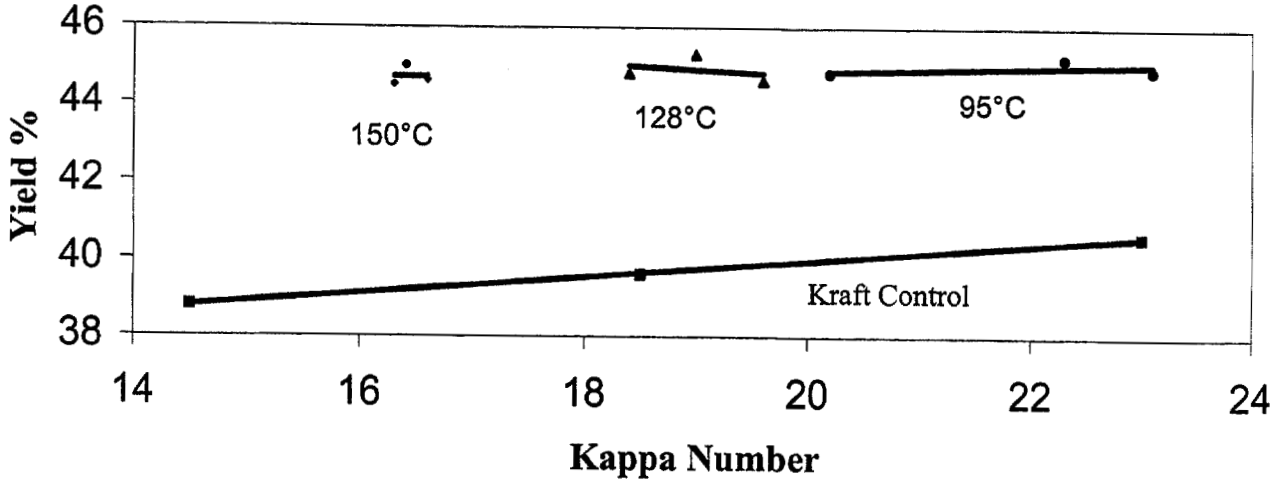

Fig. 1 - Yield vs. kappa number for conventional kraft and Green Liquor (GL) pretreated chips at 95°C, 128°C, and 150°C.

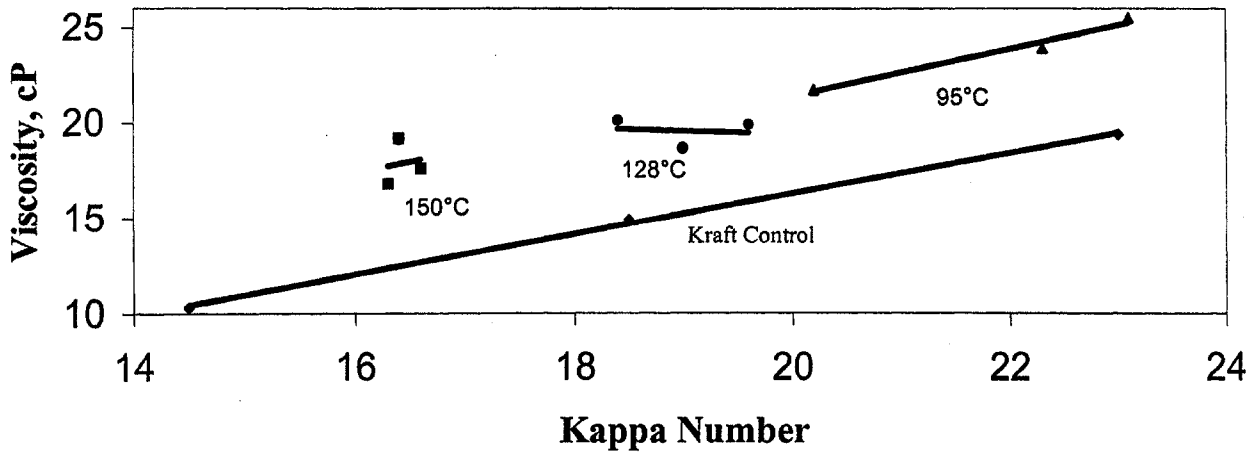

Fig. 2 - Viscosity vs. kappa number for conventional kraft and GL pretreatment chips at 95°C, 128°C, and 15

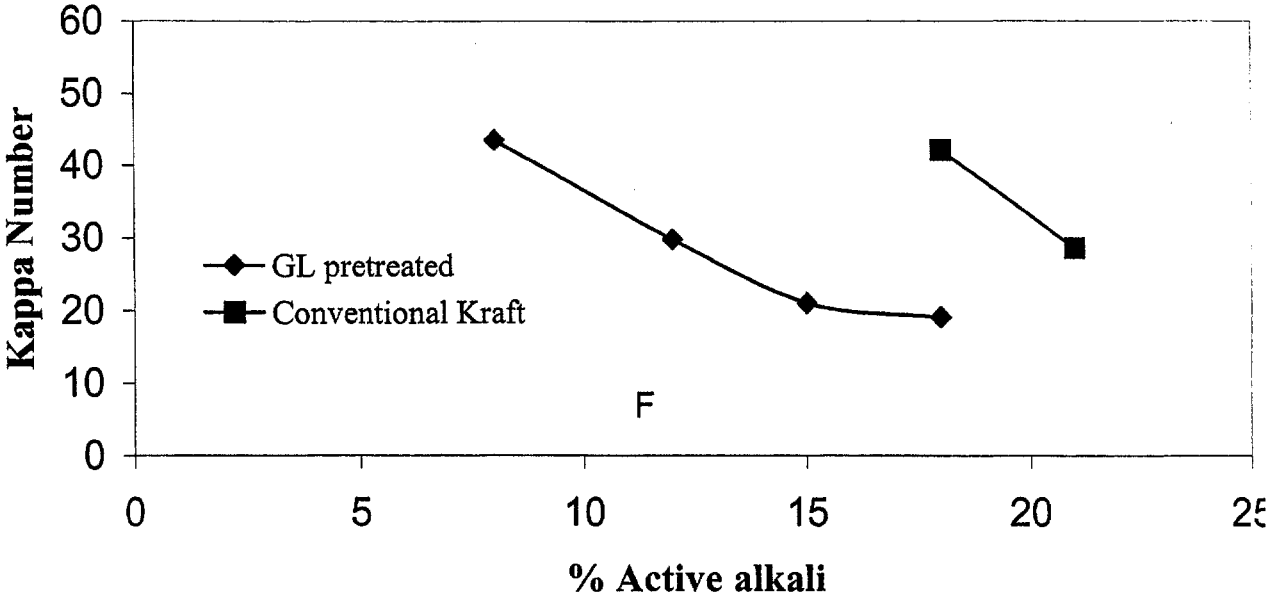

Fig. 3 - Kappa number vs. active alkali for conventional kraft and GL pretreated chips at 135°C.

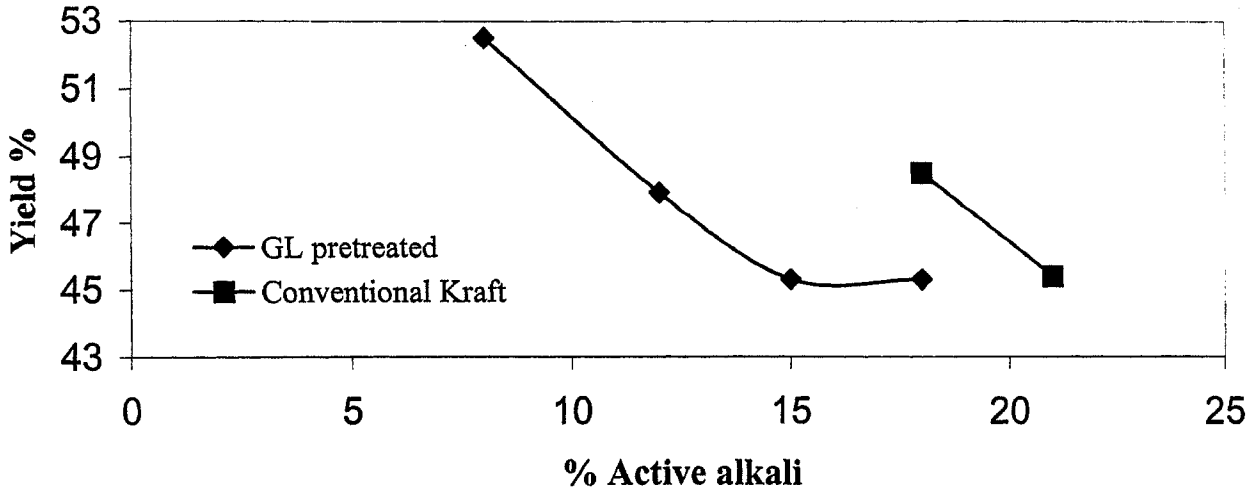

Fig. 4 - Yield vs. active alkali for conventional kraft and GL pretreated chips at 135°C.

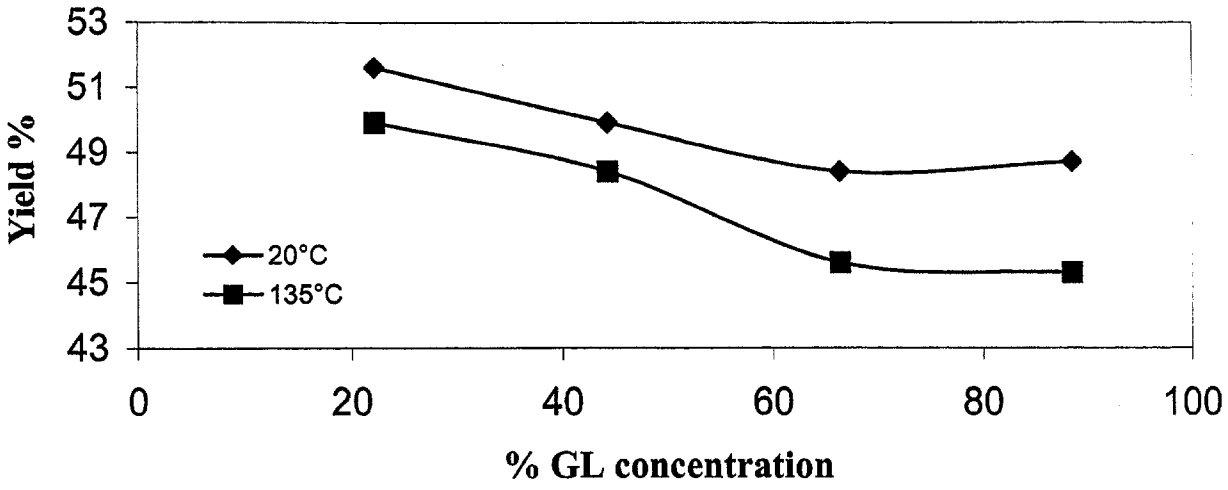

Fig. 5 - Yield vs. % GL concentration for GL pretreated chips at 20°C and 135°C.

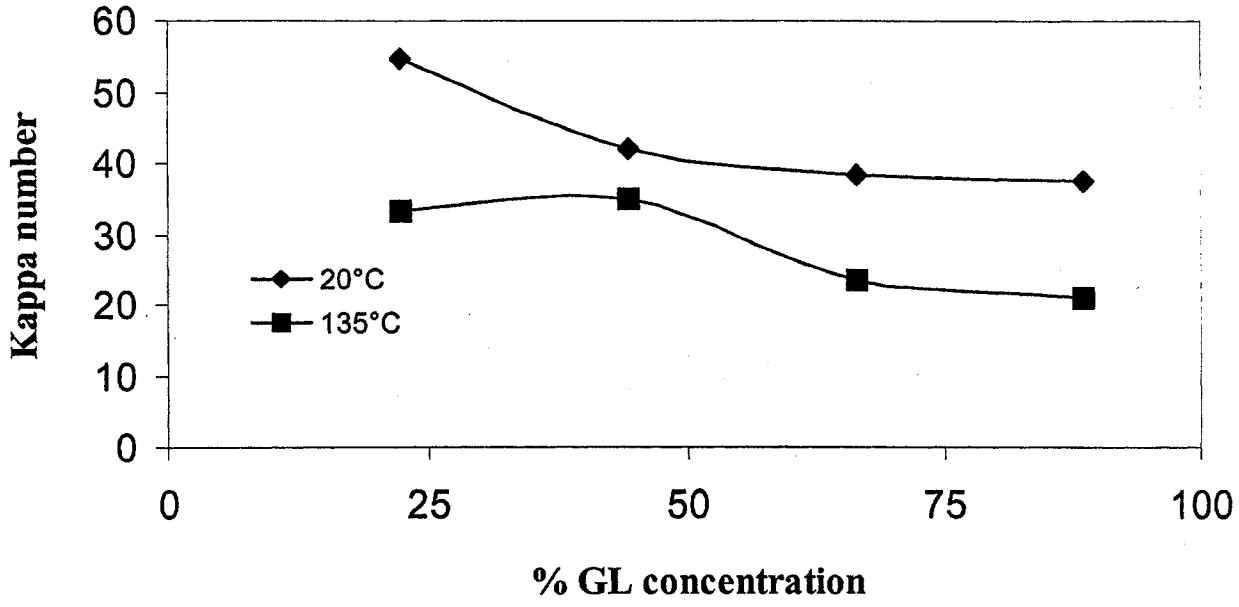

Fig. 6 - Kappa number vs. % GL concentration for GL pretreated chips at 20°C and 135°C.