Enhancing Kraft Pulping Through Unconventional, Higher Sulfide-Containing Pretreatment Liquors- A Review

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ABSTRACT

This review analyses the advances of pretreatment with sulfide-containing liquors to modify kraft pulping. In the past several decades, modified kraft pulping has advanced rapidly, based on the principle that high sulfide content at the first stage of cooking would improve both pulp quality and the selectivity of delignification. Pretreatment of wood chips with sulfide-containing liquors (i.e.black liquor impregnation) is now on industrial reality. Many research investigations for improving kraft pulping by means of pretreatment are underway, such as green liquor pretreatment, split-sulfidity cooking, and related technologies. High-sulfidity pretreatment of wood chips is one of the most promising means available to achieve significant pulping improvements. This is especially true for green liquor, an easily accessible and rich hydrosulfide source in kraft pulp mills, as part of a pretreatment stage program.

Key words: *pretreatment, sulfide-containing liquor, green liquor, modified kraft pulping, black liquor.*

INTRODUCTION

Extended delignification has received wide use in the pulp and paper industry to address environmental issues and improve mill energy efficiency. The concept from previous research arrived at the following basic principles [1-5]:

1) The concentration of hydroxide ion should be lower at the beginning of the initial cooking stage, and leveled out during cooking.
2) The concentration of hydrosulfide ion should be as high as possible initially and at the start of bulk delignification.
3) The concentrations of dissolved lignin and sodium should be low, especially towards the residual delignification phase.
4) The temperature should be kept low, especially towards the beginning and end of bulk delignification.

The active components in kraft pulping chemicals are hydroxide and hydrosulfide ions. The hydrosulfide ion plays a great role in kraft pulping technology by accelerating delignification and rendering nonselective soda cooking into a selective delignifying process. The sulfidity level around the transition point at the beginning of bulk delignification has a critical effect on the delignification efficiency.[6-8] A high sulfidity, or a high concentration of HS^-, is essential for a selective kraft cook by efficiently removing lignin with limited attack on carbohydrates.[2,9] However, a low concentration of hydrosulfide will favor an increase in the formation of enol ether structures in conventional kraft pulping, a conclusive indicator of a deficiency of hydrosulfide ions during the initial cooking stage. This impairs delignification and results in the formation of more resistant residual lignin structures [10-16].

In the most contemporary modified cooking technology for kraft pulping, pretreatment with sulfide-containing liquor is limited to the use of black liquor to impregnate wood chips before the bulk cooking. Many research and industrial applications have proven that this modification provides multiple benefits including higher pulp yield, better delignification selectivity, and some lower production cost.[16-20] However, since black liquor is limited by the relatively low levels of the sulfide in the liquor for pretreatment and it contains a high organic load and intrinsic viscosity, there are limits in its use for further improvements to the pulping process.

Based on the above mentioned modified chemistry principles, the use of a split sulfidity cooking procedure has been suggested,[21-23] that is characterized by separating the cooking chemicals into two forms, "sulfide-rich" and "sulfide-free," that are used in the course of different cooking stages. The higher sulfidity liquor is used for pretreatment whereas the lower sulfidity liquor is used for the cooking stage. The key driver behind this approach is to have a feasible separation technology. Many research efforts have been conducted using various separation methods,[24-36] such as green liquor cooling crystallization, Alby process, SCA-Billerud process, ion-exchange method, FIRESS process, and the gasification process. However, no viable industrial application has been reported yet because of the requirements of the process modification and an increase in operational cost.

Svedman et al. [37] investigated the addition of green liquor to the SuperBatch cooking system by pretreating wood chips with a combination of green and black liquor. Their results showed that pulp viscosity and strength could be increased whereas the demands for both white cooking liquor and bleaching chemical were considerably reduced. When the original mill green liquor was used, the recovery load was increased, but this load was obviated through the use of separated green liquor from crystallization, resulting in a minimal influence on the recovery cycle.

Berthold et al. [38] reported the use of polysulfide liquor-treated wood chips in one or two stages before kraft cooking. The dissolution of lignin was dramatically increased when PS was used as an additive in kraft cooking, and oxidized degradation products from lignin coniferyl alcohol and possible enol ether structures were produced. The result showed a 21% - 36% reduction of the lignin in pulp using PS pretreatment as compared to conventional cooks.

The modified pulping used in continuous cooking system is known as MCC and other designations, EMCC, ITC etc. [4, 39, 40] In batch systems, RDH, and SuperBatch cooking have been developed. [41-44] In these cases, the hot black liquor was used to pretreat the wood chips in a cooking cycle. In the case of black liquor pretreatment, previous research indicated that the sulfidity of black liquor used in the pretreatment had an important effect on delignification – the delignification rate decreased during the reduction of the sulfidity in black liquor[45]; however, the effect of sulfidity during pretreatment correlates with the alkalinity in the pretreatment liquor. When the alkalinity was reduced to a level of 4-9 g/L (NaOH), the delignification rate by modified RDH cooking was similar to that by conventional kraft cooking. This similarity in the results was observed by using either sodium sulfide solution or artificial green liquor as a pretreatment liquor, whereas both higher pulp yield and better delignification with green liquor pretreatment pulping was obtained versus the use of a sodium sulfide solution [46]. It is suggested that a synergistic effect takes place between the sulfide and the alkali. But as of yet, a clear explanation for the synergism remains to be discovered.

Profile of sulfide absorption in pretreatment of wood chips

Sulfide is easily and efficiently absorbed when chips are treated with liquors containing sulfide. The amount of sulfide absorbed depends strictly on the pretreatment conditions that are employed during cooking. When chips are treated with white or black liquor at 100°C, the total sulfide absorption is approximately 0.1-0.2 mol/kg [11]. Sulfide absorption increases with increasing concentration of hydrosulfide ions and increasing pretreatment time. The pretreatment temperature results in an increase in the total sulfide absorption. In fact, the sulfide absorption is enhanced by approximately 0.05 mol/kg wood when the ionic strength in the pretreatment liquor, defined as the concentration of sodium ions in the liquor; increases from 0.5 to 1.0 mol/L by the addition of sodium salt into the pretreatment liquor. However, the hydroxide ion concentration increase has a negative effect on sulfide absorption. Overall, to insure thorough sulfide absorption the ratio of hydrosulfide to hydroxide ions should be at least six to one.[47] Olm et.al. reported that sulfide absorption correlates with the ratio of the concentrations of hydrosulfide and hydroxide ions, as Figure 1 shows. A past study on displacement kraft batch cooking techniques showed that hydrosulfide in the recirculated black liquor greatly determines the delignification rate and selectivity, whereas the sulfidity in black liquor for pretreatment is more important for influencing overall pulp qualities compared to white liquor. [48]

There is a significant difference between alkali absorption and sulfide absorption into wood after impregnation: the alkali concentration inside wood chips is higher than that in the impregnating liquor, however, no significant difference between sulfide concentration inside wood chips and that in the liquor was demonstrated after impregnation. [49,50] A linear relationship was obtained between the concentration of impregnating liquor and sulfide absorption in wood. The amount of sodium hydroxide and sodium sulfide charged for impregnation was found to be 2.26 and 3.27 times more, respectively, than that remaining in wood chips after impregnation.[50,51]

The amount of sulfide absorbed by wood chips during pretreatment depends on the pretreatment conditions, and this will of course be a function of the chemical differences inherent in various sulfide liquors. But most of the research on sulfide absorption has focused on the black liquor pretreatment process. In general, sulfide absorption increases correlate with increases in both pretreatment temperature and time. The effect of the concentration of pretreatment liquor on the wood chips depends on both the green liquor charge and the ratio of liquor to wood. From an industrial point of view, it is possible to apply no more than 1.0 L/kg wood as a pretreatment condition without compromising mill chemicals and energy balances. Our previous work on chemical absorption by wood chips in green liquor pretreatment demonstrates that sulfide and caustic alkali were almost completely absorbed during pretreatment at a level of 1.0 L/kg green liquor charge, but only about 60% of sulfide was absorbed at 2.0 L/kg of green liquor dosage. The highest ratio of sulfide uptake in the wood chips was achieved at a GL charge of 1.0 L/kg[83] shown in Figures 2 and 3.

Bykova et al. [63] compared the impact of using artificial green liquor (at liquor to wood ratios of 0.7:1 and 4:1) on pulping. The results suggested that a low ratio of liquor to wood was sufficient to improve kraft delignification, with higher delignification selectivity and lower hemicellulose loss by using a low amount of impregnating liquor.

Nonetheless, according to previous research, the effect of alkalinity on sulfide absorption has a stronger effect than other conditions. In general, sulfide absorption deceases correlate with increasing hydroxide ion concentration, in which the ratio of hydrosulfide to hydroxide ions should be at least six to one to ensure a sufficient sulfide absorption.[47]

The profile of sulfide absorption should be the focus of any pretreatment scheme. The higher sulfide concentration and relative lower alkalinity will be helpful in providing the correct conditions to ensure a high level of sulfide absorption in wood chips. The impact of pretreatment conditions and changes of chemical components in pretreatment liquor on the pretreatment process have been investigated in the past. Yet, the rationale of the benefit of pretreatment needs to be more fully understood, especially at the chemical level where the different absorption mechanisms available to sulfide and alkali influence the overall chemical absorption profiles.

Role and forms of sulfide in pretreatment

In principle, there are three forms of sulfide in aqueous solutions: S^{-2}, HS^-, and dissolved H_2S. In highly alkaline aqueous solutions, sulfide is mainly present as HS^-, including in green liquor.[53-55] Furthermore, several studies have demonstrated that hydrogen sulfide ions in cooking liquor exist in two forms, "loosely bound" with lignin and "completely free" as HS^- ions. The amount of "loosely bound" sulfide increases rapidly in the beginning of cook, and decreases gradually as pulping proceeds, approaching zero at the end of the cook.[11] A possible mechanism which explains the benefit of higher hydrogen sulfide ion concentration in the initial cooking stage to the overall delignification is that hydrogen sulfide ions are absorbed by wood in the "loosely bound" manner.

The pretreatment of wood chips with sulfide liquor before cooking results in the benefits of increased yield and better selectivity, but the basis of this observation is not fully understood. Some early research suggested that black liquor pretreatment might prevent condensation reactions of lignin, thus enhancing delignification[56], or the synergistic effects of polysulfide ions, organic and inorganic ions as oxidants may accelerate the cleavage of lignin ether linkages.[57] Recently, dissolved extractives in black liquor improved chemical permeation into wood chips and the dissolution of lignin by acting as surfactants [58].

The β-aryl ether structure of lignin can be cleaved or form stable enol ether structures during kraft cooking through the quinone methide intermediate.[59] The shortage of hydrosulfide ions may result in the formation of enol ether structures in the early stages of cooking.[13] But other research has reported contrasting results, which indicate that no enol ether is formed during pretreatment or the initial stage in kraft cooking.[60,61] The absorption of sulfide by pretreatment may result in some cleavage of the β-aryl ether bonds in the phenolic lignin structure.[41]

Based on the chemical equilibrium of sulfide in aqueous solution under various pHs, sulfide in the pretreatment liquor may mainly exist in the form of hydrosulfide ion. On the other hand, the state of sulfide in the wood chips after pretreatment is more important and remains to be investigated. The latter point is critical since the chemical effect of sulfide on lignin during pretreatment is significant for improving delignification during cooking.

The changes observed in lignin and carbohydrates during pretreatment

Kleen and Olm[60] studied lignin and carbohydrate dissolution during pretreatment with several sulfide-containing liquors. Compared with the initial stage in kraft cooking that exhibits the removal of 5% lignin and about 20% carbohydrates on wood, less than 1% lignin was removed, *but over three times less carbohydrates were removed during their pretreatment*. The higher carbohydrate retention mainly arises from retention of glucomannan during the pretreatment process, whereas no obvious difference was exhibited for xylan dissolution between pretreatment and the initial stage of kraft cooking. Our analysis of the changes of carbohydrate in pulps produced by green liquor pretreatment displayed similar results.[85]

One reason for the improved cleavage of lignin aryl ether bonds described earlier is therefore due to sulfur absorption into wood chips during pretreatment. Another possibility may be due to the presence of polysulfide in sulfide-containing liquors from an oxidation of an α-hydroxyl group of lignin. The amount of coniferyl alcohol groups in wood after pretreatment is lower than after the initial stage of kraft cooking, especially since the coniferaldehyde groups were almost completely removed from the wood.[60] Simultaneously with the cleavage of lignin β-aryl ether bonds, enol ether structures were formed in a competitive reaction and are known to be stable to alkali. The formation of enol ether structures can clearly be attributed to a shortage of hydrosulfide ions in the early cooking stage.[13] It is reasonable to assert therefore that sulfide absorption into wood chips by the pretreatment process effectively prohibits the formation of enol ethers.

The reduction of the effective alkali dosage for kraft cooking in pretreatment is mainly due to the removal of hemicelluloses during pretreatment since these hemicelluloses are able to consume alkali during kraft cooking.[62]

Although the chemistry of lignin and carbohydrate reaction in kraft cook has been thoroughly investigated and well known, the chemistry of pretreatment process is still not well understood. The chemistry of the initial stage of kraft cook is often extrapolated to the pretreatment process, but there are many differences between the two, requiring further investigation.

Profile of pretreatment impact on pulping

<u>The ratio of liquor to wood</u>

In studies by Bykova, the effects of pretreating wood chips with model green liquor at a ratio of 0.7:1 of liquor to wood (L/W) were studied and shown to increase the delignification rate by 12% and 10% in the initial and bulk cooking phases, respectively, in comparison to that of conventional kraft pulping, but only 5 to 6% rate increases were found for pretreatment with a 4:1 L/W ratio.[63] The concentration of residual lignin decreases as the ratio of liquor to wood is lowered, with residual lignin contents of 3.0%, 3.7% for 0.7 and 4.0 L/W ratios, respectively, compared to 4.4% for conventional kraft pulping. It was suggested that diffusion and chemical redistribution were the main reasons for improving the rate of delignification in the bulk cooking stage. On the other hand, a L/W ratio increase from 0.7 to 4.0, did not cause any major differences in the viscosity of pulp.[46] These experimental results indicated that pretreatment with green liquor can be effectively achieved at a low ratio of liquor to wood.

<u>Alkalinity of pretreatment liquor</u>

The delignification rate during kraft cooking was improved by increasing the alkalinity of the black liquor used for pretreatment. Reducing black liquor alkalinity to a neutral pH raised the pulp kappa number to levels higher than those obtained in conventional cooks. Nevertheless, pulp yield was unaffected by changes in black liquor alkalinity. Remarkably, the general strength properties of pulps prepared from pretreated chips were superior to those of conventional pulps: increasing the alkalinity of pretreatment black liquor increases pulp tear strength by 10% higher compared to a typical reference kraft pulp.[64]

Pretreatment temperature and time

The pretreatment experiments using black liquor in a batch digester need a longer time for wood chip impregnation because of the limitations associated with the rate of impregnation.[40] In the case of pretreatment with sodium sulfide, pretreatment temperature demonstrated an effect on the change in kappa number. When the pretreatment temperature was increased from 120°C to 140°C, the pulp kappa number was lowered from 47 to 29, with only a minimal influence on both pulp yield and viscosity.

PS additive pretreatment

Polysulfide (PS) has been extensively investigated as an effective pulping additive agent. It was found to increase pulp yield by means of oxidizing the end group of carbohydrates.[65-68] In recent years, PS was also studied as an additive for pretreatment processes using sulfide-containing liquors. Lindström[69] indicated that PS used for pretreatment increases pulp yield, displays a slightly faster delignification, and overall improved selectivity.

Effect of sulfide concentration on pulping

Much research has confirmed the influence of hydrosulfide concentration and sulfide absorption in wood on delignification rate and selectivity.[6,8,70-72] A high [HS]/[OH] increases the absorption in wood and enhances pulping selectivity. But recent work in kraft pulping with sulfide liquor pretreatments conducted by Olm et al.[73,74] showed contrasting results with past research: both [HS]/[OH] and sulfide absorption in wood have little influence on delignification rate and selectivity. Less lignin was dissolved in the pretreatment liquor at a low hydroxide concentration than at the high hydroxide concentration, and no influence on the amount of residual lignin was afforded to any significant extent by the ratio of [HS]/[OH]. The results indicated that the delignification rate and level of residual lignin are affected mainly by the hydroxide ion concentration in the cooking stage, the high hydrosulfide ion concentration (≥ 0.3 mol/L), the [HS]/[OH] in the pretreatment liquor, whereas the sulfide absorption in wood has a minor influence on delignification.

In the investigations of displacement batch kraft pulping, much research has demonstrated that accelerated delignification with a concomitant improvement in pulping selectivity can be achieved by increasing the hydrosulfide concentration during hot black liquor impregnation. But the changes of the hydrosulfide concentration used in warm black liquor appeared to have only a slight influence on delignification.[16, 81, 82] Figure 4 and Figure 5 illustrate an improvement of pulping selectivity by means of sulfide containing liquor pretreatments in both industrial and laboratory studies.

Studies on delignification kinetics in kraft pulping demonstrate that the best pulping results can be obtained by applying all of the total sulfide charge at the beginning of the cook in the 30-45% range of overall sulfidity.[75,76] Thus, it is very important that the sulfide concentration access the reactivity sites before the beginning of bulk delignification. Pretreatment therefore provides an effective method to allow sulfide to access the reactive sites.

The amount of residual lignin dissolved correlates with the increase in the ionic strength in a range of 0.65-2.6 mol/L. At low ionic strength, little effect of ionic strength change on residual lignin was observed, but in the range of industrial cooking (2-3 mol/L), the effect was more pronounced. Some research has suggested that the effect of ionic strength on delignification is mainly attributed to the thermodynamic activity of the reactants in solution.[70] The influence of ionic strength on the amount of dissolved residual lignin is related to both the concentration of hydroxide ions and hydrosulfide ions; it has a large negative effect on residual lignin at high concentrations of hydroxide ions or hydrosulfide ions.[71]

Recent investigations on the influence of ionic strength in pulping confirm that a high ionic strength decreases the delignification rate and results in a high consumption of hydroxide ions and low pulp viscosity. At a high ionic strength (over 2.9 mol/L), cooking selectivity and pulp yield were detrimentally affected, especially for obtaining a low kappa value. Furthermore, the bleachability was negatively affected at a high level of ionic strength.[77]

Until now, the studies on pretreatment have been mainly focused on black liquor applications. However, since various sulfide-containing liquor possess different characteristics, some research has been done to enhance the beneficial function of sulfide-containing liquor by means of fortifying the sulfide pretreatment concentration or through addition in pretreatment liquors. It is anticipated that a deeper understanding of pretreatment chemistry will provide the industry with further improvements in improving pulping technologies.

Profile of pulp qualities improved by pretreatment

Modified pulping by pretreatment with sulfide-containing liquor reduces the alkali requirement, increases pulp yield, and improves the selectivity of delignification. A 25%-50% reduction in active alkali requirement was achieved by pretreatment compared to conventional kraft pulping.[62] which can be attributed to extraction of hemicelluloses during pretreatment. Since most of the alkali is consumed by carbohydrate degradation[78], the removal of alkali-soluble hemicelluloses obviously results in a lower alkali requirement.

Pulp mills using black liquor to impregnate wood chips in continuous kraft pulping systems demonstrated a 10% tear strength increase and higher burst index, easier beating, yet no obvious change in yield or bleaching chemicals consumption.[79] For the same pulp yield, a higher ratio of tear to tensile index could be achieved in a pretreatment stage with sulfide-containing liquor, as compared to conventional kraft pulp.[16,47,80] This may be attributed to higher pulp viscosity, which is derived from the improvement of delignifying selectivity. Figure 6 indicates the comparison of the tear strength of pretreatment pulps and conventional kraft pulp at a given tensile strength.

The comparison of beatability for both pretreatment and conventional pulp have conflicting results in the literature. Some research [46, 64] indicated that pretreatment pulp showed a lower beatability than conventional pulp which might be due to a loss of the hemicelluloses during pretreatment pulping. Higher tear strength was evidenced in pulps pretreated with black liquor. As compared to conventional kraft pulps, pretreatment pulps showed a higher tear-tensile index at a given pulp yield.[46] Both the higher pretreatment temperature (120°C -140°C) and alkalinity during pretreatment gave higher tear strength, but resulted in a slightly lower bleachability.[64] The same results were also demonstrated in a green liquor pretreatment case. The pretreatment with green liquor resulted in a 10% increase in the tear strength, but no obvious improvement in tensile strength was observed.[37] Other investigations in black liquor pretreatments demonstrate beneficial effects on delignification and pulp qualities at a given kappa number pulp; for example, at a kappa level of 33, the pretreatment pulping reduced the effective alkali 15%-20%, or about a half H-factor. The bleachability also improved slightly.[84]

No doubt, pretreatment with sulfide-containing liquor can improve pulp strength, especially tear strength. But the impact of pretreatment on oxygen delignification and pulp bleachability are still not fully clear. More work still needs to be done on the changes of lignin structures during the pretreatment and cook.

Concluding Remarks

As summarized above, pretreatment of wood chips with sulfide-rich liquor before cooking is an efficient approach to modifying kraft pulping. The benefits of pulping and pulp qualities have been realized by industrial practice. There is also room for more development to further strengthen the pretreatment process with sulfide-containing liquor. Green liquor, an easily accessible and rich hydrosulfide source in kraft pulp mills, can provide a powerful alternative for the pretreatment process, since its chemical nature has considerable promise as a modified pulping technology. Although much research in impregnation with sulfide-containing liquor has been conducted in the past several decades, there are still many questions to further explore. The mechanism of the process has been not fully understood, the process technology needs to be optimized, and possible synergistic combination with PS, AQ, and surfactants require further investigation.

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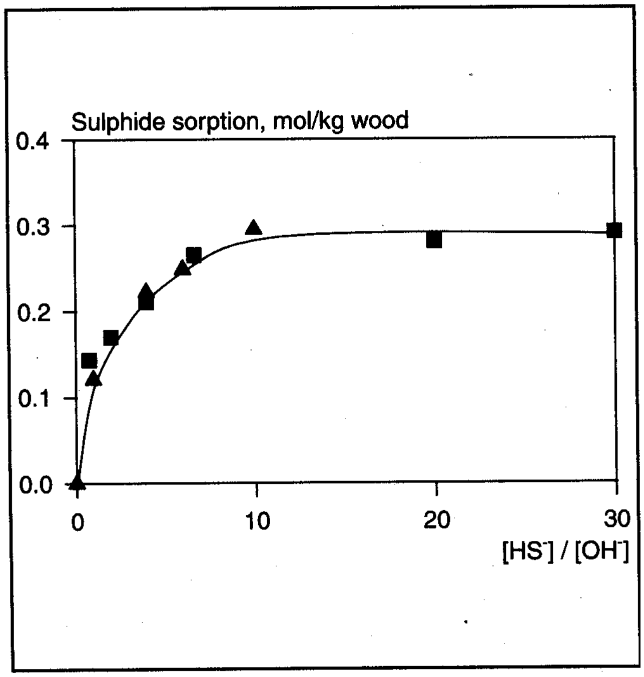

Figure 1. Sulfide absorption in wood as a function of the ratio of hydrosulfide to hydroxide ion concentration (130ºC, 30 min, Ref.47).

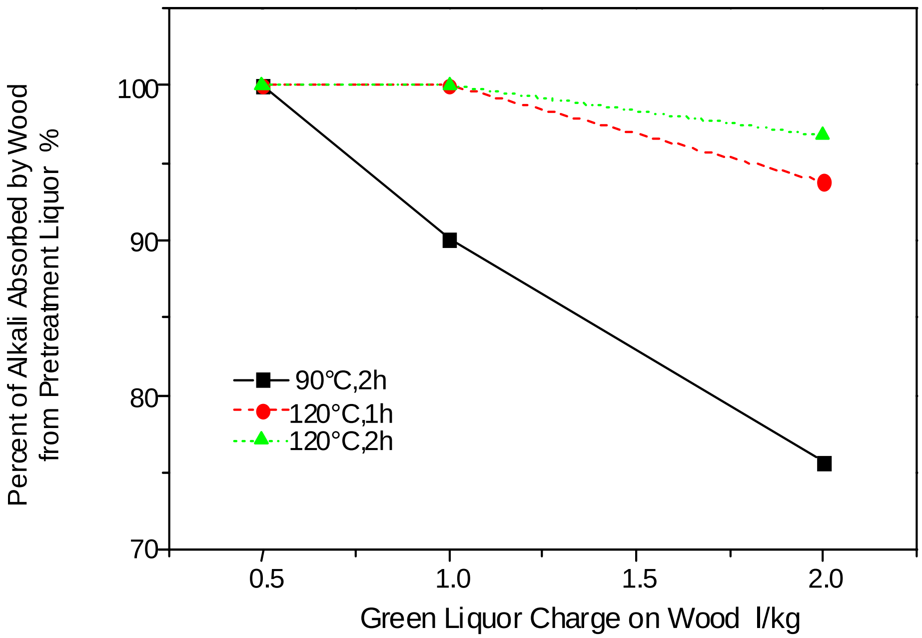

Figure 2. Percent absorption ratios of alkali in pretreatment liquor under variable GL charges (Ref.83).

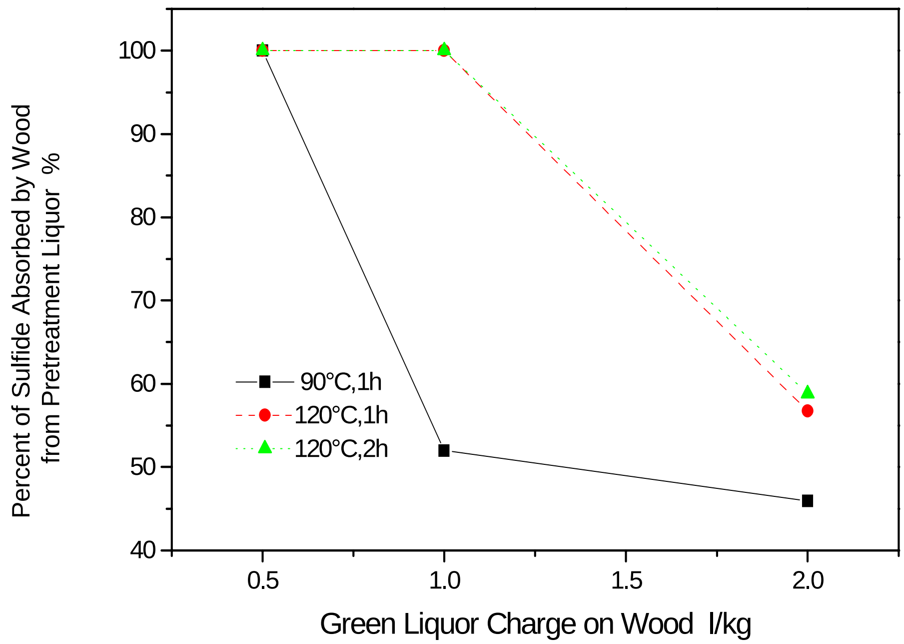

Figure 3. Percent absorption ratios of sulfide in pretreatment liquor under various GL charges (Ref. 83).

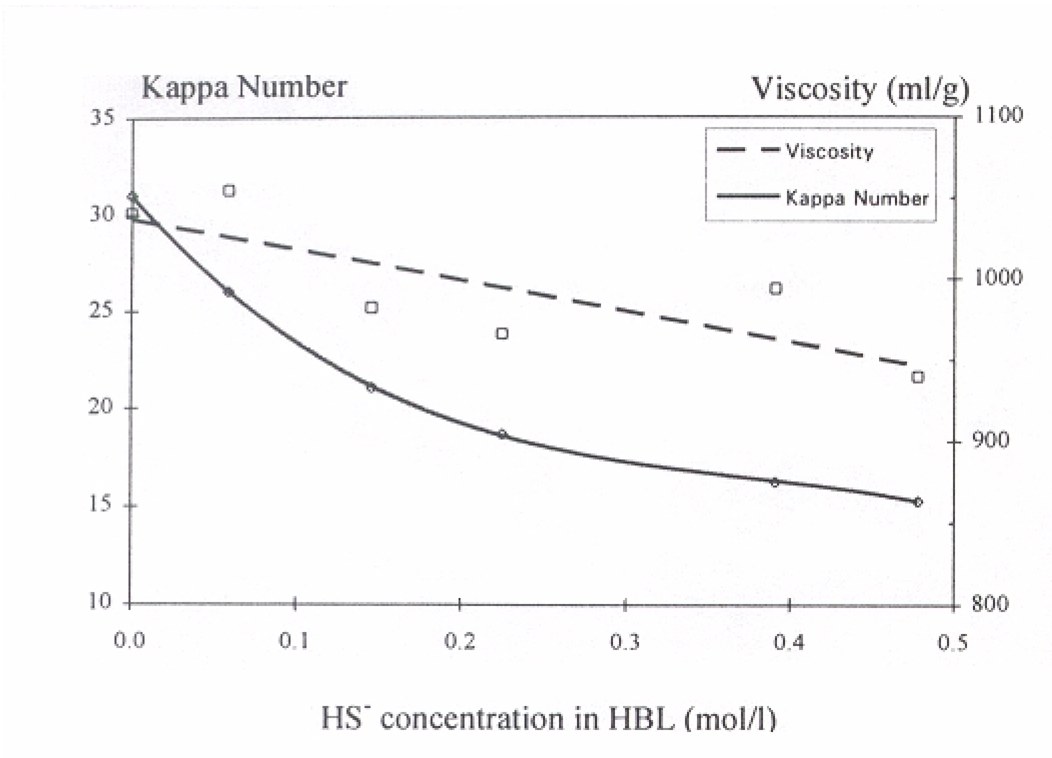

Figure 4. HS^- concentration in hot black impregnating liquor vs. pulp kappa number and viscosity (Ref. 16).

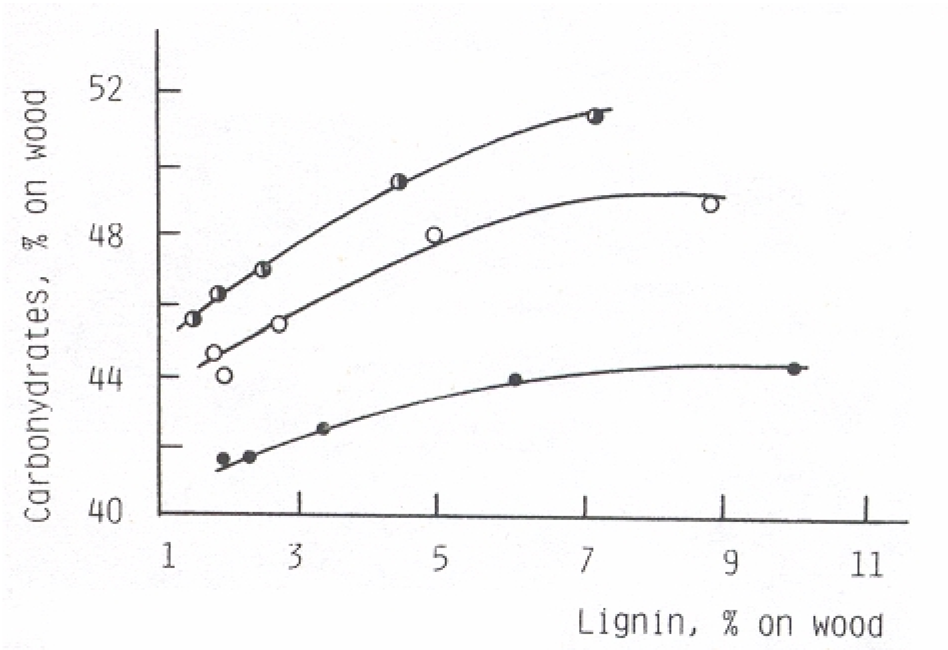

Figure 5. The effect of green liquor pretreatment on the selectivity of kraft delignification (● conventional kraft, ○ 4M GL, ◐ 0.7M GL) (Ref.63).

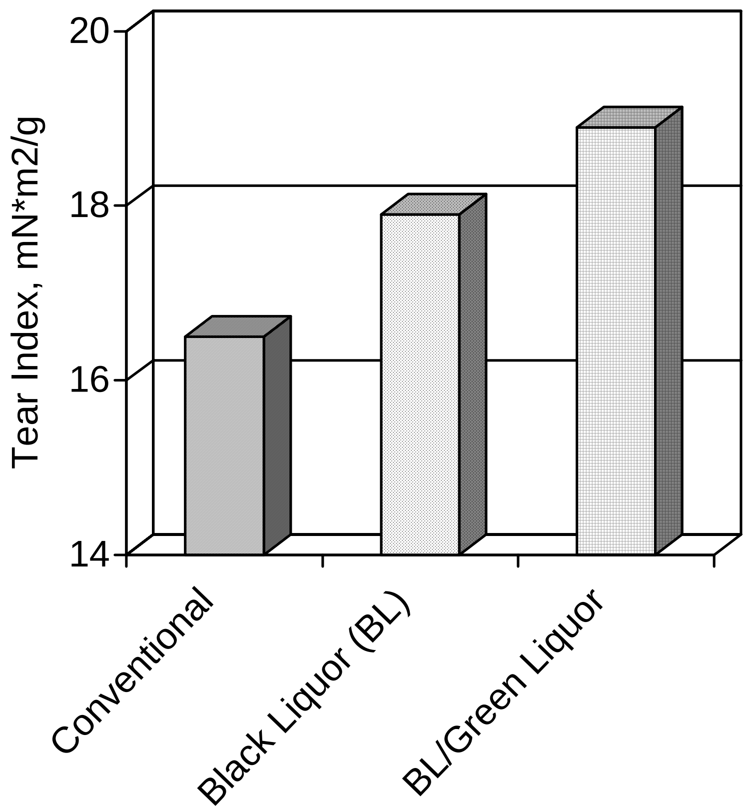

Figure 6. The comparison of tear strength at tensile index 70 Nm/g of various pulps (Ref. 37).