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ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · JANUARY 2005

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Kinetic Profiling of Green Liquor-Modified Kraft Pulping

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The kinetic features of the process of delignification in green liquor (GL) pretreatment kraft pulping were investigated in this study. GL pretreatment can accelerate pulping by providing a faster delignification rate at the onset of the bulk delignification stage of pulping. In addition, GL pretreatment increases the efficiency of the chemical reactions occurring during the pulping process. A good correlation between chemical performance and lignin removal was established for the GL-modified pulping process. The pulping chemicals were mainly consumed during bulk delignification, and the relative efficiency of reaction for the hydrosulfide and hydroxide anions for delignification were 2 and 1.6 times higher, respectively, as compared to conventional kraft pulping.

Introduction

In the past several decades, global competition for pulp quality improvement, demands in energy saving, and increasingly restrictive environmental regulations have forced the pulp and paper industry to seek modified pulping and bleaching technologies. Extended delignification pulping technologies have materialized as a result and have become a favorable approach to increasing the overall economic efficiency of the pulping process in modern operations. Several of the modified pulping processes, such as MCC and EMCC for continuous cooking systems^{1,2} and RDH for batch systems,^{3,4} have become standard pulping practices in the pulping industry to address pulping efficiency and economics. These latter technologies possess as a common motif the application of black liquor as a chip pretreatment liquor before the actual kraft cook. Based on the principles of modified delignification as suggested by researchers at STFi,^{5,6} the purpose of a black liquor pretreatment is to provide higher sulfide concentration in the initial cooking stage, which helps to ensure a higher efficiency of pulping.

The process of increasing the sulfide content in the chips can also be effected by green liquor (GL), an alternative source of higher sulfidity. GL is a rich hydrosulfide-content source and is easily accessible in all kraft pulp mills since it is a process liquor derived from the alkali recovery system. Its is uniquely positioned to pretreat the chips for maximum chemical benefit due to its naturally high sulfide-to-alkali ratio, allowing it to be a superior pretreatment liquor versus black liquor. The research that has been completed by our group and others have reported the use of GL, either the original liquor or its crystallized form, for the impregnation of wood chips in an integrated kraft cooking process.^{7–12} The results have demonstrated that modified kraft pulping through the use of GL pretreatments is beneficial for desirable pulp properties and qualities such as higher pulp yields, lower effective alkali consumption in the digester, increases in delignification, and improved pulp strength properties.

Although the chemistry has received considerable investigation recently, the kinetics of the reactions have been relatively neglected. The chemical reaction kinetics of kraft pulping have been investigated for many years.

Many kinetic models have been developed to describe delignification during the various pulping stages.^{13–16} In general, kraft delignification is considered a first-order kinetic process with respect to lignin concentration. The entire kraft pulping process may be characterized by three distinct phases: initial, bulk, and residual. Despite the many fundamental research efforts elucidating the chemistry of the GL pretreatment technology, the kinetics of GL pretreatment pulping have remained a mystery. The current work was therefore conducted to reveal the kinetic features of GL pretreatment-modified pulping and chemical behavior as well correlating their relationship during the pulping process.

Experimental Section

Wood. U.S. southern pine chips were obtained from an industrial sponsor. The chips were screened to retain the fractions whose length is between 16 and 32 mm and thickness is below 10 mm that were used for all experiments. The relative dry moisture content of the wood chips was 43.24%. All bark and knots were removed before pulping.

Green Liquor (GL). The GL used in all of the described experiments was provided from the same industrial sponsor. It was found to contain 15.91 g/L NaOH, 25.15 g/L Na₂S, and 85.36 g/L Na₂CO₃ (all concentrations expressed relative to Na₂O) analyzed by ABC titration test methods.

Pretreatment. Pretreatments were carried out in two 10 L digesters. The pretreatment temperatures were controlled by the computer program, and temperature ramps were of the order of 1.3 °C/min. Wood chips of 1 kg (o.d.) were used for each digester. Pretreatment conditions were as follows: ratio of GL to wood chips was 4:1, pretreatment time was 60 min under 120 °C, GL charge was 1 L/kg wood.

Cooking. After pretreatment, the GL was drained, and fresh white liquor was added for the ensuing pulping process. The cooking conditions were as follows: the ratio of liquor to wood chips was 4:1 (liquor adsorbed by wood chips was included); active alkali = 15% (Na₂O); sulfidity = 30%; and temperature ramps were on the order of 1.6 °C/min to reach 170 °C in 75

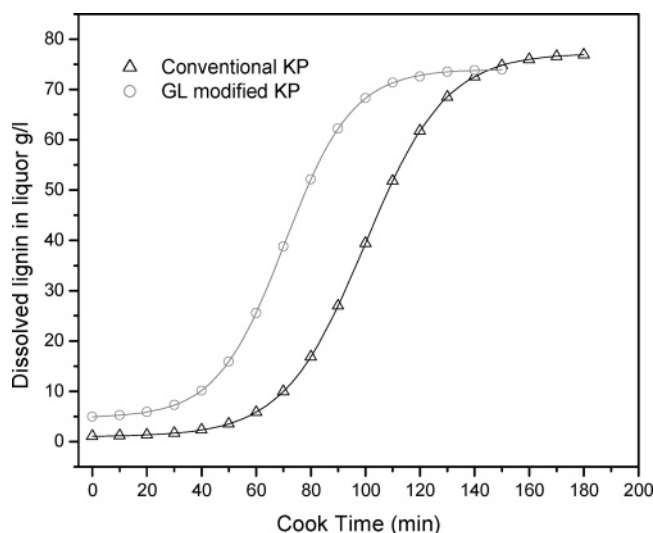


Figure 1. Kinetic process of delignification during the kraft cook.

min from the initial temperature of 50 °C, and held 75 min under the maximum temperature.

Conventional kraft cooks for comparison also were done in the same digesters with the following cooking conditions: 20% AA, 30% sulfidity, and 4:1 ratio of liquor to wood at 170 °C for 90 min. Temperature ramps were on the order of 1.6 °C/min to reach 170 °C in 90 min from room temperature and held 90 min under the maximum temperature.

All pretreatment and cook experiments were duplicated, and average results were used for all analysis.

Analysis. In all pretreatment and pulping processes, 10 mL of liquor was taken from the digester every 10 min for chemical and lignin analysis.

Sodium hydroxide in the pretreatment liquor was analyzed by the ABC titration method as modified in-house, while its sulfide and carbonate contents were analyzed by the GC method.¹⁷

Analysis of pulp κ numbers was based on TAPPI standard test method T236 cm-85. Lignin content in the process liquors was analyzed by UV spectrophotometry.¹⁸

Pulp Properties. Conventional kraft pulp had a κ number of 28.56 with a screened yield = 44.5%. GL pretreatment kraft pulp had a κ number of 30.28 with a screened yield = 46.7%.

Results and Discussion

Kinetic Features of Modified Kraft Pulping by GL Pretreatment. The salient kinetics of the process of delignification from GL pretreatment and conventional kraft pulping (KP) are displayed in Figure 1. In general, a similar profile for delignification is observed in both pulping processes. Similarly, both cooking processes may be divided into three distinct phases: initial, bulk, and residual delignification. Notably however, the delignification transition from initial to bulk and bulk to residual stage in the GL process commenced earlier and extended over a shorter time, remarkably different kinetic aspects for GL-modified pulping. To more clearly elucidate the delignification kinetics of GL pretreatment relative conventional kraft, the changes in the delignification rate during cooking are illustrated in Figure 2.

On the basis of the profiles provided for the delignification rates, the transition point of each stage was

Table 1. Summary of Lignin Removal in KP and GL Processes

cook stage	conventional KP			GL-modified KP		
	lignin removal (%)	time (min)	avg rate (g L ⁻¹ min ⁻¹)	lignin removal (%)	time (min)	avg rate (g L ⁻¹ min ⁻¹)
I Phase	4.64	0–50	0.049	9.87	0–30	0.077
II Phase	94.14	50–160	0.614	88.24	30–120	0.670
III Phase	1.23	160–180	0.071	1.89	120–150	0.066

clearly identified. Hence, three delignification phases were determined, which are summarized in Table 1. The initial stage for conventional KP was 50 min in which only 4.64% of the total dissolved lignin was removed. However, in GL-modified pulping, as high as 9.87% of the total dissolved lignin was removed in 30 min during this first stage, which is more than double than that of conventional KP. Furthermore, the average delignification rate in this stage for the GL-modified pulping was 57% faster than KP. It is known from our past work that pretreatment imparts a higher sulfide content in wood chips; however, the high delignification rate in the initial stage could not be ascribed only to high sulfide because past investigations have proved no positive effect on delignification rate increase when the sulfidity exceeds 30%.¹⁹ Therefore, the function of GL pretreatment is not to simply add more sulfide to the kraft cook but to influence the physical and chemical nature of wood adsorption and the ensuing chemistry of carbohydrates and lignin through the chemical composition of GL.

In the bulk delignification stage, approximately 90% of the total dissolved lignin was removed in both pulping processes. Similar to the conventional kraft pulping, GL-modified pulping started its bulk delignification near 100 °C, but 20 min earlier than conventional KP due to the fact that the pretreatment provided a higher initial cook temperature. Nevertheless, GL-modified pulping exhibits the following kinetic features: first, the maximum rate of delignification is 1.34 g of lignin L⁻¹ min⁻¹, which is 7.65% greater than the conventional cook (1.24 g of lignin L⁻¹ min⁻¹); furthermore, in a 20 min period of cooking (65–85 min), the rate of delignification exceeded the maximum rate of delignification during the conventional cook while during the entire bulk stage the average rate of delignification in GL-modified pulping was 10% higher. Finally, GL-modified pulping needs less time to complete the bulk delignification stage. GL-modified pulping required 90 min to complete bulk delignification (from 30 to 120 min), whereas conventional kraft pulping required 110 min (50–160 min). In summary, a faster rate and shorter pulping time are the main kinetic features for GL pretreatment delignification.

To further understand the kinetic features of GL-modified pulping, the delignification rates may be adequately summarized by kinetic expressions. The kraft kinetic model has been already determined to be a first-order reaction with respect to lignin content remaining in the pulp.¹⁴ It may be expressed as:

$$L/L_0 = A \exp(-kt) \quad (1)$$

where L/L_0 is the fraction of lignin remaining in the wood chips, L_0 is the original lignin content in wood, A is the coefficient calculated from L/L_0 values at the

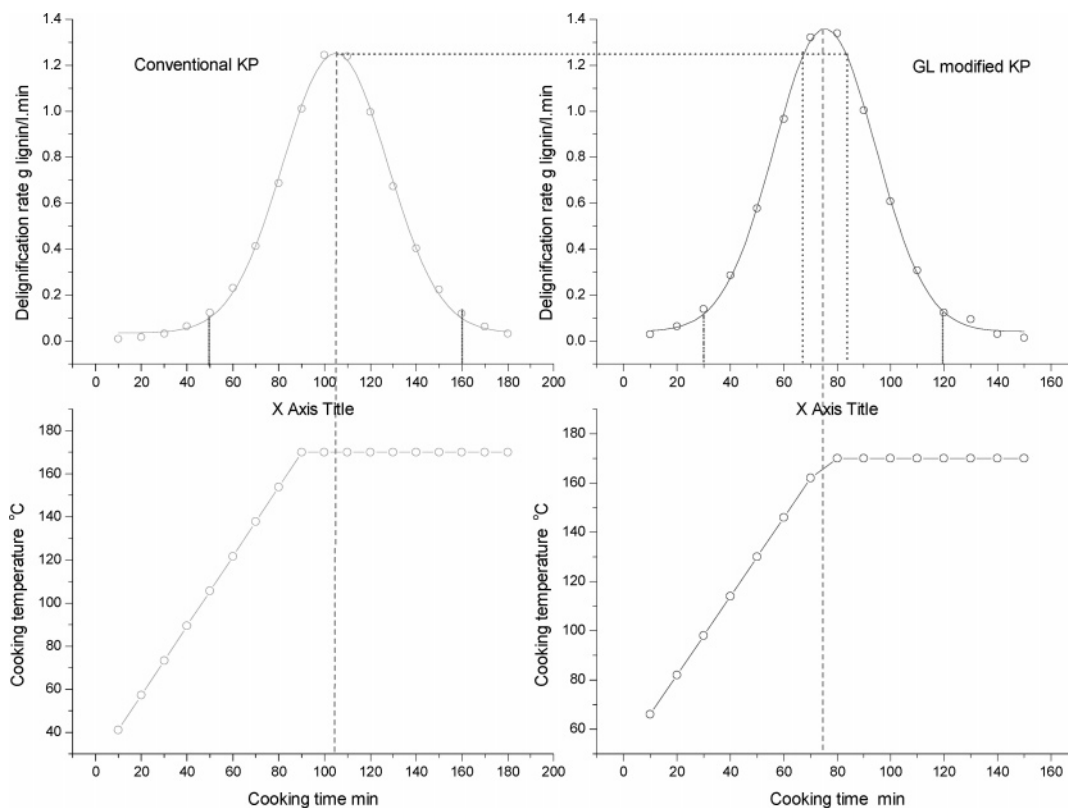


Figure 2. Comparison of the delignification rate for GL pretreatment and conventional kraft cooks.

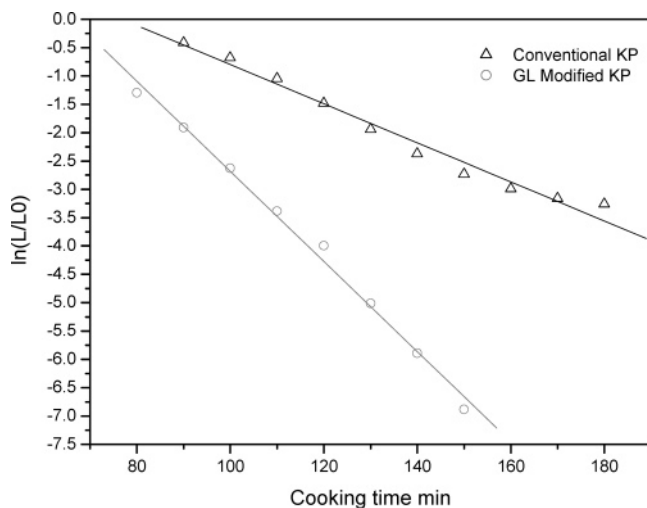


Figure 3. Kinetics for conventional and GL modified Kraft delignification at 170 °C.

beginning and end of the corresponding phases, and k is the delignification rate constant in the corresponding phase.

Obtaining the natural logarithm for eq 1 gives the following:

$$\ln(L/L_0) = \ln A - kt \quad (2)$$

Therefore, a linear correlation between the extent of lignin removal as described by the quantity L/L_0 , and the respective pulping time can be obtained. The delignification rate constant k is therefore obtained from the slope of the correlation.

Figure 3 illustrates the kinetics of delignification for both conventional and GL pretreatment kraft pulping at 170 °C. The linearity of the correlation of the log of

residual lignin content to the cooking time confirms that the GL-modified delignification process displays first-order kinetics as demonstrated for the conventional kraft case. However, it is clear that the greater slope for the GL-modified pulping case is indicative of a faster delignification rate than that of conventional kraft. Both kinetic processes can therefore be fit by the following equations:

$$\ln(L/L_0) = 2.6479 - 0.0344t \quad (3)$$

$$\ln(L/L_0) = 5.2661 - 0.0795t \quad (4)$$

in which eq 3 is the equation for conventional kraft kinetics and eq 4 is the equation for GL-modified pulping. It was found that the delignification rate constant for GL-modified pulping (k_{GL}) is 2.3 times higher as compared to conventional kraft. It is clear, therefore, that GL-modified kraft pulping accelerates the kinetics of delignification.

In the residual phase, the delignification rate was drastically reduced to approximately 10% of the bulk delignification stage. A small amount of lignin was removed in this stage, 1.9% for GL-modified pulping, and 1.2% for conventional kraft pulping, while the kinetic profiles for the two cases display no obvious difference.

While our previous studies have reported upon the physical and chemical adsorption features and the chemistry of the carbohydrate components in the GL pretreatment process,^{8,10} in this study we analyzed lignin dissolution. Figure 4 illustrates the rate of lignin dissolution during the pretreatment. Approximately 14% of the total lignin in wood was removed in the pretreatment process. The average rate of lignin dissolution was $0.091 \text{ g L}^{-1} \text{ min}^{-1}$, which was almost twice as high as conventional kraft and a little higher than

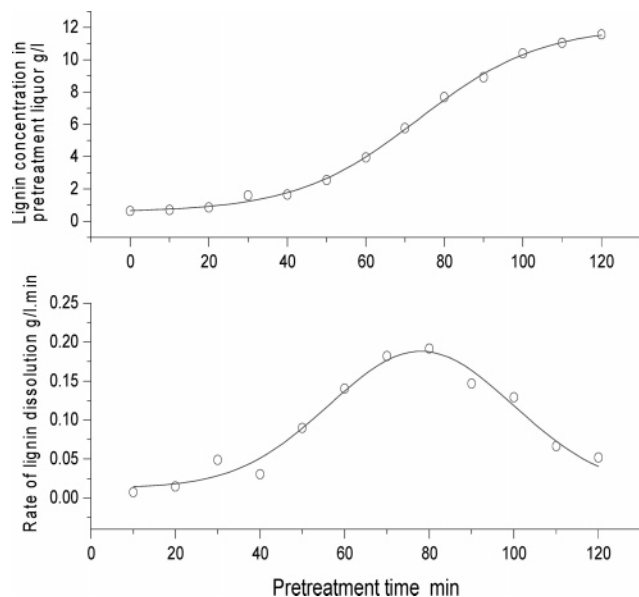


Figure 4. Rate of lignin dissolution during GL pretreatment.

that of GL-modified kraft pulping. By exploring the change in the lignin dissolution rate, similar kinetic aspects akin to conventional pulping were observed as shown in Figure 4. It can be seen that from 40 min (90 °C) the lignin content in the pretreatment liquor rapidly increased as the dissolution rate increased and the maximum rate took place at 80 min (120 °C). However, at later stages of the pretreatment process, the rate of lignin dissolution quickly decreased. During the final 20 min, very little lignin was removed; thus, extending the pretreatment time does not contribute to lignin dissolution. This result indicates that lignin removal in GL-modified pulping is limited. We speculate that the lignin removed may be low molecular weight residues. Much of the main lignin macromolecule is not decomposed under pretreatment conditions. Therefore, the primary function of GL-modified pulping pretreatments is to enhance chemical adsorption and activate the lignin structure. From our studies, it does not appear to be a practical means to delignify the substrate.

Physicochemical Characteristics of the Pulping Chemicals. There are three main salt constituents in the aqueous green liquor: sodium hydroxide, sodium sulfide, and sodium carbonate. The carbonate appears to be an inactive component during the pretreatment process as we previously reported.⁷ Thus, in the GL-modified process, the physicochemical behavior of both the hydroxide and the hydrosulfide ions merits investigation.

Figure 5 illustrates the changes in concentration of hydroxide and hydrosulfide ions during the pulping processes. The higher active alkali (AA, g/L) charge (AA = NaOH + Na₂S expressed as Na₂O) shown for conventional kraft pulping versus GL-modified pulping defines the character of conventional pulping. Notably, while the pulping proceeded, both the hydrosulfide and the hydroxide concentration in the GL-modified pulping process exceeded those of the conventional process at 30 and 90 min, respectively. Thus, the physicochemical behavior of these chemicals in GL-modified pulping is characterized by a lower consumption at a slower rate, which is predictive for a lower requirement of AA in GL-modified pretreatment pulping. Furthermore, both pulping processes proceeded in the same alkaline environ-

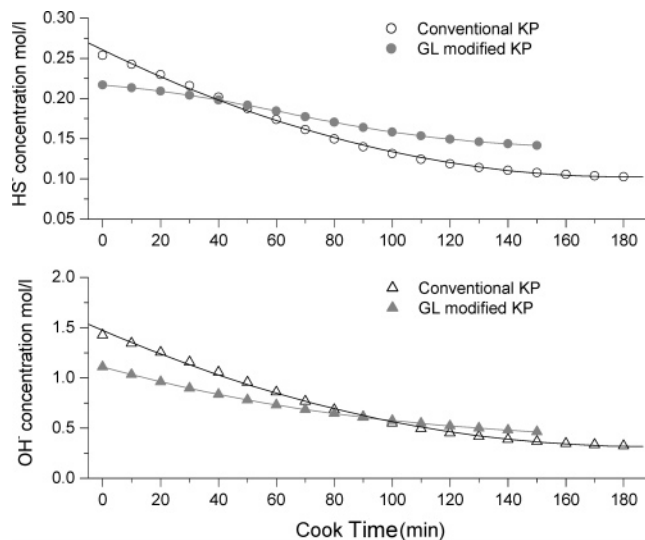


Figure 5. Changes in chemicals concentration during cooking.

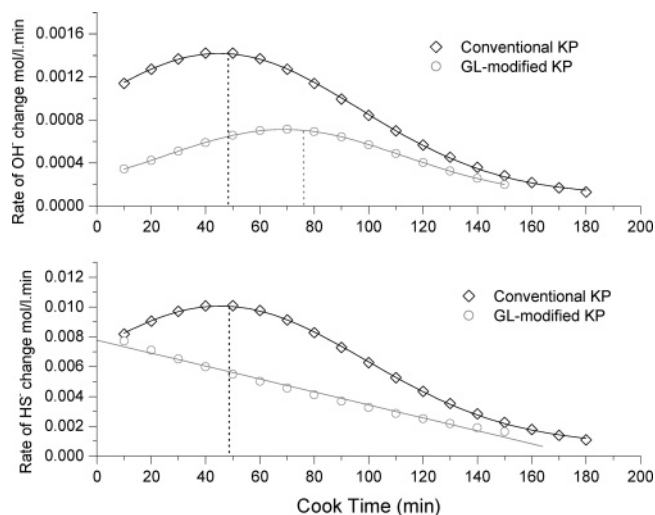


Figure 6. Rate of chemical consumption during conventional and GL-modified kraft cooks.

ment after 90 min. However, the delignification processes were quite different at this point. GL-modified pulping had already passed its maximum delignifying rate while nearing the final phase. The conventional pulping was approaching its maximum delignification rate. It was therefore found that almost 60% of the total lignin was removed in a period of 40 min, 60–100 min for GL-modified pulping, and 90–130 min for conventional kraft. Therefore, although a reduction is discovered for the amount of chemicals used in GL-modified pulping, the lower consumption in the early pulping period resulted in a higher chemical concentration in the bulk delignification period.

We further investigated the function of alkali and sulfide during pulping. The change in the rate of hydroxide and hydrogen sulfide ion concentration in pulping is plotted in Figure 6. During conventional pulping, the maximum consumption for both hydroxide and hydrogen sulfide ions occurred at 50 min at a temperature of 105 °C. However, as compared to the delignification process shown in Figure 2, this region is the transition point from the initial to the bulk phase of pulping. Therefore, faster chemical consumption does not contribute to delignification. A faster rate of chemical consumption mainly functions to degrade and dis-

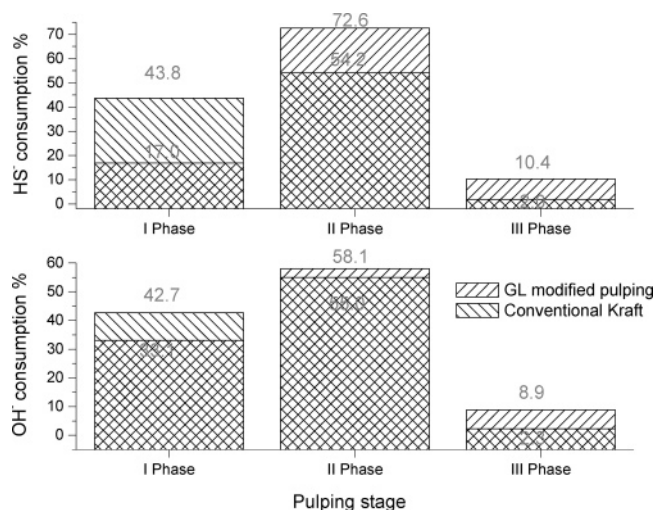


Figure 7. Percentage of chemical consumption in each pulping stage for conventional and GL-modified cooks.

solve the native wood hemicelluloses. In GL-modified pulping, the highest rate of hydroxide ion consumption occurred at 80 min, which correlates well with the maximum delignification rate *vide infra*. The data clearly demonstrate that the main function of hydroxide in GL-modified pulping is to contribute to delignification. Interestingly, hydrosulfide ion was uniformly consumed at the slower rate change, which implies that hydrosulfide has a different activity during GL-modified pulping.

In total, 58.1% of hydroxide and 34.5% of hydrosulfide were consumed in GL pretreatment pulping as compared to 77.3% and 59.6% in conventional kraft. The data indicate that GL-modified pulping requires a lower level of chemical charge to achieve a similar pulp response. Figure 7 clarifies the distribution of chemical consumption during each pulping phase. In the first stage of conventional kraft, the wood components consumed about 43% of both hydroxide and hydrosulfide based on the total consumption amount. Obviously, such high chemical consumption would not correlate to lignin removal given the previous data; therefore, the majority

of these chemicals must be consumed by the carbohydrates. In a side-by-side comparison to kraft pulping, the chemical consumptions in GL-modified pulping were at a relatively reasonable level: 33% of hydroxide and 17% of hydrosulfide were consumed.

In the bulk delignification stage in both pulping processes, the hydroxide consumption percentage is almost identical (55–58%). However, 72% of the hydrosulfide based on the total consumed amount in GL-modified pulping was consumed in the bulk stage, which is much higher than that of conventional kraft. This signifies that a higher level of hydrosulfide participates in the major delignification process.

In the residual stage, only 2% of hydroxide and hydrosulfide were consumed in the conventional kraft process, which indicates that no more delignification occurred in this stage. On the other hand, as much as 10% of chemicals were consumed in the same stage for the equivalent GL process. This higher chemical consumption, however, did not correlate to a higher lignin removal. Thus, the result suggests that attempts at further shortening the residual stage time are viable and make GL-modified pulping more efficient.

Overall, a more uniform distribution of chemical consumption in pulping may be achieved by GL pretreatment. The pulping chemicals, especially hydrosulfide, are mainly consumed in the major delignification stage, which results in an enhancement in delignification and a reduction in total chemicals usage.

Correlation of Delignification with Chemical Behavior. Figure 8 elucidates the ratio of consumption rates of hydroxide to hydrosulfide ions in both pulping processes. In conventional kraft, a flat, straight line indicates that both hydroxide and hydrosulfide were consumed at a specific ratio with little to no change over the whole pulping process. Quite a different phenomenon was apparent during the GL pretreatment pulping process. It was found that the rate of hydrosulfide and hydroxide consumption was initially slow but kept increasing as pulping proceeded. In fact, it reached its maximum value during the 90–100 min cooking time and decreased during the remainder of the pulping process. Indeed, the kinetics of hydrosulfide and hy-

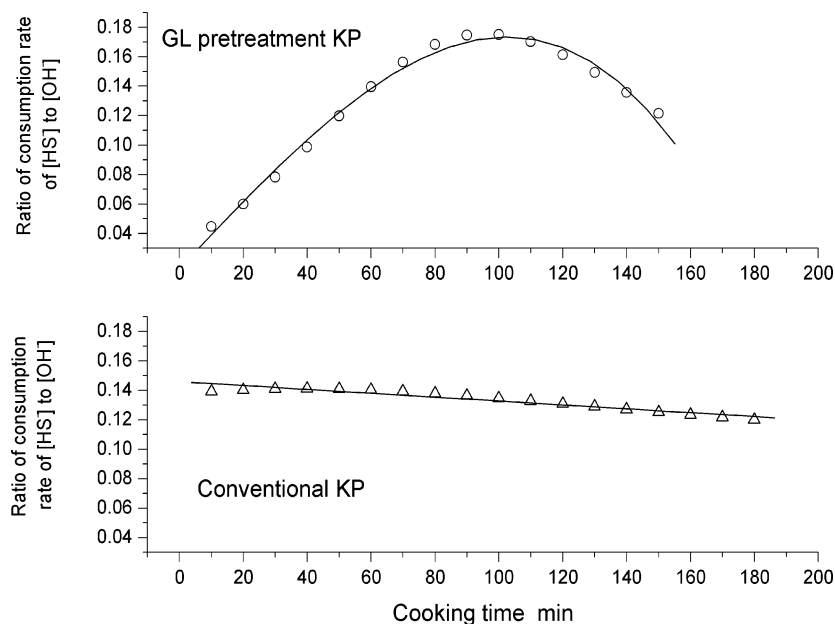


Figure 8. Change in the ratio of consumption rate of hydrosulfide to hydroxide.

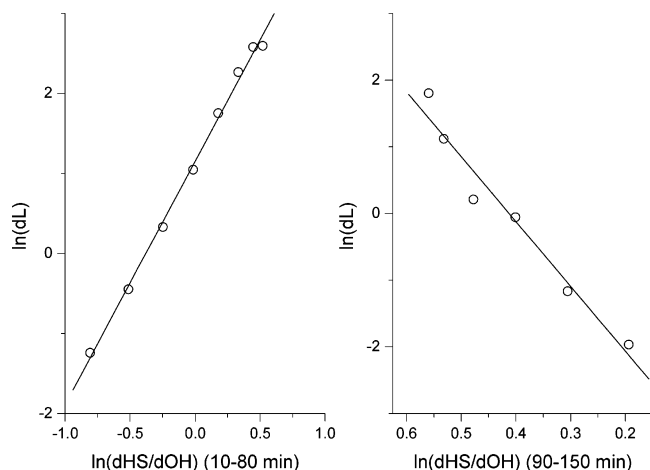


Figure 9. Logarithmic plot of delignification rate vs ratio of consumption rate of hydrosulfide to hydroxide. dL: delignification rate, g of lignin $\text{L}^{-1} \text{min}^{-1}$. dHS: HS ion consumption rate, mol $\text{L}^{-1} \text{min}^{-1}$. dOH: OH ion consumption rate, mol $\text{L}^{-1} \text{min}^{-1}$.

droxide consumption are similar in character to the kinetics of the delignification process. The phenomenon strongly suggests an intrinsic correlation between delignification and chemical consumption. Figure 9 illustrates the logarithmic plot of the rate of lignin removal versus the logarithmic consumption ratio of hydrosulfide to hydroxide. The good linear relationship indicates that chemical consumption correlates strongly with delignification, whereas the character of the pulping chemical composition, particularly the ratio of hydrosulfide to hydroxide, is more relevant in targeting the decomposition of the lignin macrostructure.

Furthermore, unlike the high hydrosulfide consumption that occurs during the first stage of conventional kraft pulping, an analysis of the hydrosulfide consumption in each stage of GL-modified pulping reveals that it more efficiently correlates to a uniform delignification process. The correlation of logarithmic lignin removal rate with hydrosulfide consumption rate is plotted in Figure 10. At the transition point of the maximum

Table 2. Contributions of HS and OH to Lignin Removal

	HS contribution (g of lignin/ mmol of HS)		OH contribution (g of lignin/ mmol of OH)	
	conventional KP	GL- modified KP	conventional KP	GL- modified KP
I Phase	0.054	0.571	0.008	0.034
II Phase	0.883	1.196	0.119	0.174
III Phase	0.314	0.178	0.038	0.024
entire process	0.509	0.984	0.070	0.115

delignification rate, GL-modified pulping can be divided into two parts: an increasing hydrosulfide consumption rate with an increasing delignification rate in the first part, while it decreases with a decrease in the delignification rate in the second part. The well-matched linear correlation between hydrosulfide consumption and delignification demonstrates that hydrosulfide in GL-modified pulping correlates very well with the efficiency of delignification that ultimately results in a higher delignification rate.

The goal of chemicals in pulping is targeted to delignification; however, an adverse action of chemicals on carbohydrates is unavoidable. Thus, how much chemicals are needed for each unit of lignin removal can be described as the pulping efficiency of chemicals during the pulping process. A higher lignin removal with less chemical consumption is optimal. The contribution of each unit of chemical consumption to lignin removal for the two pulping processes is summarized in Table 2. In general, hydrosulfide demonstrates a higher contribution to delignification in both pulping processes than hydroxide. In the conventional kraft process, the contribution by each unit of hydrosulfide to lignin removal was approximately seven times greater than hydroxide in all three stages. However, a much higher hydrosulfide contribution was exhibited in the initial stage of GL-modified pulping, almost 15 times higher than hydroxide. The higher activity of hydrosulfide can be attributed to GL pretreatment which contributes to an obvious acceleration of the delignification

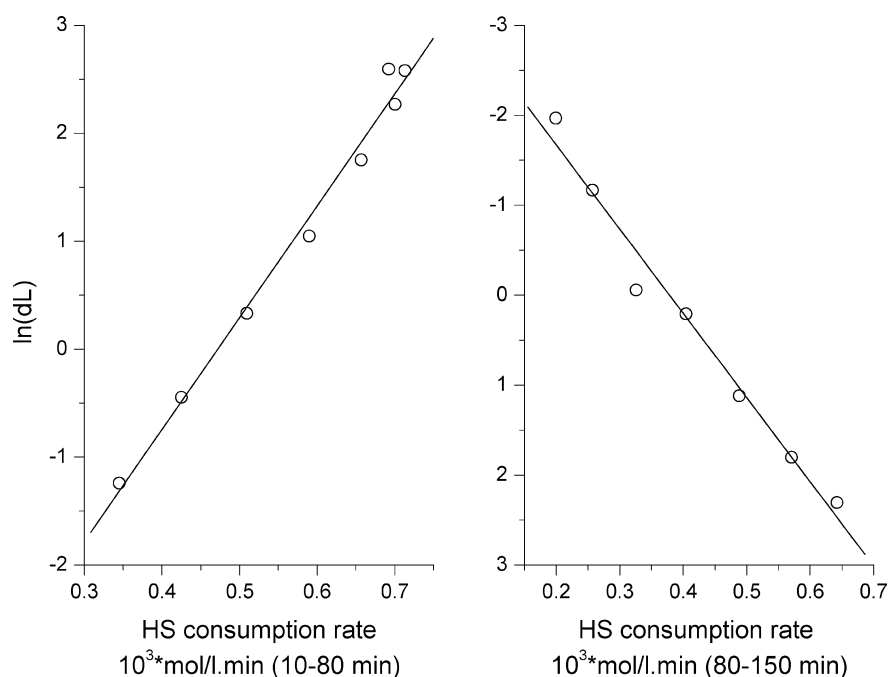


Figure 10. Logarithmic delignification rate vs hydrosulfide consumption rate. dL: delignification rate, g of lignin $\text{L}^{-1} \text{min}^{-1}$.

process. In the GL process, both hydrosulfide and hydroxide demonstrated greater contributions to lignin removal as compared to the conventional KP process. Hydrosulfide showed 10 and 1.4 times higher contributions than the conventional KP in the initial and bulk stages, respectively, whereas hydroxide showed 4.5 and 1.5 times higher contribution than KP in the same stages. Through the entire process, the contributions of hydrosulfide and hydroxide to lignin removal in GL pretreatment modified pulping were 2 and 1.6 times higher than those in the conventional KP.

In summary, one of distinct functions of GL pretreatment is to improve the efficiency of chemical delignification and, hence, result in a more selective delignification process. And more interestingly, this unique function cannot therefore be duplicated by merely adjusting the pulping chemical composition during the conventional kraft process.

Conclusions

GL pretreatment can improve the function of chemicals during delignification. First, chemical consumptions are well-correlated with the status of lignin dissolution during each pulping stage. They mainly contribute to delignification which correlates at a higher concentration; furthermore, the delignification function of hydrosulfide is strengthened by GL pretreatment. A higher consumption ratio of hydrosulfide to hydroxide in the major pulping period correlates well with a higher delignification rate while a linear relationship existed between lignin removal and hydrosulfide levels.

Delignification kinetics for GL-modified kraft pulping could be modeled as a first-order process including three successive phases. Compared to the conventional kraft pulping, the GL pretreatment pulping process features a higher delignification rate and a rapid cooking process. It required a shorter time in each stage, in which 30 min or more could be shortened in the whole pulping process. Overall, the average delignification rate may potentially be increased as much as 30% as compared to the kraft process.

Acknowledgment

This research was supported by the United States Department of Energy (Grant DE-FC36-01GO10626). The authors gratefully acknowledge International Paper and Riverwood International for their support of our work. Finally, we would also like to thank the Georgia Institute of Technology whose facilities were instrumental in allowing us to conduct this work.

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Received for review December 22, 2004
 Revised manuscript received February 7, 2005
 Accepted February 11, 2005

IE048762G