

The Effects of Lignocellulosic Fiber Surface Area on the Dynamics of Lignin Oxidation and Diffusion

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ABSTRACT: A novel preliminary experimental approach was developed to determine the effect of maximizing pulp fiber surface area for the regulation of the oxidation and diffusion of lignin through the carbohydrate matrix. The approach entailed liquid nitrogen freezing of mature black spruce kraft pulp fibers and subsequent mechanical grinding to a fine powder to test the effect of enhanced pulp fiber surface area on the efficiencies of lignin oxidation and lignin diffusion. It was found that the liquid nitrogen ground pulp samples provided higher optical reflectance (brightness) after both oxygen and hydrogen peroxide oxidation, which appears to be from chromophoric (chemical) differences and not light scattering differences as supported by UV/Vis spectroscopy. BET (absorption) experiments indicated a dramatic difference in the surface area of the pulp as a result of

the grinding, although no differences existed among the pore sizes between the samples, as determined from SEM experiments. Lignin diffusion experiments demonstrated that differences did exist in the kinetics of lignin diffusion into a bulk solution between a control and liquid nitrogen ground samples. Lignin uptake into bulk solutions was enhanced by the liquid nitrogen/pulp-grinding technique albeit not from chemical changes in the lignin because the subsequent NMR spectra did not point to any major chemical differences as a result of liquid nitrogen freezing and grinding. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 177–181, 2004

Key words: Black spruce; pulp fiber surface area; lignin oxidation; lignin diffusion

INTRODUCTION

The chemical degradation and facile removal of residual lignin from pulp fibers during bleaching reactions are the core microscopic processes for the operational efficiency of bleachable grade pulp mills. One of the chief hurdles to the complete removal of residual lignin is its inability to completely degrade under standard bleaching conditions and subsequently transfer into the bulk liquor medium. Many chemical factors can be cited for this phenomenon, in particular, condensed lignin structures,^{1–3} range of lignin molecular weights,^{4,5} fiber pore sizes,⁶ lignin–carbohydrate complexes,^{7,8} and lignin mass transfer rates.⁹ Interestingly, the effect of fiber cross-dimensional area has not received much investigation as a potential limiting factor for the bleaching of pulp fibers. Pulping work investigating the kinetics of lignin mass transfer was done by using fine pulp meal, but little else was published on the effects of fiber area on lignin mass transfer.¹⁰ Lignin diffusion studies demonstrated that the diffusional mobility of lignin is severely limited by a factor of 10^7 over what is expected from the

diffusional kinetics of lignin in water. This result was conjectured to result from lignin encountering physical obstacles in the fiber wall, namely, the macrofibrillar lamellae, thus preventing its facile migration. It was therefore believed that increasing the exposable fiber area and disrupting the macrofibrillar structure of the fiber wall would expedite the ability of lignin to degrade, escape the fiber network, and dissolve in solution. A remarkable related finding is that small differences in the dimensions of the macrostructure of lignin led to large differences in diffusion rates by as much as a factor of 10^5 for lignin molecules larger than the cell pores by 1%. The present preliminary research was therefore an attempt to apply a simple and direct method to induce severe fiber cell wall dislocations and disruptions and simultaneously increase the exposable fiber surface area. The driving force behind this work was to determine if lignin oxidation and diffusional behavior would be increased through enhanced surface area given the presumably lower barriers to lignin reactions and diffusion.

EXPERIMENTAL

Leaching

Approximately 100 g of control and the pulverized pulp (LN₂Pulp) were each suspended into large bea-

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TABLE I
Fiber Quality Analysis of the Pulp Fiber Samples

	Mean length weight (mm)	Mean length (mm)	Coarseness (mg/m)	Mean kink	Mean curl
Control	2.367	1.901	0.139	0.51	0.060
LN ₂ Pulp	1.567	0.768	<0.1	1.33	0.079

kers at 1% consistency at 0.1N NaOH content and stirred occasionally while collecting small amounts (<1 mL) of supernate for analysis.

BET measurement

Specific surface area of pulps was determined by the adsorption isotherms of N₂ at 77 K by using a Flow-sorb II 2300 BET surface area analyzer. Samples were dried in an oven at 120°C overnight and degassed at 150°C for more than 20 min prior to the adsorption measurements.

Bleaching

All pulps were hydrogen peroxide bleached in polyethylene bags at 70°C for 60 min at 3.0% peroxide charge and 2.5% caustic and 10% consistency; oxygen delignification was performed under variable times by using 2.5% base, 90 psi, 90°C, and 10% consistency in a PAPP 4282 reactor.

Analysis

Pulp brightness and UV/Vis spectroscopy were collected as reported previously by using solid-state UV/Vis directly on handsheets¹¹ with the Perkin-Elmer Lambda 900. All NMRs were collected by using the standard ³¹P quantitative procedure.¹² Kappa was conducted in accordance with TAPPI test method 236, having a mean error of ±0.3. For SEM, loose fibers were first coated with gold-palladium on SEM sample mounts. The JEOL JSM-35C scanning electron micro-

scope was used for analysis. A voltage of 15 kV was used and images were captured electronically. Focus was obtained for each image adjacent to the area of interest to avoid sample damage by the beam.

RESULTS AND DISCUSSION

All pulp was obtained from a single Northern black spruce tree that was segregated into a predominantly juvenile source (top 8 feet) and predominantly mature source (pulpwood) that was used for this study. All cooks were performed under standard kraft batch conditions at Potlatch Corp. (now SAPPi) and the resultant pulp was washed and stored in the cold. The pulp was pulverized into a fine powder by adding ~ 100 mL of liquid nitrogen (Holox Co.) to 250 g in a mortar and mechanically agitating the frozen fibers with a pestle (LN₂Pulp). Fiber analysis was done by using a fiber quality analyzer (FQA) instrument (OpTest Equipment Inc.); results of this grinding can be found in Table I. Length reduction was not as large as originally expected (~ 50%) based upon the appearance of the pulp, which is confirmed by SEM, but is large enough to enhance access of chemicals to the fiber.

Diffusional reactions

The long-term rate of efflux of lignin into a basic solution between the control and liquid nitrogen ground pulp (LN₂Pulp) was monitored over 7 days and the results are shown in Figure 1. The final differences between the two pulps are not as pronounced as expected, because both tend to level off at a kappa of ~ 16 within experimental error. However, the LN₂ pulp shows greater lignin diffusional kinetics after the first day of soaking (note a slight variation in original pulp kappas). The LN₂ pulp differs by approximately a 0.5 kappa number from the control pulp (within

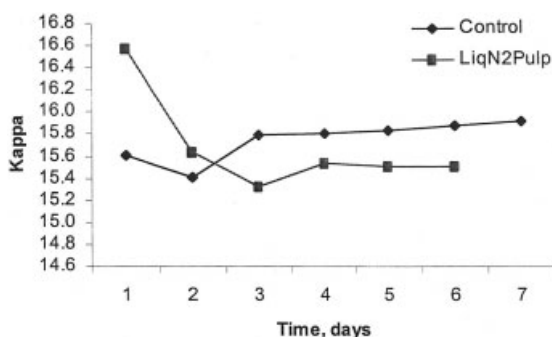


Figure 1 Differences in the changes in kappa between a control and LN₂ (LN₂ Pulp) softwood pulp.

TABLE II
The Surface Areas of the Control and LN₂ Samples as Obtained from BET

Sample no.	Specific area (m ² /g)
LN ₂ Pulp	14.8
Control	5.8

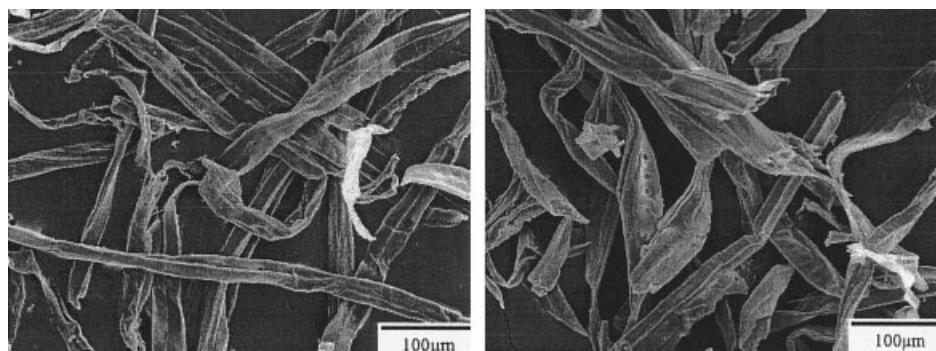


Figure 2 Scanning electron microscopic (SEM) micrographs of a control mature black spruce sample on the left and the accompanying liquid nitrogen ground sample for the mature black spruce.

experimental error), although its surface area is $\sim 250\%$ greater than the control as shown in Table II.

This result suggests that increased surface area may indeed play a role in helping to liberate lignin fragments due to the increased area, fiber damage to the cell walls, and likely physical damage to its own polymer structure. The maceration procedure likely helps liberate lignin from the cell walls and fiber interstitial spaces of the fibers. The SEM micrograph of these fibers in Figure 2 clearly prove significant physical damage to the fibers as a result of cell-wall disruption from the liquid nitrogen freeze and subsequent grinding. We noted from high-magnification SEM that the pore-size distribution between the fibers is not altered to any significant degree, thus eliminating the potential for fiber pores to impact diffusional phenomena.

Although these results indicate that the final lignin level differences are not as pronounced between LN₂Pulp and control, it appears that surface and bulk damage to a fiber are of prime importance for kinetically enhancing lignin efflux to the bulk. This result is not entirely unexpected because the final lignin concentration in a diffusion process is thermodynamically controlled, whereas the kinetic control is governed by lignin size, pore size, temperature, bulk concentration, and charge gradients. Yet, of the latter factors, not one was implicated as the most important contributor to the success of the diffusional process. Some previous work demonstrates that the efflux of lignin can be modeled as a complex migration of lignin through a maze of microfibrils with an exceedingly small diffu-

sion coefficient.¹⁰ Apparently, because of the severely low diffusion of lignin, the only pronounced efflux differences speculated to occur would require a smaller lignin size to obviate diffusional barriers, which may be the case in this study given the mechanical action induced. Certainly such an effect is akin to what is observed in mechanical pulping processes in which lignin is removed, but not chemically modified by mechanical agitation energy.¹³

Bleaching runs

All pulps were subjected to hydrogen peroxide and oxygen delignification reactions to determine how LN₂ pulp would respond to delignification and optical reflectance (brightness) changes. A control sample was created to compare LN₂ and base pulp to understand the effect of scattering on brightness. It was found that scattering accounted for an ~ 2.5 to 3-point brightness gain. For peroxide, there was a five-point brightness gain between the LN₂ and base for identical conditions, whereas for oxygen, the difference was six points. When the brightness gain from scattering is deconvoluted, there is a significant gain for both bleaching reactions with oxygen being slightly greater. This perhaps shows that surface area is indeed a significant factor for brightness chemistry. Results from these studies are depicted in Tables III and IV. Solid-state UV/Vis analysis was also conducted to attempt to elucidate the influence of surface area on the bleaching seen in Figures 3 and 4. Not surpris-

TABLE III
Peroxide Bleaching Brightness Results for the Samples

	ISO brightness
Mature bleached pulp	34.7
LN ₂ bleached mature pulp	39.8
Mature unbleached	31.5
Mature unbleached LN ₂	34.1

TABLE IV
Oxygen Bleaching Brightness Results for the Samples

	ISO brightness
Mature 60 min	32.7
LN ₂ mature 60 min	38.4
Mature unbleached	31.5
Mature unbleached LN ₂	34.1

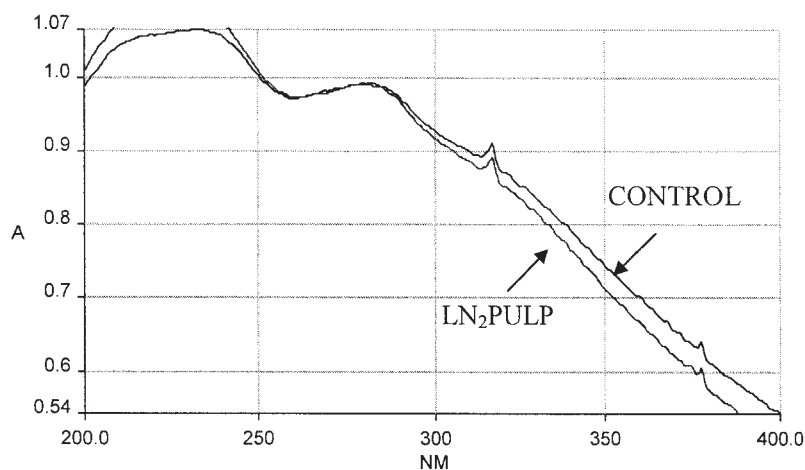


Figure 3 UV/Vis results for the hydrogen peroxide bleached samples.

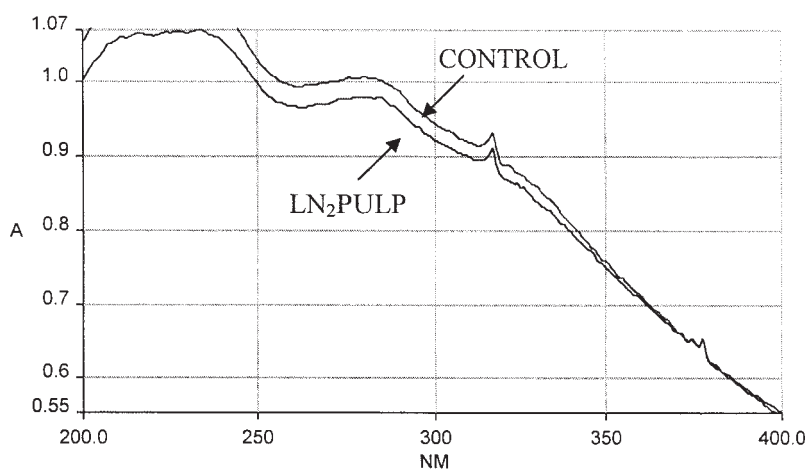


Figure 4 UV/Vis results for O₂-delignified pulp samples.

ingly, there are differences between the LN₂ and control samples for peroxide at the onset of the visible region but of low absorbance (hence, not as visually acute); yet, they are not as pronounced as the higher absorbances (and consequently more pronounced differences) in the near-UV found from in the oxygen data. This data suggest that the activation barriers for the chemical reactions are depressed for the LN₂ samples, allowing for more efficient oxidation of the lignin and thus higher brightness.

We obtained ³¹P NMRs of the LN₂Pulp and control to establish the integrity and structural similarity of

the lignin contained in each sample. Not surprisingly, we found that the lignin in each sample was nearly identical within experimental error given the differences in the starting kappa numbers of the pulps (see Table V).

CONCLUSION

The current investigation has provided a preliminary, direct method of probing the quantitative aspects of lignin oxidation and its diffusion by artificially in-

TABLE V
³¹P NMR Results Obtained for the LN₂Pulp and Control Samples

	Aliphatic lignin units (mmol/g)	Condensed 5,5'-phenolics (mmol/g)	Noncondensed phenolics (mmol/g)	Carboxylic acids (mmol/g)
LN ₂ mature	0.91	0.73	0.77	0.26
Mature	1.09	0.67	0.70	0.27

creasing the area of the pulp. Although the lignin appears to be unaffected chemically from the grinding procedure as investigated by NMR, the increased surface area appears to have a contribution to the diffusional kinetics of the lignin removal in pulp. Increased surface area also enhances hydrogen peroxide and oxygen bleaching brightening reactions. In summary, surface area thus appears to play a role in the kinetics of lignin diffusion and the efficiency of lignin oxidation chemistry.

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