PEROXYALKANOIC CELLULOSE PURIFICATION OF STEAM EXPLODED YELLOW POPLAR

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(Abstract)

Water and alkali extracted steam exploded yellow poplar fiber (log R_o 4.25) was purified through a multi-stage process. The initial stage consisted of peralkanoic acid treatment, either formic or acetic acid, at atmospheric pressure. Subsequent bleaching was achieved through treatment with alkaline peroxide in several stages. Performic acid experiments were performed by researchers at the Finnish Pulp and Paper Research Institute: K. Poppius, I.Tuominen and J. Sundquist. Peracetic experiments were conducted at Virginia Tech.

The alkanoic acid stage process parameters examined included time (3 and 6 hours primarily), temperature (40 and 60° for the peracetic trials, 80° for the performic trials), acid concentration (25, 50, and 80% for the peracetic trials), and initial peroxide charge (10 and 20 % for the peracetic trials; 2,5, and 10% for the performic trials).

The bleached fiber was analyzed on the basis of brightness (diffuse reflectance of hand sheets at 457nm), Kappa number, molecular weight (carbanilation followed by GPC), and carbohydrate composition (complete hydrolysis followed by HPLC). Peroxide concentration was monitored through iodometric titration.

The results indicated that the purified fiber may be useful as a microcrystalline cellulose. The purification process occured in three phases: lignin activation, followed by dissolution, followed by alkaline peroxide bleaching. Brightness correlated well with Kappa number. Molecular weight loss (as weight average) averaged 43%. Glucose purity of 93% was realized for the peracetic trials with residual lignin of approximately 1%. Residual

hemicellulose content was approximately 1.5%. Final brightness levels of nearly 90% MgO were attained by the performic acid samples.

In terms of percent gain in brightness per percent peroxide consumed, higher temperature resulted in greater efficiency. An alkaline extraction (no peroxide) following the initial acid stage improved efficiency. Initial peracetic peroxide charge of 20% was inefficient compared to an initial charge of 10%.

Molecular weight loss was affected by water concentration of the acid stage, but unaffected by an increase in the acid stage temperature from 40° to 60°. Molecular weight loss appeared to increase with acid stage peroxide charge up to 10%, but 20% charge did not result in greater losses.

Further research using higher temperatures and a sulfuric acid catalyst are suggested.

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Glossary

DP_n (DPn)	Degree of polymerization based on M_n.
DP_w (DPw)	Degree of polymerization based on M_w.
GPC	Gel permeation chromatography.
HPLC	High performance liquid chromotography.
L:W	Liqour-to-wood.
M_n,M_w	Number average and weight average molecular weights.
M_v,M_z	Viscosity average and z-average molecular weights.
MHS α	Mark-Houwink-Sakurada exponent.
o-;p-	Refers to ortho and para positions on the aromatic ring.
s^2	(Statistics) Sample variance.
THF	Tetrahydrofuran.
α–,β–,γ–positions	Refers to side chains present on the aromatic nucleus (lignin). The α-carbon is the carbon covalently bound to the nucleus (benzyl position). The β– and γ– carbons are the second and third carbons, respectively.
α–Cellulose	That portion which is insoluble in 17% NaOH.
α–Level	(Statistics) Probability of making a type 1 error.
δ–, δ+	Partial negative and positive charge densities.
σ^2	(Statistics) Population variance.

1.0 Introduction

1.1 State-of -the-art Cellulose Isolation

Dissolving-grade celluloses are used extensively in pharmaceuticals, regenerated fibers and films, food additives, and protective finishes and coatings. Historically, cotton linters supplied the need for chemically pure cellulose. Since world war II cotton has been replaced by woody biomass as the primary source for pure cellulose.

Dissolving pulps from woody biomass have been produced by both the sulfite and the kraft (sulfate) pulping industry. In the case of the kraft process a pre-hydrolysis step has traditionally been employed. The sulfite process may only be applied to hardwoods. Though softwoods may be pulped by the kraft process, hardwoods are preferred. Both of these processes require the use of sulfur containing chemicals. Sulfur dioxide emissions have long been implicated in the global acid rain problem; these may be produced by the recovery furnace and the lime kiln of the kraft process, as well as the bleach plant which uses SO_2 to produce ClO_2. Reduced sulfur species are responsible for the disagreeable odors produced by the kraft process: these include dimethyl sulfoxides, hydrogen sulfide, and methyl mercaptan. The sulfite process has not seen the same level of investment in the U.S. as the kraft process; thus, on an industry scale the sulfite pollution contribution is not very large. However, the major component of sulfite air emissions is SO_2. Sulfur dioxide is less noticeable than the reduced sulfur species as it has an odor threshold about 1000 times greater (1). Emissions of SO_2 from sulfite mills are a greater problem in Europe where the sulfite process has seen more investment.

Biochemical oxygen demand, BOD, is the most widely used measure of water-born organics carried in effluent streams. As a function of pulp yield, BOD appears to increase exponentially as yield decreases (1). Because traditional chemical pulping methods are low-yield processes, more organics are carried in their effluent. As noted, the kraft process incorporates a liquor recovery cycle: much of the organics are burned resulting in lower BOD. The analogous sulfite recovery cycle produces excessive amounts of SO_2, however.

Chemical purification of kraft and sulfite pulps is not a one-step process: five stages with water washing between stages are common in the typical bleaching sequence. This multi-stage approach to cellulose purification is unlikely to be replaced by a one-step, or even a two step process, due to the inaccessibility and different chemistries of the component biopolymers. New pulping techniques may reduce the number of stages required or the amount of active chemical required or increase the efficiency of the sequence.

Traditional bleaching sequences employ chlorine, chlorine dioxide, and hypochlorite. The chloro-chemicals preferentially attack the lignin component of the biomass, rendering it soluble in aqueous alkali. Two of the by-products of this process are dioxins and polychlorinated-dibenzofurans (PCB's) : these substances are extremely toxic and suspected carcinogens (2). Poly-chlorinated dibenzofurans, PCB's, and dioxins are particularly destructive as they tend to accumulate in the tissues of organisms at higher levels of the food chain. Trace amounts of these substances may remain with the fiber.

1.2 Novel Approaches to Cellulose Isolation

Steam explosion for the fractionation of biomass has received much attention recently as has organosolv pulping for the same goal. Both of these methods promise to reduce the environmental impact of isolating pure poly-anhydroglucan.

1.2.1 Organosolv Pulping

Rather than relying on reagents to react with lignin and change its structure, organosolv processes take advantage of the solubility of lignin in organic solvents, typically ethanol, to selectively dissolve the lignin portion while leaving the cellulose phase in tact. This approach allows recovery of a lignin which is uncontaminated with sulfur. Its structure is similar to that of milled-wood lignin isolations with the notable difference of fewer ß-O-4 linkages, which indicates that depolymerization has occurred. Most of the carbohydrate fraction is recoverable as well. Cellulose hydrolysis may be influenced by temperature and duration as well as through the concentration of alcohol. In the course of lignin dissolution α–O–4 ether linkages are likely broken due to the slightly acidic

conditions generated through partial hydrolysis of hemicelluloses. Higher temperatures are required to cleave β–O–4 ether linkages (approx. 200° C) (3,4). Although the organosolv process is a viable alternative to the problem of fractionating ligno-cellulosics, it creates the problem of solvent generation and recovery. The problem may have been overcome as a demonstration mill is in operation in New Brunswick. This mill uses the Alcell process, a multistage ethanol/water system.

1.1.2 The Steam Explosion Process

Steam explosion (SE) does not require any special solvents; however, high molecular weight cellulose appears to be unattainable through steam explosion of woody biomass. Experiments at Virginia Tech have demonstrated that SE is a good technique for recycling magazine stocks that have been prewetted : the molecular weight of this material might be relatively unaffected due to the mild reaction conditions that proved sufficient for pulping. (The effects of steam explosion on molecular weight of recycled fiber were not quantified.) In the SE process wood chips are saturated with steam under pressure. When the pressure is instantaneously released the steam within the wood chips expands with enough force (explosion) to cause complete fiber separation. The hemicelluloses are readily extracted with water. The lignin from this process forms micron-sized droplets that are readily extracted with aqueous alkali or organic solvents. The unextractable portion is quite accessible to bleaching reagents. The percentage of crystalline cellulose increases in response to SE but the crystalline lattice remains unchanged (5,6).

Previous research performed at the Biobased Materials Center at Virginia Tech produced a relationship between molecular weight of unbleached steam exploded yellow poplar and severity of steam treatment, represented as the logarithm of the reaction ordinate (log R_o) .The range of log R_o values depicted represents a range for optimal fractionation (7). (The reaction ordinate definition may be found in the Literature Review section). This relationship is depicted in Figure 1. The weight and number average degrees of polymerization are represented as DP_n and DP_w, respectively. Also depicted are DP values for a standard Eastman dissolving grade and a standard Whatman (CF-11) microcrystalline grade of cellulose. Note that the molecular weight of the

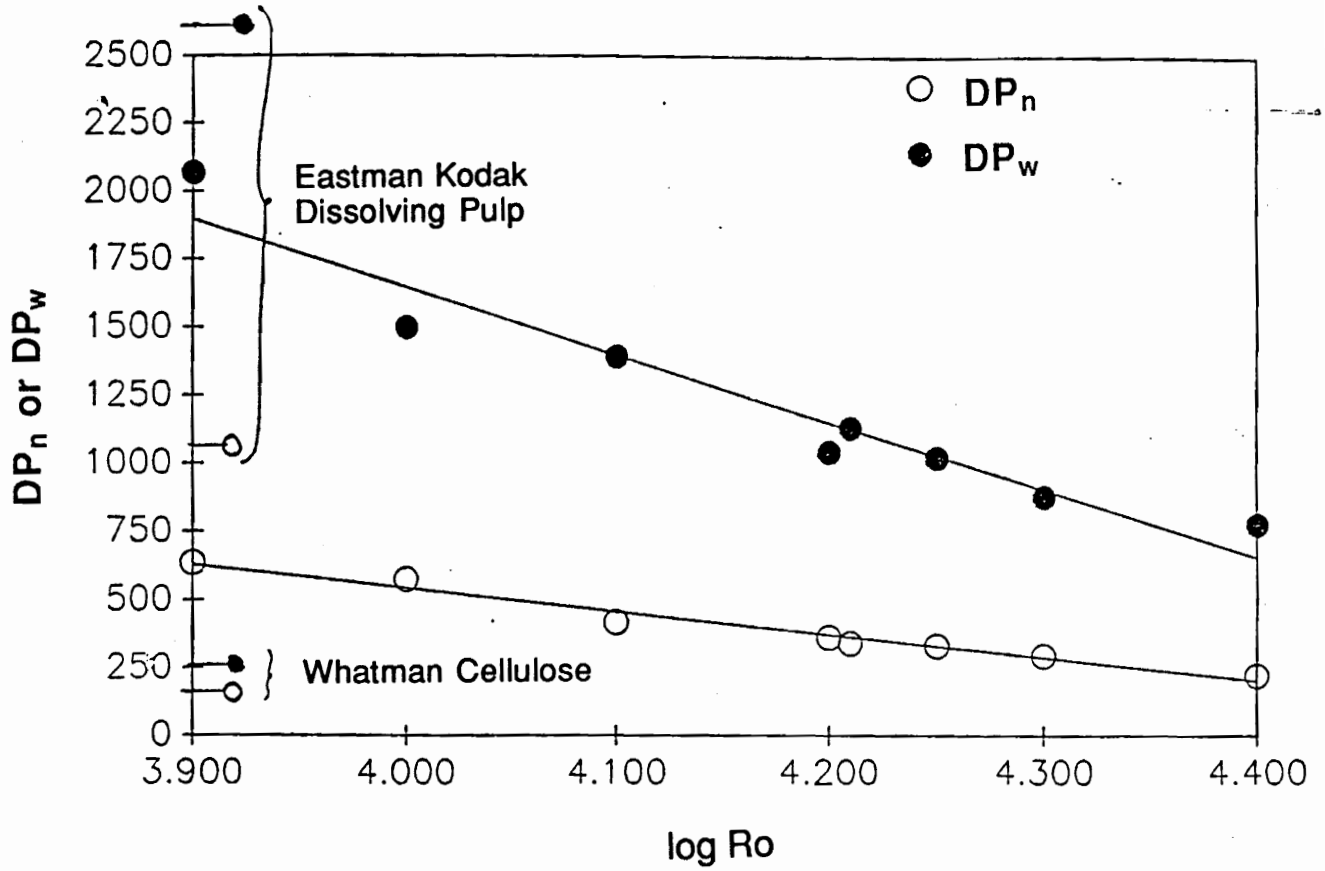


Figure 1. Molecular weight of steam exploded yellow poplar as a function of the severity of steam explosion conditions (log R_o).

dissolving grade (Eastman IV # 6) exceeds that of steam exploded yellow poplar. However, the DP for steam exploded yellow poplar is adequate for microcrystalline grades.

There are a few other end uses for which steam exploded biomass may be ideally suited: ruminant feed, enzymatic conversion,and acetylation (5). Preswelling of the biomass in conjunction with careful pH control may reduce hydrolysis and result in a suitable paper pulp (8). In this case SE would enjoy the advantages of low capital investment and smaller operating units when compared to organosolv delignification.

1.3 The Milox System

Alternative methods for cellulose purification which rely on oxygen in one of its forms (including molecular oxygen, ozone and peroxides) have been the focus of much recent research. These oxidative processes are attractive due to the low cost of producing molecular oxygen, and the minimal environmental impact. Another major advantage of such processes relates to the effluent which may be recycled to the mill recovery system (9).

There are some practical constraints to bleaching significant amounts of fiber within a pressurized vessel at the bench-scale. Both ozone and oxygen-based bleaching require pressurized conditions. Peroxides may be handled as liquid reagents ; however, they are more expensive and less efficient.

The Milox pulping process uses performic and formic acid stages at elevated temperature and atmospheric pressure to target the lignin and allow the pulp to be easily refined. Subsequent bleaching is possible using only alkaline hydrogen peroxide. Research at the Finnish Pulp and Paper Research Institute performed by Kristiina Poppius-Levlin , Ilkka Tuominen, and Jorma Sundquist, has shown that the Milox technology may be modified to give an effective bleaching sequence . They successfully applied this procedure to the bleaching of steam exploded yellow poplar fibers that had been water and alkali extracted (10). A flow chart for the combination of steam explosion pulping and peralkanoic bleaching is given in Figure 2.

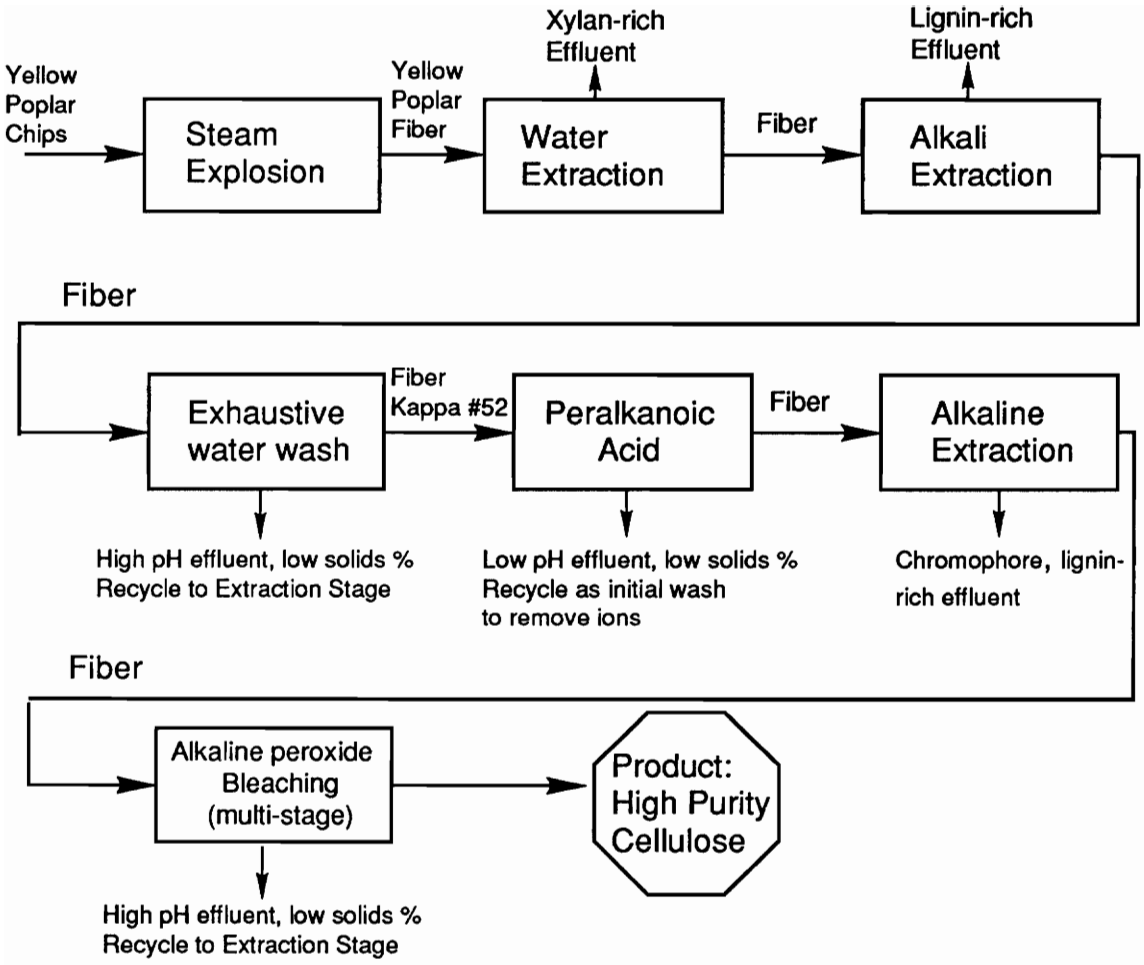


Figure 2. Process flow diagram for isolation and purification of cellulose.

Formic acid is highly corrosive, and thus it was hoped that similar success could be achieved by substituting acetic acid. The results from the Finnish study will be considered together with the results of this study.

2.0 Research Objective

The goal of this study was to investigate the chlorine- and sulfur-free purification of steam exploded biomass using hydrogen peroxide in combination with acetic acid followed by bleaching with hydrogen peroxide in aqueous alkali. Yellow poplar (Liriodendron tulipifera) , a plentiful Appalachian hardwood, was chosen as the substrate.

The primary objective was to produce a chemically pure cellulose of sufficient molecular weight for microcrystalline applications.

The parameters of molecular weight and purity were to be used to evaluate the impact of the various stages of the bleaching sequence on the final product cellulose. The objective was to identify the process stage and parameter(s) that have the greatest influence on molecular weight and purity of the product cellulose for the peracetic acid/alkaline peroxide system.

3.0 Literature Review

3.1 The Chemical Composition of Wood

Wood is composed of three constituent biopolymers: cellulose, lignin and hemicellulose. These may be thought of as an interpenetrating network of block co-polymers. The cellulose and hemicellulose fractions together comprise the carbohydrate portion of the wood. (40-50% and 20-30% respectively).

3.1.1 Cellulose

Cellulose appears to be consistent in chemical structure throughout the plant kingdom: it is a linear polymer of 1,4,β-D-anhydroglucopyranose. The degree of polymerization in naturally occurring cellulose is estimated to be 10,000 to 14,000 repeat units (11). Its syndiotactic arrangement allows cellulose to form hydrogen bonds between chains in a three dimensional lattice. These hydrogen bonds allow cellulose to exist as a semicrystalline polymer (Figs.3,4). The crystalline regions are resistant to hydrolysis by weak acids but the amorphous regions are not resistant (12).

3.1.2 Lignin

Lignin accounts for the largest percentage of the poly-phenolic portion of the wood. It comprises approximately 25% by mass of the dry wood. Softwoods contain more lignin while hardwoods contain more hemicellulose. Softwood lignins possess fewer syringyl groups than hardwoods: this lower level of oxidation may help to explain the difficulties in bleaching softwoods as compared to hardwoods (13,14). The general model for a lignin repeat unit is the phenyl propane structure. Hydroxyls or ether linkages may arise from any of the propanoid carbons. (11,12) There may also be present ethylene functionality. This variety of structure allows a complexity that complements the simple elegance of the cellulose structure (Fig.5).

3.1.3 Hemicellulose

The hemicelluloses are short chain (DP of approximately 200), branched, hetero-polysaccharides. Hemicellulose may be a compatibilizer for lignin and

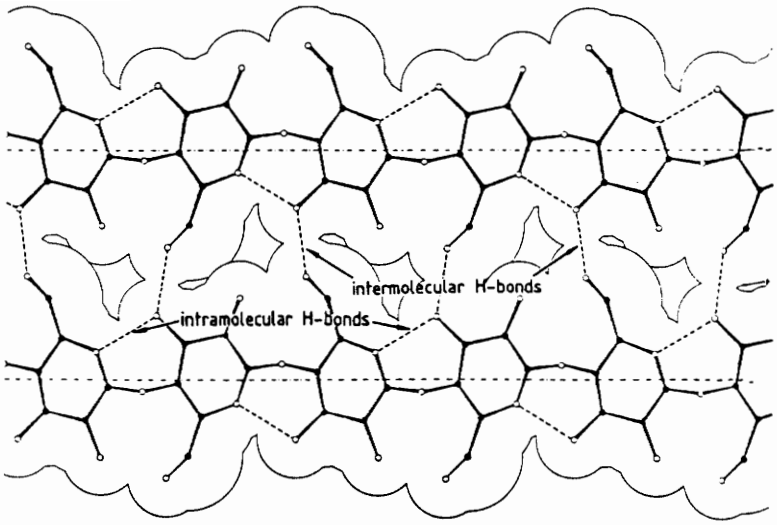


Figure 3. Intermolecular and intramolecular hydrogen bonding between cellulose chains (12).

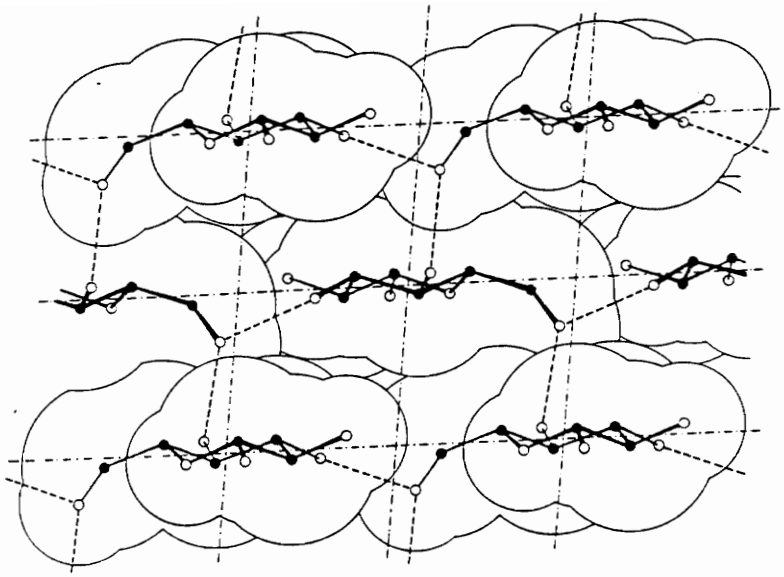


Figure 4. Depiction of unit cell with hydrogen bonding (12).

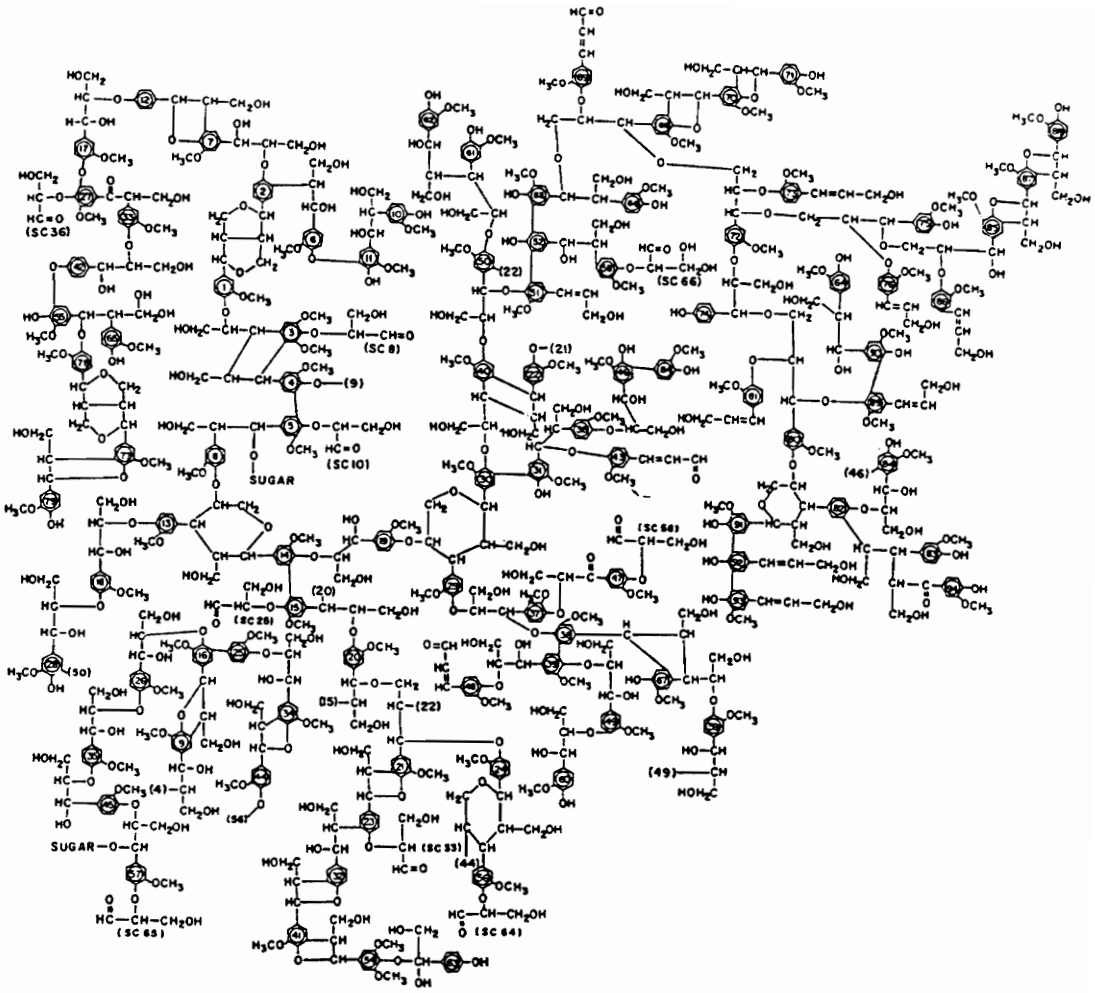


Figure 5. Computer generated simulation of softwood lignin structure.
W.G. Glasser and H.R. Glasser, Paperi ja Puu. 63(2), 71(1981).

cellulose. Hemicellulose is capable of forming hydrogen bonds but it does not normally crystallize. Softwood hemicellulose is primarily composed of galactose, glucose, and mannose; hardwood hemicellulose is composed of a xylan backbone with glucuronic acid side chains. Xylan differs from the other major carbohydrate constituents in that it is a five-carbon sugar . (While arabinose is a five-carbon sugar, it cannot be considered a major component as it typically comprises less than one percent of the wood mass.) It is more prone to decomposition than are the hexoses. Hemicelluloses are thought to be covalently bound to lignin and associated with cellulose through hydrogen bonding (Figs 6,7, and 8).

3.2 The Steam Explosion Technique

As stated in the introduction, "steam explosion" refers to a process of fiber separation where sudden decompression within the reaction vessel causes a saturated wood chip to "explode".

The degree of fiber separation and biopolymer degradation can be influenced by controlling the temperature and residence time within the reaction vessel. These two parameters have been combined into one factor . The reaction ordinate, R_o , is given as (6):

$$R_o = P \times t,$$

where t is the residence time in minutes and P = exp ((T-100/14.75). T is the reaction temperature.

Schwald, Brownell, and Saddler (15), using enzymatic hydrolysis, came to the conclusion that a single parameter such as log Ro is inadequate to characterize a steam pretreatment over a temperature range greater than 40° C. They also noted that the composition of the water soluble portion can be different and still not affect accessibility or digestibility of the cellulose. They found that the accessibility of the cellulose was governed by the amount of retained, alkali-insoluble, lignin.

Although steam explosion is clearly a physical process it also incorporates a chemical aspect. Organic acids in wood are mobilized and they control the pH during the process. This lowering of pH coupled with the saturated conditions promotes autohydrolysis (5,6). Cleavage of different ether linkages between the

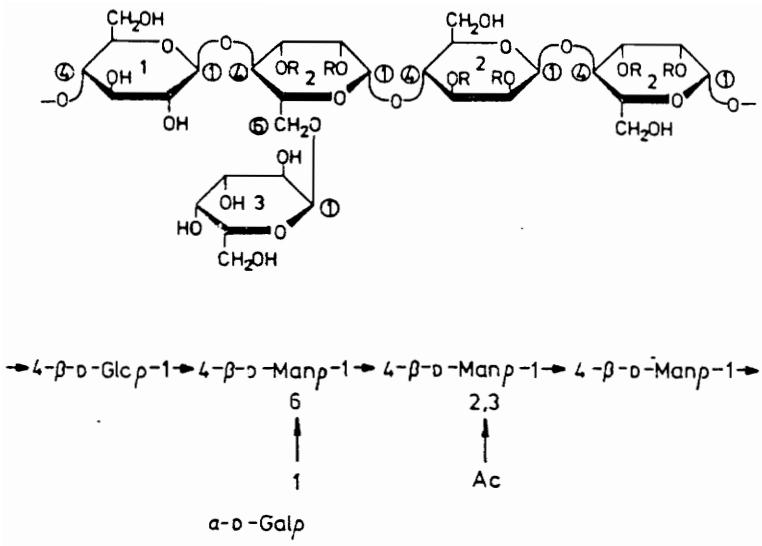


Figure 6. Softwood hemicellulose diagram (11).

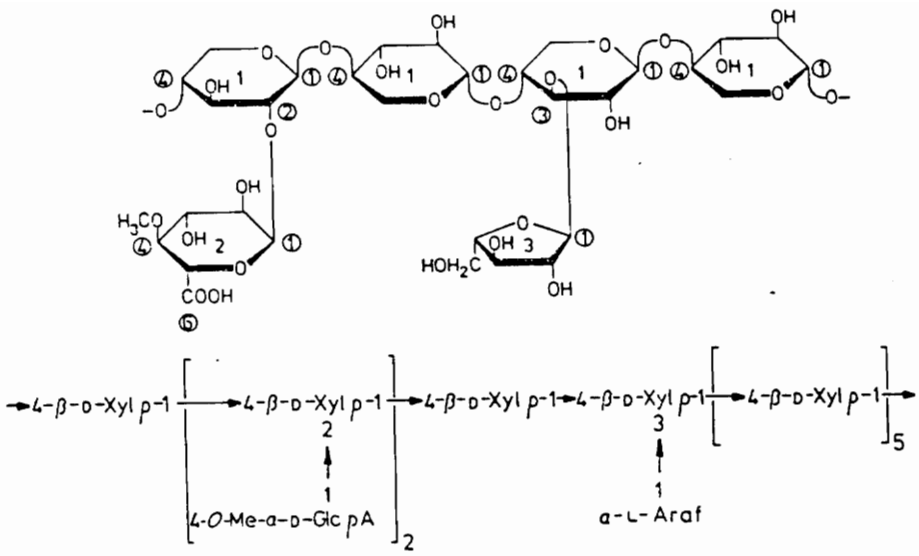


Figure 7. Hardwood hemicellulose diagram (11).

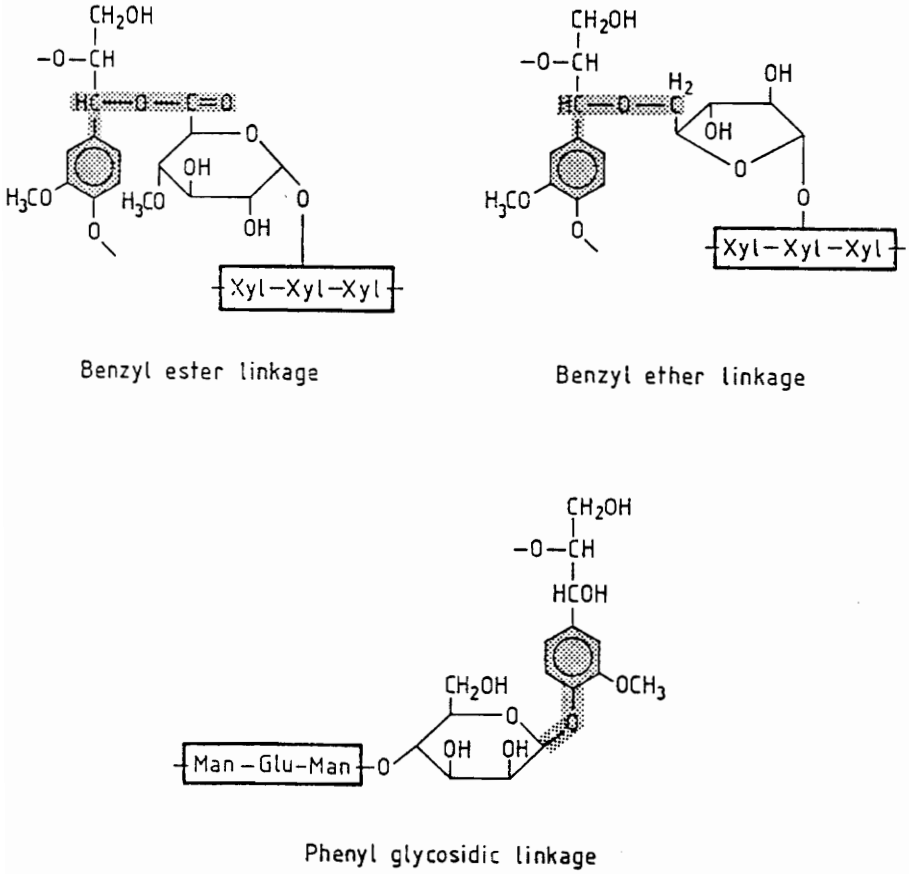


Figure 8. Probable lignin-polysaccharide linkages (12).

various components of the cell wall has been observed. Beta-aryl ether linkages in lignin are prone to this type of attack as are accessible glycosidic bonds. The covalent links between hemicellulose and lignin are also attacked (5,16). In fact, the lignin content of SE biomass may exceed the Klason content determined for the source biomass: concurrently, hemicellulose content decreases. This phenomenon has been attributed to formation of "pseudo-lignin", a composite of degraded hemicellulose and lignin (6).

Most conspicuous of the changes occurring is the coagulation of lignin into micron-sized droplets (5,6). These spheres are readily dissolved in organic solvents as well as weak alkali. Overall, this steam exploded lignin contains a larger percentage of syringyl groups, fewer methoxyl groups, greater degrees of oxidation of side chains, and a higher degree of substitution at the C-6 carbon. The greater degree of substitution at C-6 has been attributed to substitution reactions whereas the other changes have been attributed to cleavage (5,16).

The hemicelluloses are for the most part liberated or hydrolyzed by this process. They are readily extracted with water. As a result of hydrolysis they may be oxidized or deacetylated (5,17).

More important to this study is the observed increase in cellulose crystallinity. Possibly the cleaved cellulose strands have been afforded enough mobility to crystallize to a greater degree. (18)

The cellulose crystal lattice is not altered by SE, however the degree of polymerization decreases substantially: from 10,000 initially down to several hundred repeat units (5). Surprisingly these pulps have been shown to have good strength properties relative to sulfite pulps (8). Due to this low DP, classical definitions of α–cellulose have been deemed inappropriate (5). Steam exploded biomass is readily hydrolyzed enzymatically (19), further indicating that structure and arrangement of the cell wall components has changed.

The chemical and structural changes that occur in the biomass due to steam explosion allow for relatively simple isolation of component biopolymers.

3.3 Bleaching : General Aspects

The distinction between bleaching and pulping is sometimes blurred. Pulping is primarily concerned with fiber separation; whereas, bleaching is a process of highly specific chemical delignification or lignin modification. For the purposes of this study `bleaching' commenced with the first peroxide stage: the water and alkali extractions which followed steam explosion and preceded the first peroxide stage were considered part of the steam explosion fractionation process.

Most of the light absorption in pulp can be attributed to the presence of lignin (20). Lignin structure is altered by pulping to produce more conjugated fragments and hence more chromophores and leucochromophores (leucochromophores are species that may become chromophoric). This change in lignin structure makes pulps darker than the woods from which they are derived.

Bleaching is limited to residual lignin removal due to the cost of bleaching chemicals. Bleaching chemical consumption is also related to accessibility and lignin structure. Thus, different pulping processes produce different pulps with respect to bleachability, and cost of bleaching. Sulfite pulps are more readily bleached than are kraft pulps as fewer chromophores are produced by the sulfite chemistry. The inclusion of sulfonic acid groups into the fragmented lignin allows easier delignification of sulfite groups due to improved solubility in water and alkali (11).

There are two principle strategies for bleaching: lignin removal and lignin modification. For dissolving grades of cellulose the lignin must be removed. Lignin-retaining bleaching relies on chemical structure changes within the lignin to brighten the pulp. This type of bleaching has traditionally been applied to mechanical newsprint pulps which do not possess the chromophores of the chemically produced pulps. Alkaline hydrogen peroxide is employed for this purpose. Hydrogen peroxide (H_2O_2) has also been used as a final brightener in lignin-removing bleaching.

The general strategy in lignin-removing bleaching is to fragment and modify the lignin, making it more water soluble (21).

3.4 Bleaching: Chemical Aspects

3.4.1 Electrophilic Attack

All lignin-removing bleaching is initiated by an electrophilic attack (22). The electrophile may be a cation or radical species. The lignin phenyl-propane unit contains sites which vary in electron density. The electron-rich sites ($\delta-$) are determined by the para-phenolic OH group (or its substituted variant) (Fig.9). This group is an o, p- director by virtue of its free electron pairs and resonance capability. The presence of methoxyl groups at C-3 and C-5 may complicate the situation : as already stated C-6 can be a reactive site, but this site is meta- to the phenolic hydroxyl. The result of electrophilic attack can be replacement of the existing substituent with the electrophile. Multiple replacements are also possible. If the substituent contains oxygen, then cleavage (cleavage of ether linkages is the prime example) with subsequent quinone formation is likely (23) (Fig.10) .

Another reactive site exists where conjugated aromatics are present.In such instances the carbon in the β position relative to the aromatic nucleus is the target of the electrophile. Vicinal substitution may occur at the β- and γ-carbons (Fig.11). When a γ-substituent is eliminated the resultant structure may be attacked again (23,12). Further reaction may result in side chain elimination with formation of quinone methides. Quinones may also result following elimination reactions at the α-carbon.

For the special case where the electrophile is an oxidative radical, pH becomes the important parameter governing subsequent intermediate steps. The initial intermediate, regardless of pH, is a complex between the radical and the aromatic ring. In acidic media H^+ causes the complex to cleave heterolytically leaving a cation radical at the previously aromatic ring. In alkaline conditions, OH^- will replace the radical which will remove an electron from the ring. (At pH above 13, the electrophilic character of the radical is lost). Thus there will still be an unpaired electron present on the ring system and the original radical will have gained an electron to become a negatively charged ion. Resonance forms will depend primarily on whether or not the phenolic OH group is etherified (23) (Fig.12).

Figure 9. Alternating sites of high electron density within the phenyl propane and ring conjugated units (21).

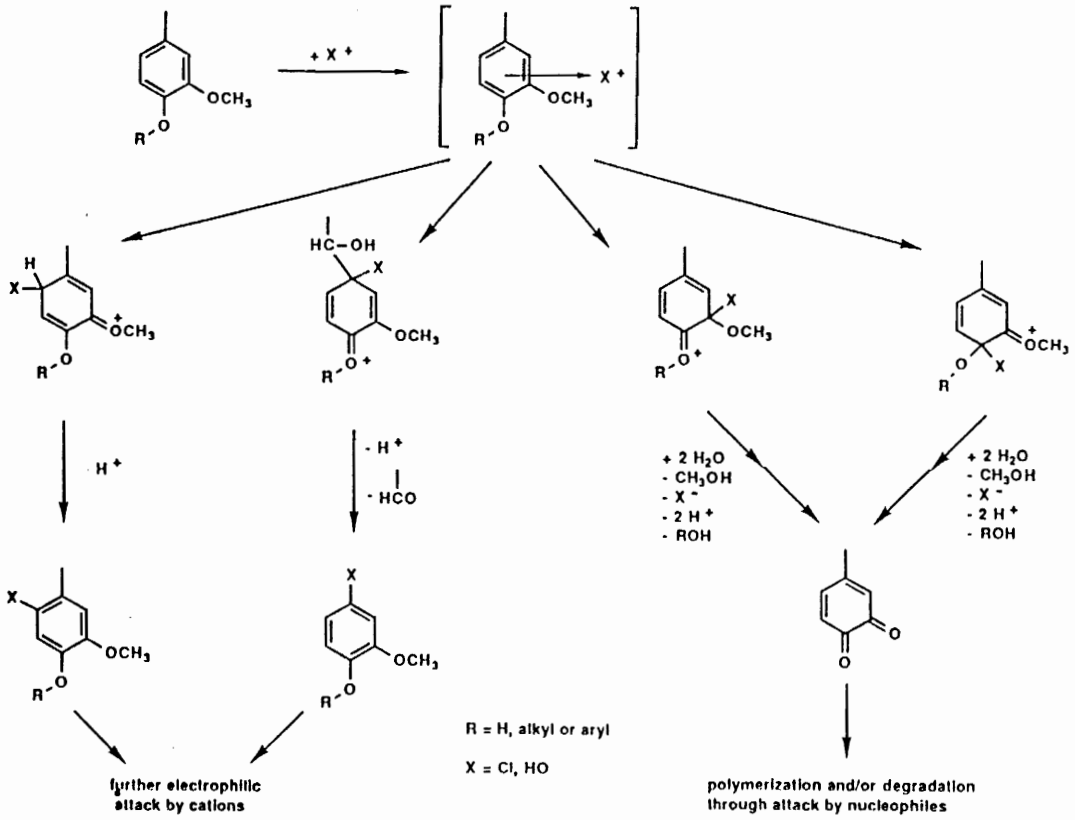


Figure 10. Cationic, electrophilic, attack of a guaiacyl lignin structure (23).

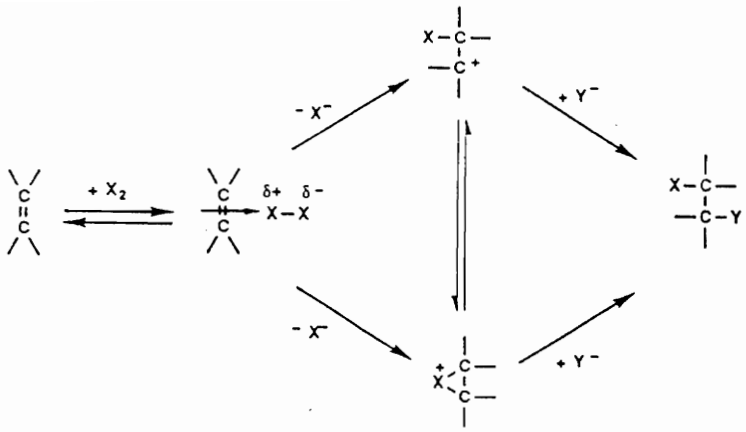


Figure 11. Cationic addition to conjugated aromatic structures (23).

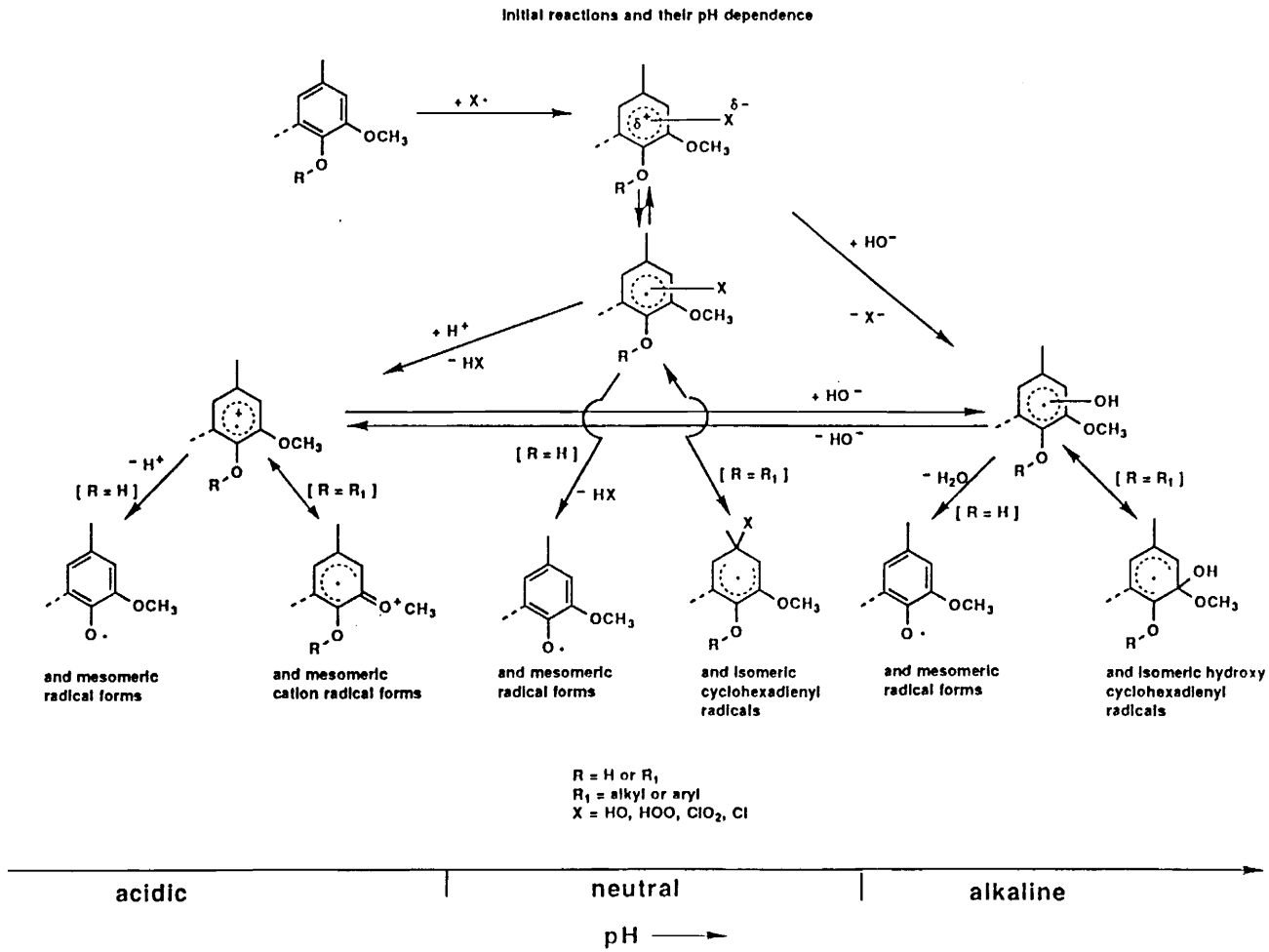


Figure 12. pH-Dependent bleaching interactions with radicals (23).

The resultant phenoxyl radicals from such processes may react in a number of different ways. Most of these paths lead to cleavage of the ring through formation of muconic acid structures, or to formation of quinonoid structures (23) (Fig.13).

3.4.2 Cationic Attack

The initial electrophilic stage will be followed by a nucleophilic stage in a typical bleaching sequence. These nucleophiles (typically OH^-) will seek out sites of lower electron density ($\delta+$) in the lignin and modified lignins. This type of reactivity is promoted when carbonyls and conjugated carbonyls are present. These structures are created by electrophilic attack in preceeding stages (24). Initial attack of nucleophiles is likely to cleave the side chain. Subsequent attack can lead to ring opening. Both of these changes result in increased solubility of the lignin fragments. In the case of alkaline extraction, phenolic hydroxyls and carboxyls may be converted to their more hydrophilic sodium salts (11).

3.5 Bleaching: Traditional Reagents

3.5.1 Electrophiles: Chlorine and Chlorine Dioxide

The most commonly employed bleaching reagents are chlorine and chlorine dioxide. Chlorine will form an equilibrium with hypochlorous acid and hypochlorite ion depending on the pH of the system. At pH=7 hypochlorous acid predominates. Below pH 7 an equilibrium between HOCl and Cl_2 is present with all Cl_2 at the lowest pH range. Above pH 7 an equilibrium between HOCl and OCl^- is present. The reactivity order, given in descending order, is : HOCl, Cl_2, and OCl^- (25). Under bleaching conditions of elevated temperature and low pH, Cl_2 can rapidly decompose into Cl^* radicals which are indescriminate in their attack : they will attack carbohydrates, resulting in higher oxidation states. To moderate the effects of these radicals a scavanger is often included in the liquor : chlorine dioxide. Chlorine, when present on the aromatic ring, will increase the acidity of the phenolic hydroxyl : chlorine dioxide exhibits higher reactivity towards the dissociated phenolate ion. Thus Cl_2 and ClO_2 complement one another in more than one way (22). Also of concern at the low end of the pH

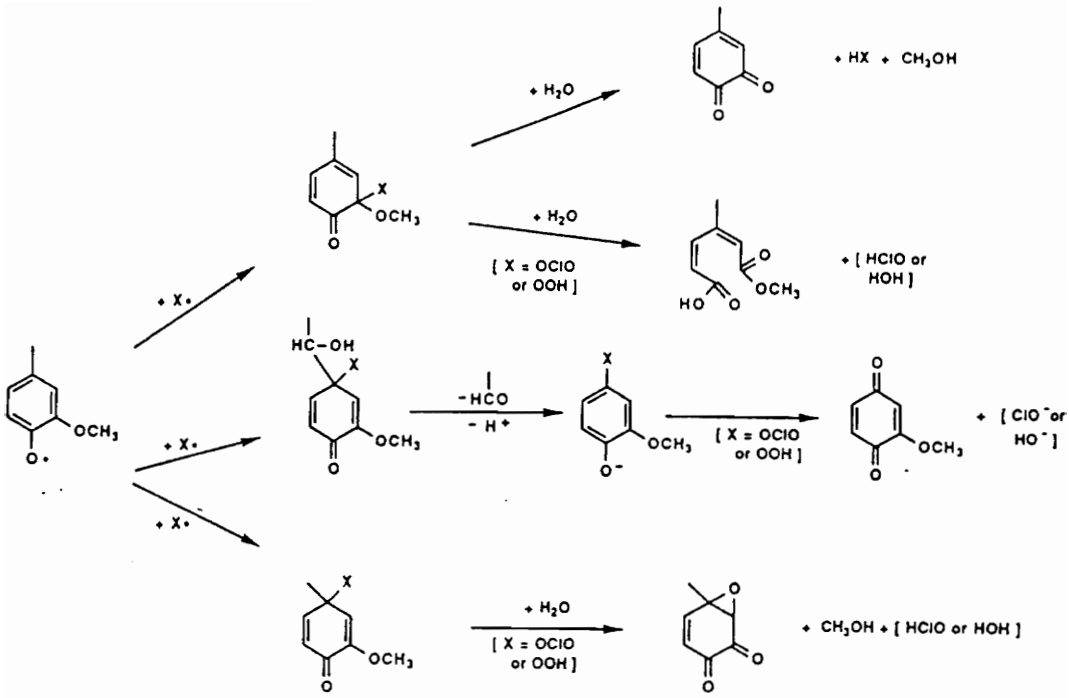


Figure 13.Reactions of phenoxy radicals (23).

scale is acid hydrolysis of glycosidic ether linkages. Either the glycosidic oxygen or the ring oxygen may be targeted by this hydrolysis.

Chlorine acts as an electrophile and affects depolymerization of lignin through elimination of side chains and oxidative cleavage of aryl-ether bonds (23). Dissolved lignin fragments are high in carboxyls following this stage : it is believed that 50% of the chlorine is consumed in such oxidations (11). Bound chlorine is found predominantly on the aromatic ring (25).

Chlorine dioxide is toxic and explosive. It is highly selective towards lignin as well as unsaturated acids (25,26). As already noted, ClO_2 moderates the degradation of carbohydrates resulting from chlorine radicals. It also traps chloro-anions that result from heterolytic cleavage of the chlorine molecule. Chloro-anions can degrade carbohydrates by extracting protons from hydroxyls. ClO_2 reacts with lignin to give phenoxy radicals : ClO_2 has 19 valence electrons and therefore contains an unpaired electron giving it free-radical reactivity (25). Dicarboxylic acids are the primary product of the reaction with lignin present in the spent liquor. Traditional barriers to the use of ClO_2 have been hazards in handling. Initially it was expensive relative to chlorine but this has been overcome and is no longer a deterrent to use (25).

Dioxin (2,3,7,8-tetrachlorodibenzo-p-dioxin) and PCB's (poly-chlorinated dibenzofurans) have been shown to be produced in the initial chlorination stage of a typical bleaching sequence. The substances tend to remain with the fiber through the chlorination stage and are released in largest concentrations in the effluent of the alkali extraction stage (27).

Published chemical syntheses of these materials include alkaline condensation of chlorophenols and acid-catalyzed coupling of catechols with chlorobenzenes and chlorophenols. Direct chlorination does not appear to be a route to the creation of these compounds during bleaching reactions (28).

One solution to this problem entails substitution of ClO_2 for Cl_2 . A 50% substitution level has been shown to decrease dioxin to undetectable levels. (This would require a large capital investment). Another approach is to lower the chlorine- to-lignin ratio, as chlorine in excess of that consumed by lignin is believed to be responsible for dioxin formation (29).

The most logical solution to dioxin and PCB formation is the complete elimination of chlorine from the bleaching process. The Milox hydrogen peroxide-based system is one example of a chlorine-free bleaching sequence.

3.5.2 Traditional Nucleophile: NaOH

Treatment with NaOH follows the initial chlorination and may actually be more than one stage (termed "alkaline extraction"). Chloro- and oxidized lignins are dissolved in this step. Seventy per cent of the chlorine present on the lignin will be removed and simultaneously free phenolic hydroxyls will be created (a substitution of OH^- for Cl^- , which results in increased hydrophilicity---more solubility) (11). More concentrated alkali will result in dissolution of hemicelluloses.

The spent alkaline liquors are much darker than their acidic counterparts, reflecting structural changes in the dissolved organics which render them stronger chromophores (attributed to ionization of phenolic OH groups) (9). If oxidized cellulose is present, ß-alkoxy elimination is likely to lead to depolymerization (12) (Fig. 14). Alkaline hydrolysis is also a possible mechanism for cellulose degradation.

Although alkaline extractions have traditionally been used in conjunction with chlorine-based bleaching, they have also found use in oxygen-based bleaching sequences. With respect to ozone bleaching it has been found that bleaching efficiency and pulp viscosity may be improved through alkaline extraction. For systems where ozone is followed by alkaline peroxide, an extraction stage resulted in higher final brightness with less peroxide demand. The negative aspects of alkaline extractions have been reduced selectivity and lower yield (9).

The chemical species responsible for delignification and brightening in oxygen-based bleaching may similarly be classified as electrophilic or nucleophilic. These reagents are addressed in the next section.

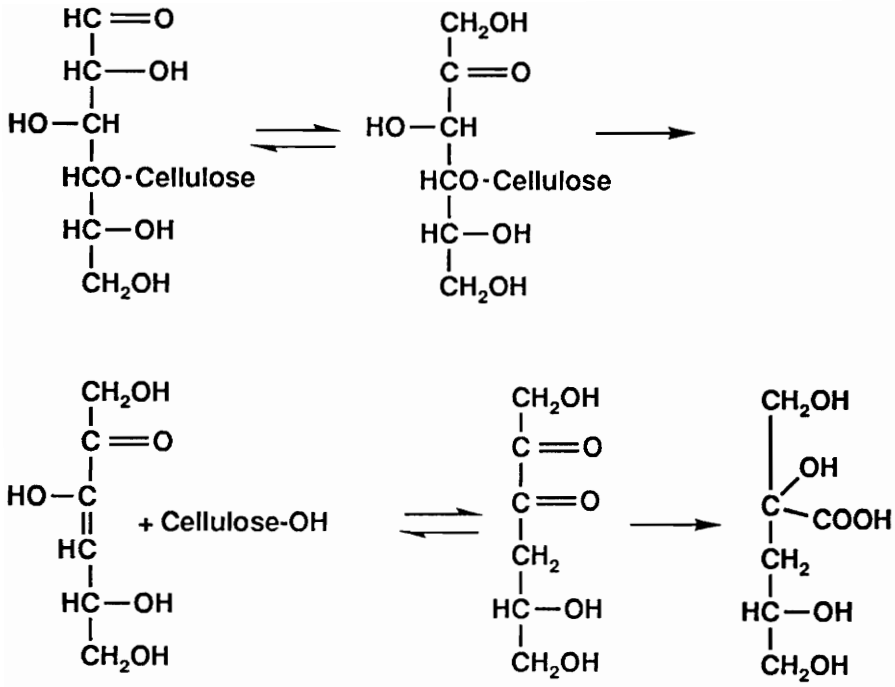


Figure 14. β–Alkoxy elimination or "end-wise peeling" (11).

3.6 Oxygen-based Bleaching Chemistry

3.6.1 Oxygen (O_2)

Oxygen and peroxide give rise to the same chemical species in alkaline solution. They differ in the proportions of these active species and in their initial reaction with lignin (30,31).

Molecular oxygen is unreactive towards non-phenolic lignin : it reacts readily with carbanions which are produced from phenolic or enolic lignins in basic media. (Contrast this reactivity to chlorine which will react with etherified phenolic, C4, lignins as well.) O_2 is an electrophile and is therefore directed o- or p- to the phenolic OH group. Chromophoric lignin and fragments are produced (12,22).

O_2 is believed to react as a di-radical. It may remove a proton from the lignin anion or it may remove an electron. In either case a lignin-based radical may result which can react again with an oxygen radical through addition, resulting in a peroxy anion (22). This step is the fastest step in the mechanism due to the radical-scavenging property of the oxygen di-radical and accounts for the highest consumption of oxygen and substrate (32). Hydroperoxide anions may result from O_2 reduction (through a one electron transfer). These anions are nucleophilic and preferentially add to the quinonoid structures which may be present following electrophilic attack of the O_2 di-radical (30). The hydroperoxide anion is thought to be the major reactive species produced by hydrogen peroxide in alkaline conditions ; in O_2 bleaching it is the minor reactive species (30).

Oxygen bleaching can result in oxidized cellulose which is prone to depolymerization in the alkaline medium through ß-alkoxy elimination. Hydroxyl and perhydroxyl radicals are thought to cause this oxidation by removing a proton from cellulose. In the presence of oxygen, C2-C3 bond cleavage may occur (31). Therefore, complete delignification with O_2 is not practiced. Generally, 50% removal of lignin is the target in an oxygen-only stage (33).

3.6.2 Ozone (O_3)

Gierer (22) classifies ozone as a cationic electrophile. Ozone is believed to react with alkenes and aromatics by initially forming a cyclic species which

breaks down through cleavage of the double bond, yielding two carbonyl-containing fragments (Fig.15) (2). Epoxides are possible products when ozone is reacted with hindered olefins (22). Ozone itself is not thought to degrade carbohydrates; however, radicals that do degrade cellulose may result from reaction of ozone with lignin or water. Degradation takes the form of carbonyl formation which leads to depolymerization in subsequent alkaline extractions (33).

Ozone is highly electronegative : it is almost as electronegative as fluorine (2). This might account for its superior solubility in water when compared to molecular oxygen. Ozone stages have proven most effective at pH 2 to pH 3 with respect to degradation of carbohydrates. Low consistency (less than 25%) tends to preserve viscosity and yield, while higher consistency improves the efficiency of the ozone (33). Free hydroxyl ions (OH^-) promote decomposition of ozone.

The combination of an oxygen stage followed by an ozone stage has proven more effective than the reverse sequence : both sequences show improvements when compared to oxygen or ozone alone (9).

Ozone shows promise as a delignifying agent and is receiving scrutiny in pilot operations: recently Union Camp in Franklin, Virginia brought on line an ozone stage (34). It would seem that its general utility will be somewhat limited due to the detrimental effects that increased charge has on viscosity : cellulose must be chemically protected if charge exceeds 1% (33). There might be other limitations related to the manner in which it is produced : oxygen gas is passed through an electric arc, liberating a small percentage of atomic oxygen which then reacts with molecular oxygen to give O_3 (2).

3.6.3 Hydrogen Peroxide (H_2O_2)

Conceptually, H_2O_2 is a novel bleaching reagent because it is capable of functioning either as an electrophile or as a nucleophile. In alkaline media it gives up one proton to form the hydroperoxy anion HOO^-, a nucleophile:

$$H_2O_2 + OH^- \rightleftharpoons HOO^- + H_2O.$$

The equilibrium favors hydroperoxy anion production at high pH (above 11). However, at pH levels above 12 decomposition may occur (35):

$$H_2O_2 + HOO^- \rightleftharpoons O_2 + H_2O + OH^-.$$

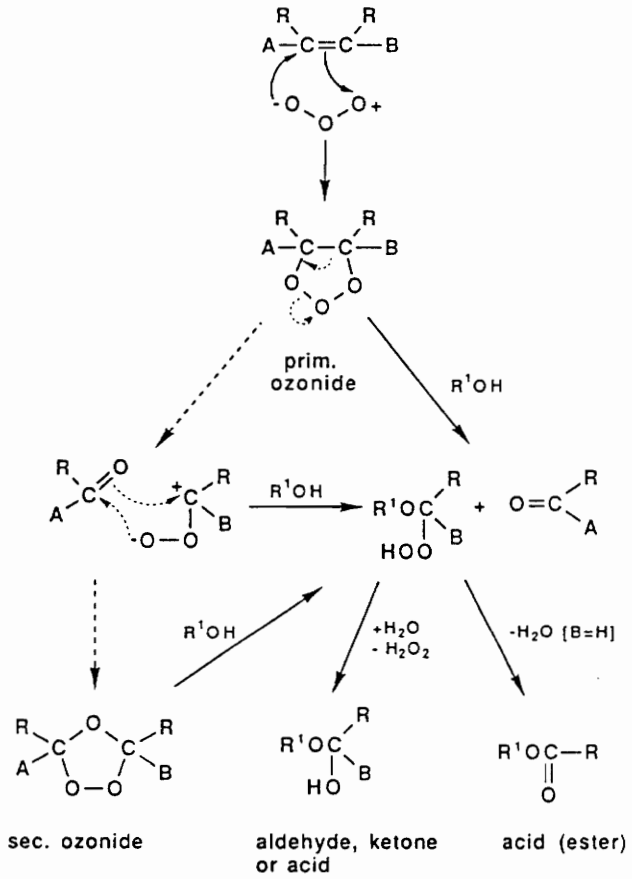


Figure 15. Ozonolysis cleavage of ethylene bond (23).

In alkanoic acid media an equilibrium arises between the acid and peroxide and their addition product, peralkanoic acid (peracid)(2):

$$RCOOH + H_2O_2 \rightleftharpoons RCOOOH + H_2O.$$

Peracids give rise to an unusual electrophile, OH^+.

Free radicals may also be produced, particularly in alkaline conditions. These are responsible for the degradation of carbohydrates through oxidation and may play a role in delignification (36).

The decomposition products of hydrogen peroxide are oxygen (O_2) and water. Therefore, H_2O_2 poses a smaller threat to the environment than chlorine-containing compounds that result from traditional bleaching. The oxygen is capable of reacting as in the oxygen-based bleaching system discussed previously. Decomposition will be a minor reaction and therefore oxygen will be a minor component of the system.

Decomposition may occur in alkali or acid and is catalyzed by metal ions, in particular Fe^{2+} (31):

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO^* + H^+$$
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^* + OH^+$$
$$HO^* + H_2O_2 \rightarrow H_2O + HOO^*$$
$$HOO^* + Fe^{3+} \rightarrow H^+ + Fe^{2+} + O_2$$
$$HOO^* + Fe^{2+} \rightarrow HOO^- + Fe^{3+}.$$

Note the different radicals produced. The ultimate product of these electron transfer reactions is water and oxygen.

As with oxygen bleaching, cellulose degradation may result from the attack of hydroxyl and perhydroxyl radicals. These radicals and their anions may also participate in beneficial bleaching reactions. The concentration of these radicals increases with pH above a threshold of approximately pH 11.5; below this threshold cellulose degradation is not significant. (The threshold has been shown to vary with initial hydrogen peroxide charge) (37). Because the optimal pH for peroxy anion production is 11, a trade-off between cellulose degradation and optimal production of nucleophiles (hydroperoxy anions) exists.

One way to tip this balance in favor of bleaching is to chemically protect the cellulose : magnesium sulfate is used for this purpose. There are different theories as to the method by which magnesium sulfate protects cellulose: it may complex with metal ions or it may complex with the vicinal hydroxyls of the

cellulose molecule (Fig.16) (38). Chelating agents are also employed to tie up the iron ions.

Hydrogen peroxide has been shown to have an additive interaction with oxygen when added to a first-stage O_2 treatment (39).

Specific reaction parameters and their effects on H_2O_2 bleaching will be addressed in the discussion section.

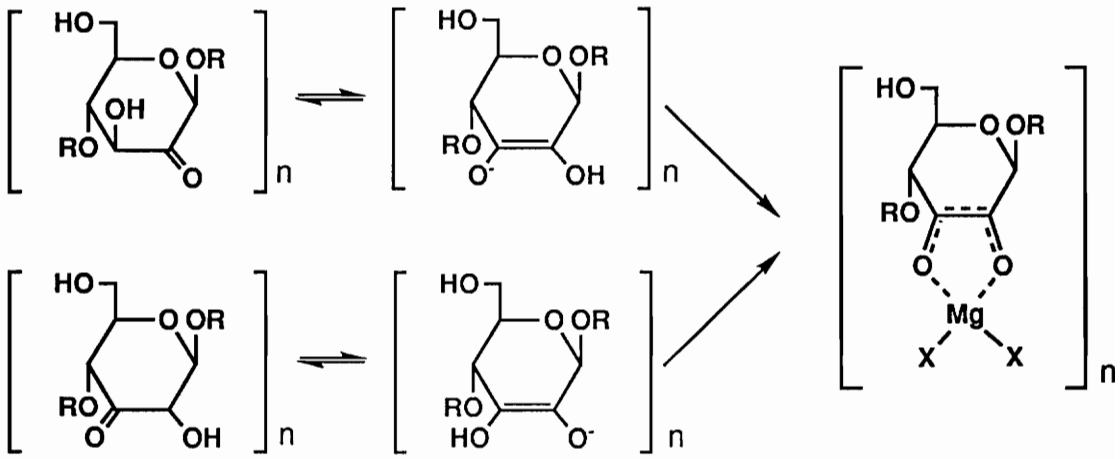


Figure 16. Proposed magnesium/cellulose complex (38).

4.0 Discussion of Cellulose Product Parameters

4.0.1 Specifications for Dissolving Grades

Two important parameters for the evaluation of dissolving grades of cellulose are purity and molecular weight. Purity refers to the percentage of material present in the form of cellulose. Specifications for acetylation grade pulp call for an α-cellulose content of 95.6% (11). (α-Cellulose is that portion of the isolated fiber that is insoluble in 17% NaOH; this generally correlates to cellulose chains of DP 200 or more). Other dissolving grades do not require this level of purity (40). For acetylation grades, the presence of pentosans is detrimental and leads to the formation of "haze". Ash content must also be controlled.

For microcrystalline grades, the requirements are somewhat less stringent: carbohydrates other than cellulose may be acceptable in larger concentrations. The specifications for microcrystalline cellulose require 97% carbohydrate, *calculated* as cellulose (41).

Microcrystalline cellulose has traditionally been produced through mineral acid hydrolysis of α–cellulose. The "leveling off" DP is the lower DP at which further hydrolysis becomes much more difficult. The leveling off DP is therefore closely related to the size of the cellulose crystallites, which varies with the source biomass and the isolation procedure. The DP_n range for microcrystalline cellulose is 140 to 400 repeat units (42). Data for purity and molecular weight specifications for dissolving and microcrystalline celluloses is presented in Table 1.

Industrially, α-cellulose content of bleached fiber has been increased through treatment with hot alkali. As might be anticipated, yield suffers as a result of these treatments and may be as low as 30%. Historically, ash content and other impurities have been reduced through extensive washing. Both of these techniques may supplement the peralkanoic acid/alkaline peroxide purification examined in this study.

Table 1. Cellulose specifications per end use for dissolving grades.

Application	α- Cellulose (%)	Pentosans (%)	Ash (%)	Iron (ppm)
Acetylation Grade	95.6	<2.1	<.08	<10
Micrcrystalline	97*		<.05	<10**
General Dissolving	87			

* Carbohydrate calculated as cellulose.

** Total heavy metals percentage expressed as lead.

4.1 Cellulose Purity

4.1.1 Methods for Assessing Purity: Monitoring Lignin Content

There are many techniques which have been employed to yield information relevent to the determination of purity. Some of these techniques have focussed on determination of residual lignin rather than determining the carbohydrate fraction directly. Methoxyl determination, Klason lignin determination, chlorine number, and permanganate number are examples of common traditional wet chemistry methods for lignin quantification.

Methoxyl Determination

Methoxyl groups may be present in hemicelluloses as well as in lignin. The hemicelluloses are soluble in alkali of varying strengths and may be extracted. The remaining methoxyl groups may be determined by reacting the extracted pulp with boiling hydriodic acid. The dissolved alkyl iodides may be analyzed through gas chromatography (GC) (43).

Klason Determination

The Klason lignin determination typically employs 72% sulfuric acid to completely hydrolyze the carbohydrate portion of the lignocellulose. The insoluble portion is determined gravimetrically and termed "Klason lignin". Problems with the acid hydrolysis of carbohydrates may result in inaccuracy. If conditions are too mild, incomplete hydrolysis may occur; if conditions are too harsh, then the carbohydrates may be degraded to insoluble fragments. The traditional method of optimizing the Klason technique has relied on the methoxyl determination.

Oxidative Methods

Chlorine number and permanganate number are two examples of lignin determinations that take advantage of selective oxidation of the aromatic nucleus. Chlorine gas consumption in milliliters, or "chlorine number", is monitored by a pressure sensing apparatus. Improvements to this procedure have focussed on replacing the gas phase with a liquid phase. Tappi T-235 is an example of an accepted standard method in which hypochlorite has been substituted for the chlorine gas.

The permanganate number relies on iodometric titration to monitor the consumption of a known initial amount of permanganate. The permanganate number is sensitive to residual permanganate volume and permanganate concentration. The Kappa number is an improvement over the permanganate number as it specifies an initial amount of pulp that will consume between 30 and 70 percent (average consumption of 50%) of the initial permanganate. The resulting value is then corrected to reflect 50% consumption, 0.1N $Na_2S_2O_3$ basis.

Kappa Number

Kappa numbers were chosen in preference to other wet chemistry techniques because they can be performed quickly (20 minutes) and consistently once all of the reagents are standardized. (Klason lignin determinations were performed as part of the chromatographic carbohydrate analyses). Kappa numbers were performed according to Tappi T236- cm-85 with one modification: the oven dry fiber sample size was limited to 4 grams. This limitation was necessary due to the scale of the bleaching reactions. For the more completely bleached samples, 30% of the initial permanganate was not consumed.

Spectral Measures

Residual lignin may also be quantified by FTIR (Fourier transform Infra-Red) spectroscopy. (44,45,46) Unlike previous techniques, FTIR techniques may be performed using dry fiber specimens. Peaks in the aromatic region (1505-1605 cm^{-1}) of the spectrum may be integrated or quantified by peak intensity after subtracting out an appropriate standard. FTIR data have been correlated to Kappa number and Klason lignin (44).

Diffuse-reflected brightness is another spectral method which gives information about purity. The major chromophoric component of extracted lignocellulose is lignin. Thus the relative brightness of pulp samples gives an expedient measure of lignification (purity), in the case of lignin-removing bleaching. The brightness parameter is used extensively in the pulp and paper industry where brightness is of key importance from a marketing perspective.

4.1.2 Methods for Assessing Purity: Monitoring Cellulose Directly

Direct methods rely on chromatography, which requires an initial hydrolysis (Klason determination) (43).

Chromatography has been defined by the IUPAC as: "A method used primarily for the separation of the components of a sample, in which the components are distributed between two phases, one of which is stationary while the other moves" (47). Separations may be performed based on any of a variety of different chemical affinities but ionic interactions are most commonly exploited for chromatographic separations. These separations are particularly useful as composition (%) of hemicellulose may also be determined. Chromatographic methods applied to lignocellulosics have included paper, thin layer (TLC), gas (GC), gas-liquid (GLC), and high performance liquid (HPLC).

HPLC was developed to overcome the slow diffusion rate of solute particles in traditional column (liquid) chromatography. Higher diffusion rates have been achieved by decreasing the particle size of the packing materials. This decrease in particle size causes an increased pressure drop accross a column. Pumps and couplings have been developed to withstand the high pressures necessary to drive such a system. This equipment was unavailable until the late 1960's; other chromatographic methods had firmly been established by this time (47). Since then, the advantages of the HPLC technique have led to its more wide-spread use.

HPLC allows for automated sample introduction and continuous flow monitoring; and, HPLC columns are reusable. GC requires the creation of volatile sugar derivatives and elutes slowly. Paper chromatography may require more than two days to complete. Gas-liquid chromatography may produce multiple peaks (48,49,50).

4.2 Cellulose Molecular Weight

4.2.1 M_n, M_w, and M_z

Molecular weight is an equally important parameter for characterizing dissolving grades of cellulose (polymers in general). The molecular weight of polymers cannot be adequately represented by a single value because the chain lengtts (degree of polymerization) of polymers follow a statistical distribution. There are several different average molecular weight values that may be derived from this distribution.

The number average is simply the summation of mass for all of the molecules divided by the total number of molecules:

$$M_n = (\Sigma M_i N_i) / (\Sigma N_i).$$

The weight average is proportional to the square of M_i, and therefore better reflects the influence that higher molecular weight fractions exert on physical properties:

$$M_w = (\Sigma M_i^2 N_i) / (\Sigma M_i N_i).$$

The 'z' average is calculated as with M_w, except that M_i is raised to the next higher power:

$$M_z = (\Sigma M_i^3 N_i) / (\Sigma M_i^2 N_i).$$

Hence, M_z is more sensitive to the higher molecular weight material than either M_w or M_n.

The ratio of M_w to M_n is referred to as the polydispersity and gives an indication of how broad the distribution is. A monodisperse system occurs when the molecular weight may be given as one value, i.e. M_w=M_n.

4.2.2 Viscosity-based Measure

Intrinsic viscosity is calculated from viscosity measurements performed on several solutions of increasing solute concentration. The intrinsic viscosity results from graphically extrapolating back to a zero concentration. Automated differential viscometers are now used as detectors inline with GPC equipment. These detectors when coupled to a suitable micro-processor allow the determination of intrinsic viscosity.

Traditional cellulose solvents are strongly alkaline copper-based reagents and which are prone to oxidizing cellulose in the presence of atmospheric

oxygen. By performing dissolution under a nitrogen atmosphere, oxidation can be minimized. Newer solvent systems that rely on DMSO or DMAC and LiCl are not believed to be sensitive to atmospheric oxygen but these materials present other hazards in handling.

Viscosity is a material property related to solvent/solute interactions that determine the hydrodynamic volume of the dissolved solute. This hydrodynamic volume is also dependent on the molecular weight or chain length (degree of polymerization) of the dissolved polymer. Thus, viscosity measurements on a solvent/solute system allow a determination of molecular weight.

Relative viscosity measurements have proven useful in pulp manufacture because they are less time-consuming than intrinsic viscosity measurement: only one solution concentration is necessary for comparison purposes. Tappi T-230 is an example of one of these comparitive techniques.

The viscosity-average molecular weight is derived from intrinsic viscosity measurements and has the form:

$$M_v = [(\Sigma M_i^{1+a} N_i) / (\Sigma M_i^2 N_i)]^{(1/a)}.$$

The exponent 'a' varies with the shape of the solute particle in solution and is therefore a function of both the solvent and the solute. Values for *a* vary from 0.6 to 0.8 for many cellulose solutions (11). For carbanilated cellulose in THF, Evans and Wallis (51) report a value of 0.85. When $a = 1$ the viscosity average and weight average are equal.

If the M_v for a sample is known, the exponent *a* for the solute may be calculated from the Mark-Houwink equation:

$$[\eta] = K M_v^a.$$

Where K is a constant and $[\eta]$ is the intrinsic viscosity. The exponent *a* is often referred to as the Mark-Houwink (M-H) constant. The M-H constant is known to decrease for higher molecular weight materials as the chain length increases: this has been attributed to chain folding for polar polymers such as polyesters (52).

4.2.3 Alternative Traditional Methods

Molecular weights may be characterized by other methods such as osmotic pressure, and titration of end groups. End group analysis is recognized as the least accurate method (43). Typically, it requires the titration of reducing

ends present in the carbohydrate fraction with the assumption that one and only one reducing end is present.

An example of such a method is the copper number determination. The copper number is the number of grams of copper reduced from the cupric to the cuprous state by 100g of cellulose, as determined through permanganate titration of the filtrate. The inaccuracy in this method arises from non-stoichiometric behavior: more than two cupric ions per cellulose carbonyl group may be reduced (43).

Osmotic pressure is a colligative property: it is the pressure exerted by a fluid across a semipermeable membrane as it dilutes a polymer solution on the opposite side of the membrane. Whereas modern osmometry presents a fast , reliable alternative to viscometry, viscometry has seen more universal acceptance. The molecular weight value obtained from osmometry is a number-average: this may explain part of the reason for the preference for viscometry, as viscometry yields an average molecular weight that more closely approximates the weight average. The primary reason for the preference of viscometry is the simple, inexpensive, apparatus which requires less than ten milliliters of cellulose solution.

4.2.4 Size Exclusion Chromatography (GPC)

Gel permeation, or size exclusion, chromatography (GPC) makes use of a verticle column packed with a porous particulate that slows the elution of smaller particles as they pass into and out of the pores. The advantages inherrent to HPLC are applicable to GPC (47).

Historically, cellulose has been derivatized through nitration. The nitrated cellulose may be precipitated through addition to a nonsolvent. By repetition of this process a molecular weight distribution may be developed though gravimetric and viscometric analysis of the precipitate.

Carbanilation offers a better alternative: the resulting product is more stable as compared to cellulose nitrate and completely substituted without cellulose degradation. Cellulose tri-carbanilate is soluble in tetrahydrofuran, a preferred solvent for HPLC.

A sample molecular weight profile from the GPC data is shown in Figure 17. Because each repeat unit is expected to have each hydroxyl hydrogen

substituted by a phenyl-isocyanate group the repeat unit will have a mass of 519g per mole (the displaced hydrogen is bound to the nitrogen of the cyano-group in the carbanilated product). The values for M_n, M_w, and M_z given in Fig.17 are given in terms of this carbanilated repeat unit. The tabulated DP values quoted throughout this report have been calculated by dividing the respective molecular weight by 519.

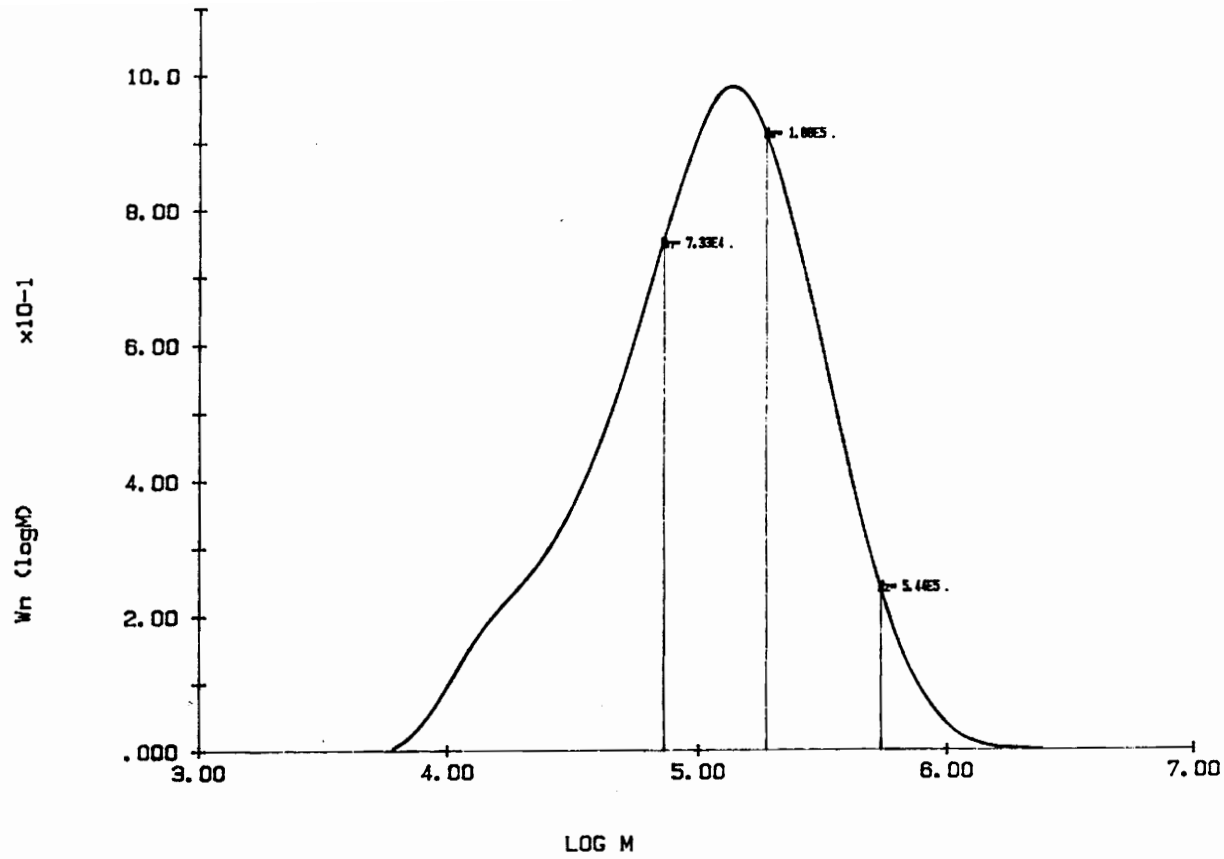


Figure 17. An example of a GPC trace for carbanilated cellulose.

5.0 Experimental Design

5.1 Discussion of Factorial Experiments

A factorial experiment is an experiment in which a response is observed at all factor-level combinations of the independent variables. In statistical terminology a variable is a "factor" and a particular value for this variable is a "level". Such a design allows for analysis of interactions between the independent variables as well as analysis of the main effects from these variables.

For this study, four different factors for the acid stage were examined: time, temperature, acid concentration, and peroxide charge. Temperature and peroxide charge were examined at two levels, while acid concentration and time were examined at three levels (the three levels for time were 3 and 6 hours, and "extended" ~ 20 hours). For the alkaline peroxide treatments two different sequences were investigated and water washing was compared to alkaline extraction. Thus, the alkaline extraction factor was composed of three levels. The number of factor-level combinations necessary to complete a full factorial experiment for these factors would have been 2x2x3x3x3, or 108.

Two trials are necessary to allow an estimate of the variance and mean of any response. Therefore, 108x2, or 216 trials would have been necessary to allow a basic statistical analysis.

If a more accurate measure of the true mean response at each factor-level combination were desired, then more than two trials would have been required. Table 10, page 95, to be discussed more thoroughly in Section 7.5.4, is a tabulation of molecular weight data for the bleached samples that were analyzed through carbanilation and GPC. Samples A60.80.106 and A60.80.106(2) allow an estimation of the number of samples which might be required to yield an accurate approximation to the true mean for any factor-level combination. For this sample calculation the less variable DP_w data will be used.

An acceptable confidence level and range of error must be specified in order to make this approximation. Accepted levels are 90% or 95%. To minimize the number of samples required, 90% will be chosen for this calculation. The acceptable range may be determined based on prior experience; since the range

of the two samples considered is 19 units, this sample calculation will use 20 units as an acceptable range for error. In this case the acceptable error would be ±10 units. The equation to estimate the appropriate sample size, assuming a normal distribution about the mean, is given as (53):

$$n_o = (Z_{\alpha/2})^2\sigma^2 / E^2,$$

where n_o is the number of samples necessary, and $Z_{\alpha/2}$ is the area under the standard normal curve given for an α value equal to 100- (the specified confidence interval), σ^2 is the population variance, and E is the specified, acceptable error.

The population variance, σ^2, may be estimated by the sample variance, s^2. The formula for s^2 is given as (53):

$$s^2 = \Sigma\ (y-y)^2 / (n-1),$$

where y is an actual sample value, and y is the average value for the number of samples, n. From the DP_w values of 388 and 407 for the two samples a sample variance of 180.5 may be calculated.

The $Z_{\alpha/2}$ value may be obtained from a standard table. For an α level of 10% (100% minus a confidence level of 90%) this value is 1.65 standard deviations. Substituting s^2 for σ^2, 180.5 , and filling in the values for E, 10, and $Z_{\alpha/2}$, 1.65, the sample size, n_o, is approximately 5 samples. Thus 5 trials at each factor-level combination are necessary to produce an acceptable estimate of the true population mean, in this case the true DP_w. (Note that for the preceeding calculation it was assumed that a DP_w value from a single GPC trial was representative of the individual sample. Replications of the same sample would also display a range of values, this aspect is addressed in the section concerning accuracy and precision of experimental methods).

If 108 factor-level combinations are multiplied by 5 trials at each factor-level combination, then 540 trials would have been necessary. At the rate at which experimental data was completed for this study, the carbanilation and GPC work alone would have required a minimum of 108 weeks to complete. Even the statistically mandated minimum of 216 trials would have required more than 42 weeks.

A full factorial design for the process variables examined in this study was not feasible.

5.2 Implemented Design

The experimental design as implemented was an attempt to derive information about trends without using a full factorial design. The factor-level combinations which were explored are diagrammed in Table 2. The top row of the table gives the column headings for the different acid concentrations.The left column gives the row headings for the two temperatures explored. The intersections of these rows and columns are outlined in bold. Within these blocks are listed the peroxide charge levels and the acid stage reaction times. Each chosen factor-level combination was replicated once with the exception of two factor-level combinations which were duplicated. It was recognized that one trial would not allow for a statistical analysis: it was anticipated that strong trends in the data would be present and that these trends would guide future, statistically valid, research projects.

The chosen factor-level combinations allowed for one-at-a time comparisons for each factor. Assessment of interaction was generally infeasible given the chosen factor-level combinations.

Brightness data were generated at each stage of the bleaching sequence for each factor-level combination. Molecular weight samples were chosen from the bleached material after brightness data had been generated. Some samples were eliminated from molecular weight analysis based on the brightness data. Samples for carbohydrate analysis were chosen following the molecular weight and brightness analyses.

Table 2. Factor-level combinations for the controlled peracetic acid experiments.

Temp.° C		Acid Concentration %								
		80				50			25	
40	Peroxide charge % :		10	20					10	20
	Time (hrs) :		6 19	3 6					6	3 6(c)
60	Peroxide charge % :	0	10	20		10			10	20
	Time (hrs) :	6	3 6(d) 23	3		6(a)			3 6(b)	3 6(b)

Normal sequence: peracetic acid, alkaline extraction, and 2 alkaline peroxide stages.
One trial was performed per factor-level combination unless otherwise noted.
(a) Additional trial conducted with extensive water washing instead of alkali extraction.
(b) Additional trial conducted with 4-stage alkaline peroxide sequence.
(c) Duplicate trial conducted under 'normal sequence'.
(d) One additional trial per each of the preceeding notes.

6.0 Experimental

6.1 Materials

Yellow poplar chips were steam exploded using a Stake-Tech continuous feed digestor. Reaction conditions were chosen to approximate a log R_o value of 4.25 (retention time of 3.44 minutes at 226° C.) The material for the performic acid trials came from a different batch than that used for the peracetic experiments: both were log R_o 4.25.

The steam exploded fiber was extracted with water at 80° C for 1/2 hour. One alkaline extraction proved sufficient for the first batch of fiber that was bleached by the Finnish Pulp and Paper Institute. This extraction was performed with 20% NaOH on fiber at 80 degrees for 1/2 hour. Following the alkaline extraction the fiber was washed extensively. This material had a Kappa # of 53.9.

The second batch of material, which was used in the peracetic experiments, was found to contain significant amounts of alkali-soluble lignin following the first extraction. Therefore, a second extraction was performed with 4% NaOH on fiber. This material had a Kappa # of 52.

6.2 Methods

6.2.1 Preliminary Peracetic Trials

Several preliminary peracetic acid bleaching trials were conducted in a 500mL beaker on a heated stir plate with typically 25g of steam exploded fiber, log Ro 4.2, pre-washed with acetic acid. Different sequences of alkanoic and alkaline peroxide with extensive water washing between stages were tried. Temperatures ranged from 60° to 80°. The liquor-to-wood ratio was necessarily high (approximately 10:1) to allow for stirring with a magnetic stir bar. Distilled water was the diluent, thus the acid strength of the liquor had been reduced to approximately 50 to 60%.

Subsequent trials were conducted at higher consistency (6:1): these were agitated with an electric motor. One trial was conducted at room temperature for an extended period.

6.2.2 Peralkanoic-acid Based Bleaching

The water and alkali extracted steam exploded fiber was rinsed with waste peracid to solubilize and remove metal ions that might catalyze peroxide decomposition. Acid concentration and liquor-to-wood calculations accounted for initial moisture retained on the extracted fiber. Total liquor-to-wood ratio for all of the trials was 6:1. The hydrogen peroxide concentration was calculated on fiber mass on a volume-to-mass basis. This amount of hydrogen peroxide was added to the total volume of acid and allowed to equilibrate at reaction temperature for approximately twenty minutes. For the performic acid trials the peroxide doses examined were 2, 5 and 10%. For the peracetic acid trials the doses examined were 10 and 20%. The formic acid was 85% concentration whereas the acetic acid strengths were 25, 50, and 80 %. (In order to attain the higher acid concentrations the fiber was air dried to approximately 50% solids content). The fiber was then added and temperature again raised to reaction temperature. Reaction temperature for the performic acid trials was 80°C: the peracetic trials included samples reacted at 60° and samples reacted at 40°. The performic acid trials were agitated whereas the peracetic acid trials were tumbled in a rotary evaporator, Yamato RE-71 with 12 liter capacity, at atmospheric pressure. Initial fiber mass for the peracetic trials was typically either 100 or 200g.

The performic acid samples were washed extensively and then reacted in aqueous-alkaline hydrogen peroxide, pH 11.5 . Alkaline hydrogen peroxide doses ranged from 1 to 5 percent of original mass. Diethylene triamine pentaacetic acid, DTPA (0.2%), a chelating agent, was added with water to the pulp prior to addition of alkali or peroxide. The aqueous alkali (NaOH), hydrogen peroxide, and $MgSO_4$ X 7(H_2O) (0.5% on pulp) were added to the mixture at the same time. The liquor-to-wood ratio was estimated as 10:1. The mixture was heated for one hour at 80°C, cooled, and then washed with water. This stage was repeated four times (five alkaline peroxide stages total) with decreasing amounts of charged peroxide; and reaction time was extended to three hours.

The peracetic acid samples were washed to a pH of 3-3.5. This typically required three liquor volumes of water (distilled water was used throughout). This was followed by a mild alkaline extraction (NaOH) designed to raise the suspension to pH 12. This extraction was performed at 60° for one half hour,

after attaining 60°, with liquor-to-wood ratio of approximately 8:1. This extraction was followed by water washing (approximately 2 liquor volumes). Two alkaline peroxide bleaching stages of 5% H_2O_2 on fiber (25-30g oven-dry typically) were performed at 60° for three hours with liquor-to-wood (l:w) ratios of 7.3:1 and 6.5:1 for the first and second stages, respectively. These were conducted in 400 ml beakers within a Fisher Scientific Versa-Bath. Stirring was by hand at 15 minute intervals. Ethylenediamine tetraacetic acid, EDTA, was substituted for DTPA. Initial pH was approximately 11 for these two stages. For comparison purposes two samples were run using extensive water washing as opposed to alkaline extraction (approximately 10 liquor volumes were required to raise the suspension to pH>6). Multi-stage alkaline bleaching was conducted with three samples. The multi-stage sequence included 4 stages, the only difference between them being the amount of charged H_2O_2: 4% for the first stage, 3% for the second stage, 2% for each of the final two stages. Peroxide was administered in two half doses for each of these stages.

6.2.3 Brightness Testing

Fiber samples (approximately 1.5g) were formed into handsheets according to the Tappi Standard T205 om-88. After the final stage, fiber samples were also taken for viscosity determination, Kappa #, molecular weight by GPC, and carbohydrate analysis by HPLC. Diffuse brightness testing at 457nm was conducted according to Tappi T525 om-86. The brightness tester was an Electrodyne S-4 Brightness Tester & Colorimeter calibrated to ceramic tile standards. The sheet former and fiber disintegrator, as well as the fiber press, were manufactured by the Hermann Manufacturing Co. of Lancaster, Ohio. Solids content measurements were performed using an Ohaus MB200 Moisture Balance.

6.2.4 Titration for Residual Peroxide

Liquor samples were titrated for residual peroxide using an iodometric titration. Liquor (5mL) was acidified with 25mL 5% H_2SO_4, to which had been added 0.25g KI. The residual peroxide was allowed to react with the iodide for fifteen minutes. The resultant iodine was titrated with 0.1N $Na_2S_2O_3$ and a starch indicator was used near the end point.

6.2.5 Extraction Liquor Solids (%)

Extraction liquor samples (150mL typically) were frozen in a round-bottomed flask in an ethanol bath at -50°. Lyophilization yielded a dry precipitate. Solids content was corrected to reflect the total volume of extract recovered. No correction was made for sodium content.

6.2.6 Kappa Number

Kappa numbers were performed according to Tappi T236 cm-85 with one modification: all Kappa numbers were performed on 4 grams of oven dry equivalent fiber. This limitation was necessary due to the scale of the bleaching reactions. For the more highly bleached samples, 30% of the permanganate was not consumed: for these trials the consumption factor was calculated according to equation 7.2 as given in the test standard:

$$\log K = \log p/w + 0.00093\,(p-50).$$

Where p is the amount of 0.1N permanganate actually consumed by the test specimen and w is the weight of moisture-free pulp in the specimen, grams.

6.2.7 Molecular Weight Determination (GPC)

6.2.7(a) Procedure

Fiber samples (250 mg) were dried overnight in a 125 mL Erlenmeyer flask. A stir bar was added to the flask and the flask was sealed with a septum. Pyridine (25 mL) was introduced into the flask using a syringe transfer technique. A different syringe was used to add 5 mL of phenyl isocyanate to the mixture. The temperature of the flask was maintained at 80° by placing the flask in a thermally regulated oil bath which was placed on a hot/stir plate. Pressure increased within the flask as the reaction proceeded and was vented with a syringe needle. The reaction was allowed to continue until the solution was clear (two days maximum). The reaction was stopped by the addition of 4 mL of methanol to the cooled solution. The solution was precipitated into a 250 mL volume of a 50/50 solution of methanol and water. The precipitate was isolated through filtration and rinsed with methanol until the pyridine odor was eliminated. The samples were dried in a vacuum oven at 55 degrees. For the GPC (gel

permeation or size exclusion chromatography) determination a sample of this material was dissolved in THF.

6.2.7(b) Apparatus

The GPC analysis was performed on a Waters Ultrastryragel column, 30cm x 7.8cm inside dia. This column was packed with a styrenedi-vinylbenzene copolymer with pore diameters of 10^3 , 10^4, and 10^6 Å. The system was pressurized by a Waters 510 HPLC pump. Detection was via differential refractive index as well as differential viscometry using a Viscotek 410 Differential Refractometer and model 100 Differential Viscometer. Temperature was 40°.

6.2.8 Tappi Viscosity

Tappi T230om-82 was used with the following modification: a sealed 50mL erlenmeyer flask was substituted for the dissolving bottle. Oven dry fiber (0.250g) was dispersed in 25mL of water. The flask was purged with nitrogen. Cupriethylenediamine (1.0M in cupric ion and 2.0M in ethylenediamine) solution (25mL) was added to the suspension. The fiber was found to be dissolved completely after 45 minutes. Viscosity was measured with a Cannon-Fenske capillary viscometer (size 100). Temperature, according to the standard, was set to 25°C. The viscosity in centipoise (mPa * s) was calculated from this formula:

$$V = Ctd$$

where C is the viscometer constant, t is the average efflux time (sec), and d is the density of the pulp solution(1.052).

6.2.9 HPLC Determination of Carbohydrates

6.2.9(a) Procedure

The chromatographic determination of sugar content followed Tappi T 249 cm-85, "Carbohydrate composition of extractive-free wood and wood pulp by gas-liquid chromatography" with these modifications: the autoclaving stage of the hydrolysis was performed in a sealed vessel to retain the volatile portion; HPLC (high performance liquid chromatography) was substituted for GLC (gas-liquid chromatography) , thus eliminating the need for derivatization of sugars. Though

the volatile portion was not calculated its determination is possible using this technique. This method has been described by Kaar et. al. (54,55).

Hydrolyzate (10 mL) and 1mL of a 2g/mL solution of erythritol (IS) were pipetted into a beaker. The pH of this solution was adjusted to 5.3 with $Ba(OH)_2$ and centrifuged. The supernatant was concentrated by rotary evaporation to approximately 2 ml. The concentrate was passed through an ion-exchange column prepared with layers: 0.2 ml of Bio-Rad AG 50w-X8, 100-200 mesh H+ resin covered by 0.4 ml of Dowex1X-8, 200-400 mesh $CO_3^{(2-)}$. Water (0.5 mL) was used to rinse the column following elution. This rinse was collected with the first elution and analyzed by HPLC. Degassed and distilled water was the solvent. Column temperature was 85° C. Pump flow rate was 1.0 mL/min. Detection was via refractive index.

6.2.9(b) Apparatus

A Bio-Rad-Cation H:30x4.6mm guard column was driven in series with an Aminex HPX-87P 300X7.8mm HPLC carbohydrate analysis column. These were pressurized by a Waters 510 HPLC pump. Detection was by a Waters 410 Differential Refractometer .

6.3 Statement of Precision and Accuracy for Methods

6.3.1 Brightness (Diffuse reflectance at 457 nm)

The repeatability for the brightness data was calculated with data from bleached fiber generated for this study. Each brightness test result was produced from an average of five measurements. Four different test results were used to produce the average repeatability.

The range in brightness for all four test results was from 58.8 to 72.5% MgO basis. In this case, the average Tappi repeatability represents the range of test results that may be expected 95% of the time, a test result being an average of five measurements on the same sample. This value was calculated as 1.2% of the mean value.

The initial brightness which Poppius et. al. (10) indicated for the extracted, steam exploded, log R_o 4.25, yellow poplar fiber was 16% MgO. The initial brightness for the fiber that supplied the peracetic-acid-based experiments, which was extracted with alkali twice and should have been brighter initially, was lower in initial brightness by nearly 2%. Therefore, conservative rather than optimistic values for these samples were expected.

6.3.2 Molecular Weight (GPC)

The values of repeatability reported in this section were generated from GPC data that was produced from elutions of carbanilated Aldrich cellulose. The same sample of carbanilated Aldrich cellulose was eluted five times. The range of molecular weights, reported as DP_w , was from 256 to 321 repeat units.

The repeatability was calculated according to Tappi T1206 rp-86. The value generated was 37.4 repeat units, or approximately 12.8% of the mean for the five replications. This value represents the range of values that may be expected 95% of the time for similar experiments with five replications.

For individual trials, the repeatability was estimated from the sample standard deviation and a 95% confidence interval. This calculation resulted in a value of 59.0 repeat units, or 20.1% of the mean value. This value may be interpreted as representing the range of values which could be expected 95% of the time for individual trials.

The polydispersity was similarly analyzed. The range of values was from 2.87 to 2.33. Tappi repeatability, expressed as percentage of the mean, was calculated as 10.8%. The per-trial repeatability was found to be 17%.

The chosen GPC technique relied on a universal calibration with polystyrene standards. Such a method is recognized as being capable of producing accurate results if the column packing is chosen to allow for high resolution and if the standard is reprensentative of the polymer to be investigated. Using commercial grades of cellulose over a DP_n range of from 164 to 2000 repeat units, the correlation coefficient, R^2, between GPC data and intrinsic viscosity data (produced by capillary viscometry) was found to be .978.

A better method of assessing the accuracy of the data would be to compare the results reported here for steam exploded yellow poplar to published results. No published results were found.

6.3.3 Carbohydrate Analysis (HPLC)

The repeatability for the carbohydrate analysis was calculated from data reported by Kaar et. al. (54). Quaking aspen (*Populus tremuloides*) and white fir (*Abies concolor*) were examined. For each wood, three samples from the same batch were extracted and hydrolyzed. The hydrolyzate for each of the three samples was eluted once.

The ranges reported for aspen glucan content and xylan content were 47.92 to 48.05%, and 14.35 to 14.54%, respectively. The Tappi repeatability for the glucan and xylan, expressed as a percentage of the mean, was calculated as 0.3% and 1.1%, respectively. The repeatability per trial was calculated as 0.3% and 1.3% for glucan and xylan, respectively.

The ranges reported for white fir glucan and xylan contents were 44.87 to 44.98%, and 4.16 to 4.36%, respectively. The Tappi repeatability for the white fir glucan was calculated as 0.2%. The analagous value for xylan was found to be 4.2%. The estimate for repeatability per trial was calculated as 0.3% for glucan and 5.1% for xylan.

The accuracy of this method is difficult to assess due to the natural variability of wood and the difficulty in separating the wood components. Cellulose content for quaking aspen was given as 49.4, 42.7 and 51.0% by three different researchers (12). Pentosans content was given as 17.2%. The total

glucan content of approximately 49% for quaking aspen reported by Kaar (54) appears to be an acceptable value. The total xylan content was reported by Kaar as approximately 16% which also agrees well with the older data.

Similarly, the glucan content found for white fir agrees well with tabulated data for cellulose content in other firs and pines. Data for the xylan content was not readily available.

7.0 Results and Discussion

7.0.1 The Sample Identification Code

The fiber samples are coded consistently throughout this report. Referring to Table 3, the sample designated 'F80.85.023' was reacted in formic acid, the first letter of the code is either "F" for formic or "A" for acetic; the second two digits give peralkanoic acid temperature, 80°; the middle two digits give the acid concentration, 85% ; the next two digits give the peroxide dose for the acid stage, 2%; and the final digit gives the length of time of the peralkanoic acid stage, three hours.

7.1.0 Performic Acid Results: Brightness Data

Water and alkali extracted, steam exploded yellow poplar , log R_o 4.25, was bleached by a sequence which featured an initial performic acid stage that was followed by five alkaline peroxide stages with extensive water washing between stages. The performic acid and fiber suspension was heated gradually to 80° and this temperature was then maintained for a total reaction time of three hours. The formic acid concentration was 85% and the liquor to wood (L:W) ratio was 6:1. Three different initial peroxide charges of 2, 5, and 10% fiber basis were employed. Citric acid was experimented with as a stabilizer for performic acid but was found to be unnecessary if the fiber was rinsed first with formic acid. The alkaline stages were conducted at pH 11-12 with a L:W ratio of approximately 10:1. Peroxide charges for these stages varied from 4% to 1% on fiber. Diethylenetriamine penta acetic acid (DTPA), 0.2% was added to chelate metal ions. $MgSO_4$ was also added to protect the cellulose from oxidation. The final stages were charged with peroxide at the 1% level . The data from these trials and a control sample are presented in Table 3.

The data in Table 3 show the expected behavior in response to bleaching agent: each stage resulted in an increase in brightness, given as % MgO, for all of the samples. This increased brightness resulted from the consumption of hydrogen peroxide.

Table 3. Hydrogen peroxide charge and consumption for performic acid experiments.

Sample	Initial Stage**	Alkaline Peroxide Stages				
		Stage 2	Stage 3	Stage 4	Stage 5	Stage 6
Control(no PFA)	Water wash					
H2O2 Charge (% Fiber):	n/a	5.0	4.0	4.0	3.0	3.0
H2O2 Consumption:	n/a	5.0	4.0	4.0	3.0	3.0
Brightness (% MgO):	16.2	27.7	41.6	54.4	62.1	65.9
F80.85.023*	PFA					
H2O2 Charge (% Fiber):	2.0	4.0	3.0	3.0	1.0	1.0
H2O2 Consumption:	2.0	3.5	2.0	0.9	0.4	0.4
Brightness (% MgO):	22.7	53.6	72.9	79.0	81.1	83.1
F80.85.053*	PFA					
H2O2 Charge (% Fiber):	5.0	3.0	3.0	3.0	1.0	1.0
H2O2 Consumption:	5.0	2.9	2.2	0.7	0.6	0.3
Brightness (% MgO):	28.0	54.2	78.6	83.0	84.3	85.9
F80.85.103*	PFA					
H2O2 Charge (% Fiber):	10.0	3.0	3.0	1.0	1.0	1.0
H2O2 Consumption:	10.0	2.1	0.5	0.4	0.3	0.4
Brightness (% MgO):	39.0	76.3	84.4	85.4	87.0	88.4

Data from experiments at the Finnish Pulp and Paper Institute.

* Sample I.D. code: F=formic acid; 80= acid stage temperature; 85=acid concentration (%); 02, 05, and 10 are the acid stage peroxide charges (% on fiber initially); 3=duration of acid stage, hours.

** Initial stage=performic acid (PFA) treatment, subsequent stages (stage 2 through stage 6) are alkaline peroxide.

Previously it was reported that increased alkaline peroxide charge led to increased consumption (37). Comparing H_2O_2 dosage with consumption for the control sample, it can be seen that complete consumption of H_2O_2 occurred for each of the alkaline peroxide stages. The other samples listed in the table consumed a varying amount of alkaline H_2O_2 relative to the initial concentration. Sample F80.85.053 consumed nearly the same amount of peroxide in stage 5 as in stage 6, though the charge varied from 3.0 to 1.0, respectively. Sample F80.85.103 displayed similar behavior in stages 3 and 4. Alkaline peroxide charge did not influence consumption in a consistent manner for the performic acid pretreated samples.

Increased initial peroxide charges in the acid stage , however, exhibited a distinct trend to increased gains in brightness for the initial stage: initial charges of 2,5, and 10% resulted in brightness values of 22.7, 28.0, and 39.0%, respectively.

Stage 2 was characterized by high consumption of peroxide relative to charge, but absolute consumption decreased when peroxide consumption in the preceding performic stage increased. This trend indicates that a trade-off in consumption between the initial acidic stage and the alkaline stages exists.

Figure 18 presents the brightness data as a function of peroxide consumption. The four profiles depicted are the same four samples that were listed in Table 3. A brightness level approaching 90% was achieved by the sample that was charged initially with ten percent acidic peroxide, sample F80.85.103. This level of brightness is extraordinary considering the high initial Kappa number, 53.9, for the extracted steam exploded yellow poplar. (Kappa numbers in the 28-35 range for kraft softwood pulps, the worst case, are considered normal for bleaching (56)).The lowest final brightness depicted in this figure was for the sample which was bleached entirely with alkaline peroxide, the control sample. High brightness levels are unobtainable without the initial peralkanoic stage.

Brightness levels of 83 and 86% were achieved by samples F80.85.023 and F80.85.053, respectively. While these samples weren't as bright as F80.85.103, they were significantly brighter (about 20 brightness percentage points) than the control sample.

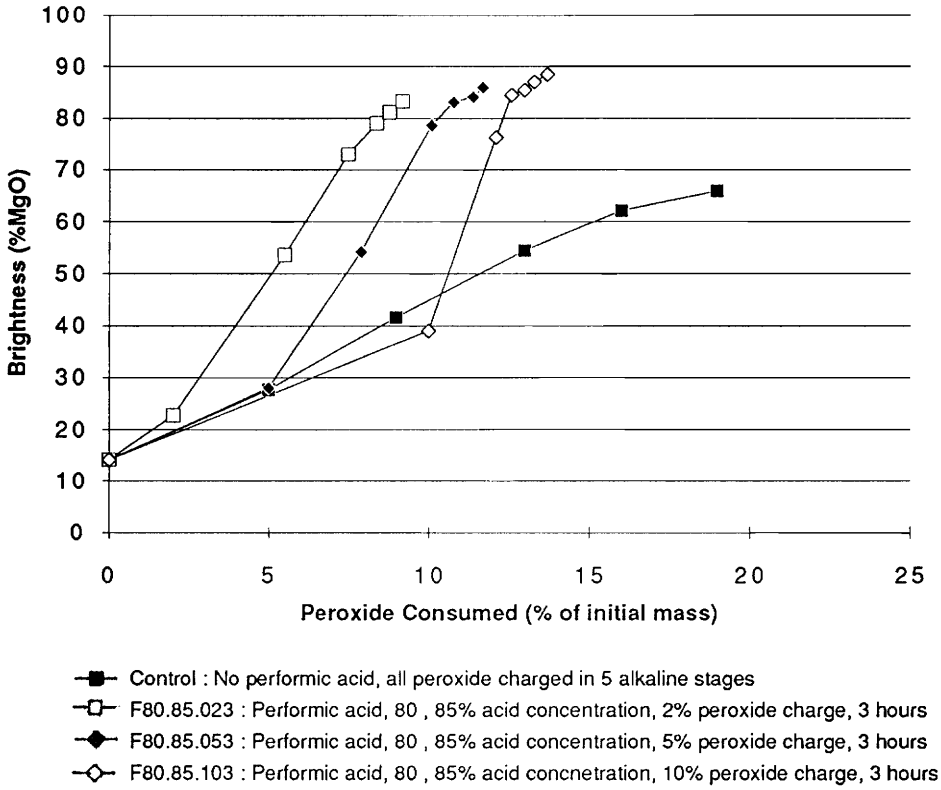


Figure 18. Brightness vs. peroxide consumption for performic trials conducted by K.Poppius-Levlin, J.Sundquist, and I.Tuominen of the Finnish Pulp and Paper Research Institute.

The three performic acid traces in Fig.18 may be characterized by three phases. The first phase displayed a shallow slope: not much brightness was gained relative to peroxide consumption. The second stage was characterized by a steep slope: large gains in brightness with low peroxide consumption. This second phase carried through the second and third bleaching stages. The third phase which was composed of several stages was characterized by small, gains in brightness with decreasing efficiency (% MgO gained per % H_2O_2 consumed). These three phases correlated well with the bleaching theory of Gierer (21,22,23,24): initial electrophilic attack followed by nucleophilic dissolution. Because not much lignin was dissolved and chromophores were actually created, the brightness gains of the first phase were modest. The changes to residual lignin structure from the first phase rendered a large percentage of it soluble in alkaline peroxide, the second phase. The residual lignin following these two phases was readily accessible to alkaline peroxide bleaching, the third phase.

The efficiency by bleaching stage for each of the performic acid samples is presented in Table 4. The general trend was an initial phase of low efficiency followed by a phase of very efficient brightness gain, and a final phase of intermediate efficiency (the control sample, F80.85.003, demonstrated fairly uniform efficiency). The efficiencies for stages 2 and 3 increased with alkanoic peroxide charge: this effect may be seen by noting the sequence of values in descending order within the corresponding columns. The *overall* efficiency decreased as alkanoic acid peroxide charge increased, however.

The efficiencies for samples F80.85.053 and F80.85.103 were very low in stages 5 and 4, respectively. The efficiency increased again following these stages. Returning to Figure 18, it appears that a transition in slope, efficiency, is occurring near a brightness level of 80%. This level of brightness was found to correspond to complete delignification in the peracetic experiments, to be described subsequently. Based on this information, it appears that delignification is essentially complete when the 'dip' in efficiency occurs and that a transition in bleaching mode may be occurring. In terms of stages, the higher initial acid peroxide charge required one less stage to attain this efficiency 'plateau'.

Table 4. Peroxide efficiency for performic trials

Sample*	Final Brightness (% MgO)	Rate of brightness Gain (%MgO / %H2O2 Consumed)						
		Stage 1	Stage2	Stage 3	Stage 4	Stage5	Stage 6	Overall
Control	65.9	xxx	2.3	3.5	3.2	2.6	1.3	2.6
F80.85.023	83.1	3.2	8.8	9.6	6.8	5.3	5.0	7.3
F80.85.053	85.9	2.4	9.0	11.1	6.3	1.7	6.3	6.0
F80.85.103	88.4	2.3	17.8	16.2	2.5	5.3	3.5	5.3

Data from experiments conducted at the Finnish Pulp and Paper Research Institute.

*See figure 18 for definition of sample I.D. code.

7.2 Performic Acid Results: Molecular Weight Data

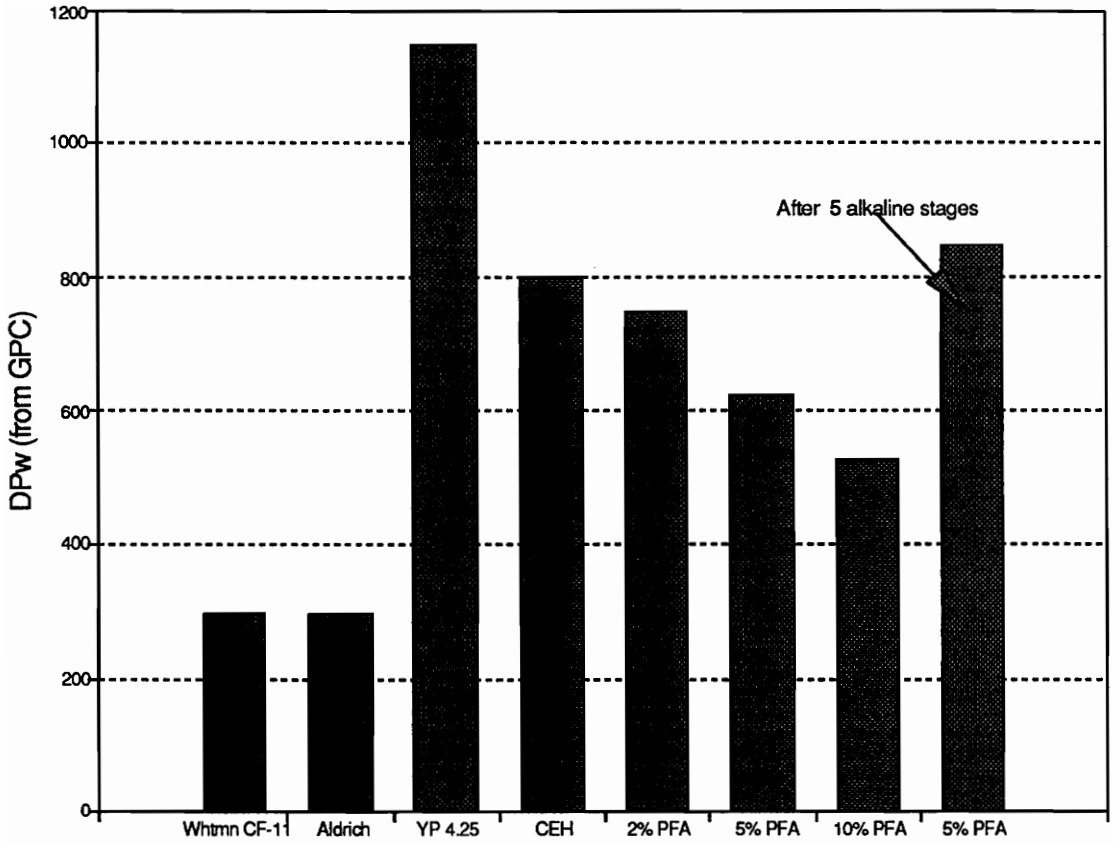
Performic acid samples were carbanilated and analyzed for molecular weight by gel permeation chromatography (GPC). The results from this analysis are presented graphically in Figure 19. Whatman CF-11, Aldrich microcrystalline cellulose, steam exploded log R_o 4.25 yellow poplar, and a standard CEH (chlorination, extraction and hypochlorite) bleached yellow poplar sample are displayed along with four samples from the performic acid experiments. The samples designated 2, 5, and 10% PFA are samples isolated following the initial acid stage of the performic acid sequence. The trend in the data indicates that increasing peroxide charge in the initial acid stage results in lower DP_w. The yield (not tabulated) also decreased with increasing alkanoic peroxide, from 98.5% for F80.85.023 to 90.6% for F80.85.103. These data support the conclusion that cellulose was hydrolyzed to a greater extent as peroxide dose increased.

However, this loss is somewhat mitigated by the effects of the alkaline peroxide stages which result in increased DP_w. This phenomenon has been well documented and has been attributed to hydrolysis or alkaline peeling of the low molecular weight material (57).

If the molecular weight loss due to peralkanoic peroxide bleaching is expressed as a percentage of initial molecular weight then the range in loss for the acid samples is 35 to 55%. The fully bleached sample has lost approximately 30% of its original DP_w.

The fully bleached material exceeds the molecular weight of the sample bleached with the more common CEH sequence. This fact indicates that the selectivity of the peralkanoic bleaching sequence is good relative to traditional methods.

The final observation to be made from Figure 19 concerns comparisons with Whatman CF-11 and Aldrich grades of microcrystalline cellulose: the DP_w for performic/alkaline peroxide-bleached fiber exceeds the DP_w for commercial grades. This fact indicates that the severity of the steam explosion stage could be increased and still produce fiber of suitable molecular weight. This increased severity could lead to more efficient bleaching by rendering more of the lignin extractable.



Whtmn=Whatman; YP 4.25=steam exploded yellow poplar log R_O 4.25; CEH=chlorination, alkaline extraction, hypochlorite; PFA=peroxyformic acid.

Figure 19. DP_w data for microcrystalline cellulose and performic-acid bleached yellow poplar. Also included is data for a yellow poplar sample that was bleached with a CEH sequence.

In summary, the performic acid trials resulted in cellulose with brightness of 90%, essentially complete delignification. The bleaching process began with lignin activation by performic acid. This first phase was followed by a nucleophilic phase of high efficiency in terms of brightness gain per consumption of peroxide: the major portion of the residual lignin was rendered soluble in alkaline peroxide. The third phase was characterized by alkaline bleaching of residual chromophores. The steam explosion process effectively substituted for the first two stages of the Milox process. Molecular weight was well above that required of microcrystalline cellulose grades, indicating that a more severe steam treatment could be tolerated. It appears that it is possible to produce microcrystalline grades from steam exploded biomass with the Milox process.

7.3 Results from Preliminary Peracetic Acid Trials

Preliminary trials were conducted on water and alkali extracted steam exploded, log R_o 4.21, extracted yellow poplar fiber samples (25g) within 500mL beakers. Typically, these beakers were stirred on a hot plate with a stir bar; dilution of the peracetic acid was necessary to allow this. The resulting acid strengths ranged from 50 to 60%. Table 5 summarizes the most successful results from the preliminary trials. Sample B was produced through a bleaching sequence that alternated peracetic (H_2O_2 concentration: 10% on fiber for the first acid stage, 5% on fiber for the second) and alkaline peroxide stages (H_2O_2 concentration: 5% on fiber for both) for a total of four stages. The L:W ratio was approximately 9:1. Sample G was conducted at room temperature and high consistency, L:W ratio of 6:1, over an extended period (several days) with intermittent , manual, stirring . Sample H was conducted at high consistency and was stirred with an electric motor. Samples H and B were conducted in the same temperature range, 60 to 80°. Both samples G and H were bleached with a four stage sequence that began with a peracetic stage (10% H_2O_2 on fiber) and was followed with three alkaline peroxide stages (5% H_2O_2 on fiber). Alkaline peroxide charges of 5% were chosen in response to the performic acid data which indicated that consumption of peroxide was not dependent on

Table 5. Data from preliminary peracetic acid trials.

Sample*	DPn	DPw	Klason (%)	Glucose (%)	Xylose (%)	Brightness (% MgO)
B	105	285	3.2	96	0.54	81.4
G	180	721	1.0	98	0.99	71.1
H	179	441	0.9	99	0.67	77.0

* Sequence and conditions for each sample:

B- peracetic stage (10% peroxide on fiber initially) followed by alkaline peroxide (5%) followed by second peracetic stage (5%) followed by alkaline peroxide (5%). L:W of approx. 10:1, acid conc. of 50%, 6-hour stages.

G- peracetic stage (10%) followed by three alkaline peroxide stages (5% each). L:W of approx. 6:1, acid conc. of approx. 80%, stages conducted at room temp. over several days.

H- same conditions as G with heating and mechanized stirring and 6-hour stages.

charge. A charge of five percent insured that an excess amount of peroxide was present.

Sample H resulted from certain refinements in technique as compared to previous trials. A mechanized stirrer allowed higher consisitency than was previously tried and careful pH monitoring during the alkaline peroxide stages was practiced to prevent peroxide from decomposing to oxygen.

Sample B achieved the highest final brightness (81.4% MgO) of the preliminary experiments. But it also produced the lowest molecular weight (the molecular weight data are from GPC traces of the carbanilated cellulose): DP_w was half of that for sample H and nearly one third of that for sample G. Since sample H and sample B were conducted at about the same temperature, and the alkaline stages were similar, the acid treatments must have been responsible for the difference in DP_w . As sample B was exposed to the acid for a longer period of time it was speculated that duration of the acid stage may be a key variable influencing molecular weight. Acid concentration was also different between samples B and H.

Sample G was only one repeat unit better than Sample H in terms of Mn but nearly 300 units longer in terms of Mw (DP_n and DP_w respectively). These facts support the interpretation that hydrolysis of high molecular weight glucans has resulted in a higher percentage of low molecular weight substance in the case of sample H, and that the degree of hydrolysis varies with temperature.

Klason lignin determinations are also included in Table 5 as are carbohydrate compositions. Sample B produced the largest Klason percentage. The lowest glucose percentage was also recorded by sample B, but all three samples exceeded 95% glucose. Other sugars were also present in small amounts. Sample H presented the highest percentage of glucose and moderate DP_n losses and was also similar to the protocol that was employed for the performic trials : this sequence became the basis for a more controlled series of experiments.

Preliminary experiments on water and alkali-extracted material, which had been produced specifically for this study, revealed that a large percentage of extractable lignin remained on the fiber. (The Finnish research group also noted brightness gains simply by water washing the already water- and alkali- extracted fiber.) A 10% peracetic acid stage(acetic acid concentration was approximately

75%) at 60° produced no visible change in the fiber mass though the peroxide was substantially consumed. Normally, the fiber color changed from brown to brick-orange during the peracetic acid stage. Brightness gains were minimal. Subsequent alkaline peroxide stages proved ineffective as well. It was speculated that extractable lignin was still present on the fiber: a second alkaline extraction under mild conditions was performed (4% NaOH on fiber (w/w), 60°, 8:1 liquor-to-wood (L:W), for $^1/_2$ hour). The second extraction resulted in an additional mass loss of 2%.

The dried fiber following this second extraction was more similar to the fiber used previously in brightness and texture. This twice-extracted material was used exclusively for the quantitative work that followed.

In summary, the preliminary data showed that molecular weight of the final product cellulose may be influenced by temperature and acid concentration and possibly by consistency. Brightness levels exceeding 80% MgO basis were achieved. Glucose percentages exceeding 95% were attained with the retention of approximately one percent hemicellulose. An additional extraction was required prior to bleaching for log R_o 4.25 material resulting in an additional loss of 2% yield.

7.4 Justification for Selection of Process Parameters

Consistency

Higher consistency has been shown to be more efficient for both alkaline and alkanoic peroxide stages (34, 58). In terms of liquor-to-wood (L:W) ratio, the practical limit has been given as 4:1 (34,58). At the scale of these experiments, consistency of acid concentration between trials and effective mixing were primary concerns in the peracetic stage. A liquor-to-wood ratio of 6.5:1 was found to be satisfactory for mixing and allowed the addition of enough water to the suspension to maintain uniform acid concentration between trials.

Fiber swelling became an issue in the alkaline stages as it opposed adequate mixing. A minimum L:W ratio of 6.5:1 allowed adequate mixing and was therefore chosen for the alkaline peroxide stages of the peracetic-acid based

sequence. This L:W ratio was lower than that used in the alkaline stages of the performic-acid based trials (10:1).

Acid concentration

Acid concentration was identified as a possible variable influencing molecular weight of the bleached fiber. The upper practical limit for acid concentration was 80%, as retained water on the air-dry fiber diluted the acid. (Oven drying was undesireable due to difficulties with diffusion of non-swelling solvents such as acetic acid). This acid concentration was lower than the 85% concentration used in the performic acid experiments.

Temperature

Acid hydrolysis of carbohydrates generally increases with temperature (12). In order to preserve as much of the starting DP as possible through the initial peracetic acid stage and still achieve high brightness, intermediate temperatures (between room temperature and 80°, the temperature used in the performic experiments) were chosen for the peracetic acid experiments: 40° and 60°.

Reaction Time

The equilibrium reaction that results in the production of peracetic acid was shown to be much slower than the performic equivalent (58). Therefore, two reaction times for the peracetic acid stages were examined: 3 and 6 hours.

Peroxide Charge for the Initial Stage

The performic experiment which employed 10% hydrogen peroxide on fiber produced the brightest pulp. Preliminary experiments were performed with peracetic acid at 2,5 and 10% on fiber. Visual inspection showed 10% to be significantly brighter than the lower concentrations. The Finnish researchers did not report data for any trials with greater than 10% initial acidic peroxide concentrations. Therefore, two peroxide concentrations were examined: 10 and 20%.

Alkaline Extraction

Gierer lists the OH^- ion as being an effective nucleophile (22,24): this fact, together with the observation from preliminary experiments that peroxide may be consumed by the liquor (a similar observation has been reported concerning ozone bleaching (9)) led to a modification of the Milox (performic acid) sequence for the peracetic acid trials: an alkaline extraction was inserted following the peralkanoic acid stage.

The second stage alkaline extraction served three functions: it removed alkali-soluble organics, it reduced the amount of water required for washing the acid fiber as some of the alkali is consumed neutralizing residual acid, and it raised the pH of the fiber prior to alkaline peroxide stages.

7.5 Results from Controlled Peracetic Experiments

The results reported in this section were produced from experiments in which the process variables discussed in the previous section were carefully controlled. Water and alkali extracted yellow poplar was reacted with peracetic acid within a rotory evaporator under atmospheric pressure. Alkaline extractions were performed in large beakers on heated stir plates. Subsequent alkaline stages were conducted within 250mL beakers within a closed water bath set to 60°.

7.5.1 Peroxide Consumption

The concentration of peroxide as a function of time at two different temperatures (40 and 60°) is depicted in Figure 20. This graph was generated from intermediate scale (200g of fiber) peracetic acid stages conducted with strict temperature control. The initial peroxide concentration reflects a 10% charge on fiber. Approximately 75% of the starting peroxide concentration was consumed after six hours for both temperatures. There was no difference between the two temperatures in terms of peroxide concentration after six hours. The remaining peroxide was consumed at a much slower rate although more was consumed by the 60° trial. Based on the consumption of peroxide, six to nine hours appears to be optimal.

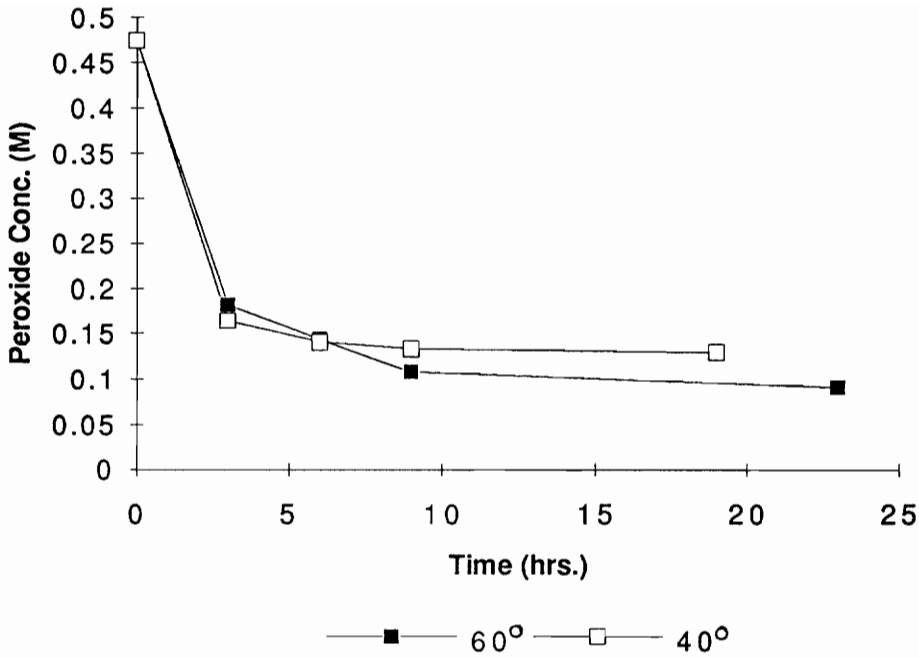


Figure 20. Hydrogen peroxide concentration vs. reaction time for 40° and 60° peracetic acid stages.

Alkaline peroxide concentration data are plotted against time in Figure 21. This data was generated from the second alkaline peroxide stage (stage 4) of a large scale (5kg) trial and reflects an initial peroxide concentration of 3% charge on fiber. The rate of alkaline peroxide consumption appears to level off after an initial period of high consumption (Fig. 20). Again, about 75% of the starting charge has been consumed after six hours.

Figure 22 presents brightness data as a function of peroxide consumption for the carefully controlled peracetic acid trials. Several trials with different initial peracetic acid conditions are depicted in this figure. Initial brightness for all of the traces was 14%. The first segment reflects peroxide consumption and brightness gain for the peracetic acid stage. Initial peroxide concentrations of 10% and 20% on fiber may be readily compared: 20% inital peroxide charge was inefficient in terms of percent gain in brightness per percent peroxide consumed. The 15-16% consumption of two of the traces reflected a 20% initial charge. Regardless of charge and time (3 and 6 hour trials are presented) about 75% of the charged peroxide was consumed in the first stage.

The second stage was an alkaline extraction in which no peroxide was charged. The line segment for the second stage is vertical, reflecting no peroxide consumption.

The initial peroxide charge for the first alkaline peroxide stage, stage 3, was 5% on fiber. As can be seen from the figure more than 80% of charge was consistently consumed in this stage (compare peroxide consumption in stage 3 to the initial 5% concentration), which was three hours long (a much higher rate of peroxide consumption than that described for the fourth stage of the large-scale trial). A smaller consumption of peroxide was observed for the second alkaline peroxide stage (also 5% peroxide charge), stage 4. The difference in peroxide consumption between the alkaline peroxide stages is due to differences in lignification. The peroxide targets the lignin and will therefore react faster in the presence of a higher lignin concentration.

In summary, peroxide consumption in the initial peracetic acid stage was consistently 75%. Temperature, reaction time, and acid concentration did not markedly influence this level of consumption. Alkaline peroxide consumption was higher for the third stage but tapered off in the fourth stage. This phenomenon

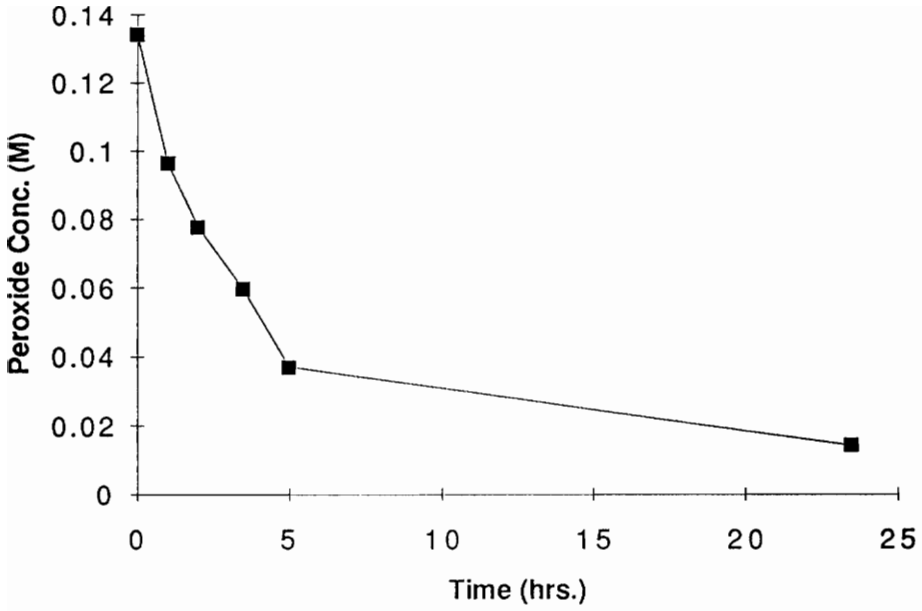


Figure 21. Hydrogen peroxide consumption vs. reaction time for alkaline hydrogen peroxide, fourth stage.

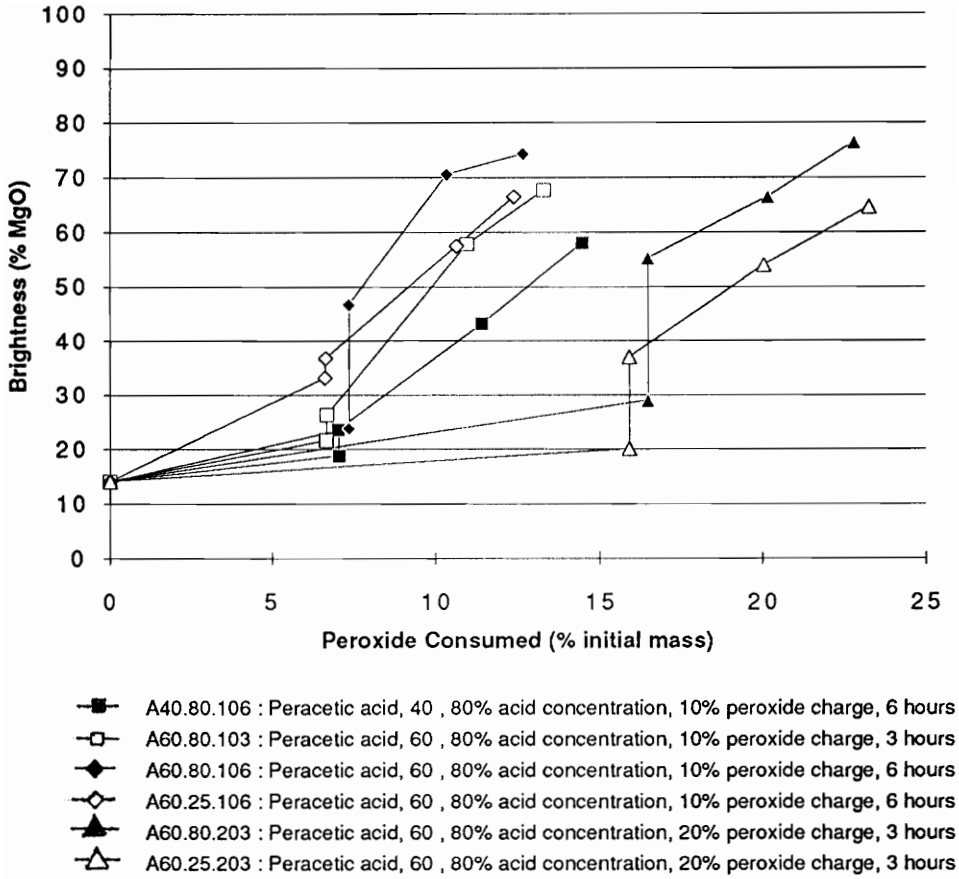


Figure 22. Brightness vs. peroxide consumption for peracetic acid trials with differing acid stage conditions. Note verticle segment which reflects alkaline extraction without peroxide.

was attributed to residual lignin percentage which was higher in stage three.

7.5.2 Reaction Kinetics for the Peracetic Stage

Based on the data presented in Figure 20, a rough estimate of the energy of activation for the peracetic stage may be calculated. It was assumed that the reaction was first order with regard to peroxide concentration. This assumption was based on analagous findings with regard to alkaline peroxide systems (59) and chlorine-based bleaching (60). (Alkaline peroxide systems have also been found to be first order with respect to lignin concentration (59) in bleaching of sugar cane bagasse).

Given the assumption of first order kinetics with respect to peroxide concentration, the rate constant (k_{temp}) for the peracetic stage may be found from the slope of the linear regression of $\ln[H_2O_2]$ against time (referring to concentrations given in Figure 20). The initial concentration, which was calculated from the initial peroxide charge and the volume of aqueous acetic acid, was omitted from the calculation. These calculations resulted in k_{40} of 3119 min^{-1} with a regression correlation r-value of -0.79. The k_{60} value was found to be 1520 min^{-1} with an r-value of -0.89. The r-values were improved by omitting the last data point in both cases: k_{40} was found to be 1584 with an r-value of -0.96, and k_{60} was found to be 688 with an r-value of -0.99.

Using this second set of k values and the corresponding temperatures, the activation energy for the reaction may be calculated from an equation which has been derived from the Arrhenius equation (61):

$$\ln (k_{40} / k_{60}) = -(Ea / R)\{(1/T_{40}) - (1/T_{60})\},$$

where Ea is the activation energy, R is the gas constant (2 cal / Kelvin / mole), and T is the temperature in Kelvins. This calculation resulted in an Ea value of 8.7 kcal / mole.

Activation energy values provide a means of assessing which aspect of the reaction is rate determining. For rate processes which are limited by chemical reaction, the activation energy is typically much higher (25-50 kcal / mole)(59,60) than the calculated value (8.7 kcal / mole) for the peracetic acid stage. Reaction processes which are diffusion-controlled, however, are found to have activation energies of approximately 5 to 10 kcal / mole.

The calculation presented here was based on sparse data and would be ideally replicated with more data points over a shorter time interval. However, the magnitude of the calculated value suggests that the rate of the peracetic acid attack on lignin is diffusion controlled.

Figure 23 is a schematic indicating the physical nature of the bleaching process. The ligno-cellulosic material may be treated as a stationary phase relative to the active chemical. The active reagent, whether it is H_2O_2 or NaOH or peralkanoic acid, must diffuse through the liquid medium. A stationary film surrounds each fiber and this layer has a lower diffusivity than the bulk media. Once through the surrounding layer of fluid the active reagent must diffuse through the polymeric matrix of the cell wall, which may also contain pockets of stationary fluid. Removal of the reacted materials must then follow the reverse of this course.

Experiments conducted with water transport through cellophane indicated that the rate of diffusion was five orders of magnitude less than that of water through itself (60). If this cellophane/water model is accepted as a reasonable approximation to the peracetic acid/lignocellulose system explored here, then it is not surprising that the estimate of activation energy indicated that this system is diffusion controlled.

Diffusion control is not unusual in pulping and bleaching of ligno-cellulosics. It has been shown in relatively recent studies to be rate determining in chlorination stages (60), in alkaline pulping (11,62), and in alkaline peroxide systems (59).

7.5.3 Brightness Data

Cellulose and hemicellulose are almost colorless, though bleached grades appear bright white: the whiteness results from light scattering. The purpose of bleaching is either the removal of color or the removal of non-cellulosics depending on the targeted application of the product. Color and UV absorption result from electronic transitions in conjugated systems. Chromophoric structures are present in native lignins, but their concentration increases following chemical changes in structure which occur in the initial electrophilic stage. Because most of the color in woody biomass can be attributed to these lignin-derived chromo-

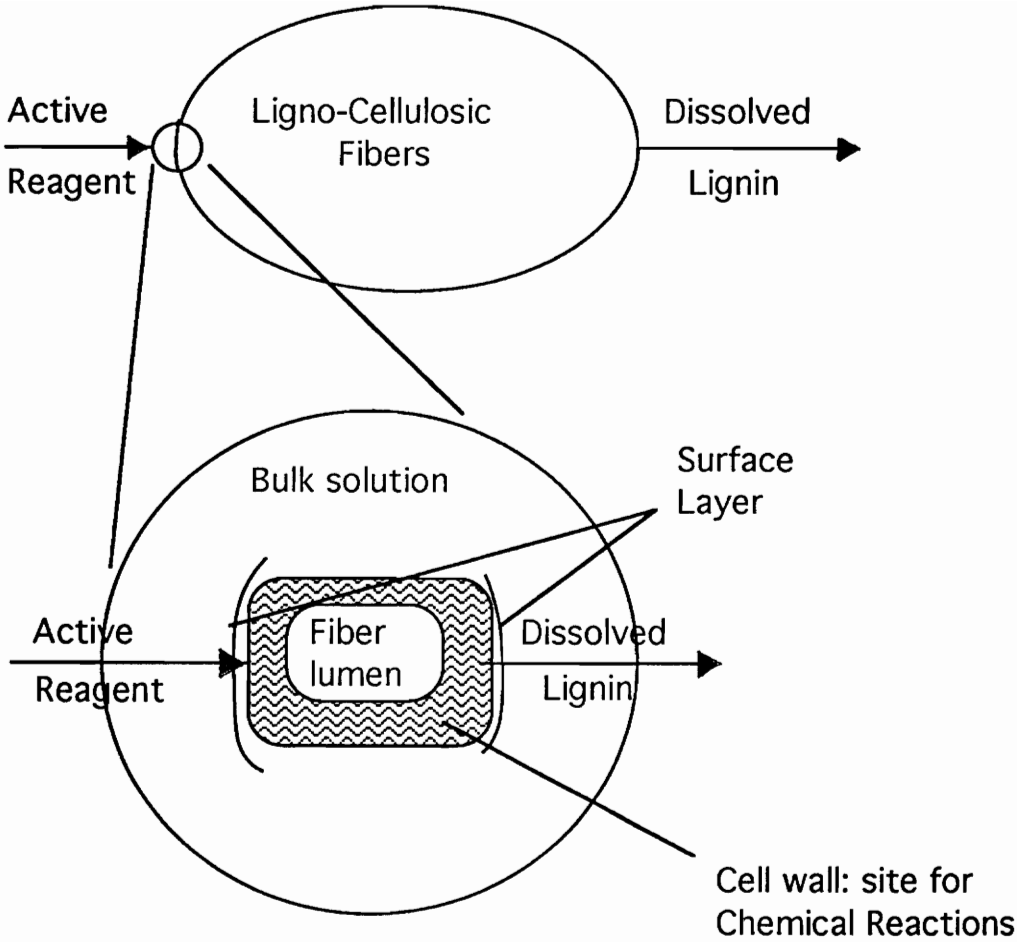


Figure 23. Schematic of mass transport during heterogeneous phase reactions. Diffusion is occurring through bulk solution, surface layer, and cell wall. Within the cell wall diffusion may be occurring across stationary pockets of liquid phase as well as through polymeric matrix.

phores, the degree of delignification should correlate with brightness.

Kappa number was the method used in this study for quantifying the residual lignin on fiber . Figure 24 is a graph of brightness vs. final Kappa # for sixteen peracetic-acid-bleached samples. The relationship between these two parameters is strongly linear. A simple linear regression gave this equation

$$\text{Brightness (\%)} = 80.133 - 2.212*(\text{Kappa \#}).$$

The regression correlation coefficient, R^2, was given as .971 for the best-fitting line. Some deviations are seen at the lower end of the Kappa# scale: these deviations may be the result of consuming less than the Tappi-specified amount of permanganate (fiber sample size was limited to 4g for all Kappa numbers reported for the peracetic trials), or they may derive from nonuniform delignification. Extrapolating to zero, complete delignification should occur when 80% brightness is attained (this assumes that the relationship holds for Kappa # below 2). Based on the data, it appears that brightness correlates well with lignin content .

Referring to Fig.22, note that the profile does not exhibit the smooth contour of the Milox data. The three phases that were apparent in the trace for sample F80.85.103 are accentuated in the peracetic traces. Figure 25 displays more vividly the activation due to the acidic peroxide. The initial stage for sample A60.80.003 was an acetic acid stage without peroxide. The first stage was followed by an extraction. There was virtually no brightness gain; the symbols for stages 1 and 2 overlap on the y-axis. After approximately 10% peroxide consumption the difference in brightness between A60.80.003 and A60.80.106 was about 30%. This difference may be attributed to the gain in brightness of 25% that occured in the alkaline extraction of sample A60.80.106. Peroxide is necessary in the initial peralkanoic stage for lignin activation.

Brightness from the final stage has been plotted as a function of alkaline extraction liquor solids (%) in Figure 26. This data displayed a general trend towards higher brightness as more lignin was dissolved. These data indicate that the amount of lignin removed in the first two stages has a strong influence on the brightness level achieved.

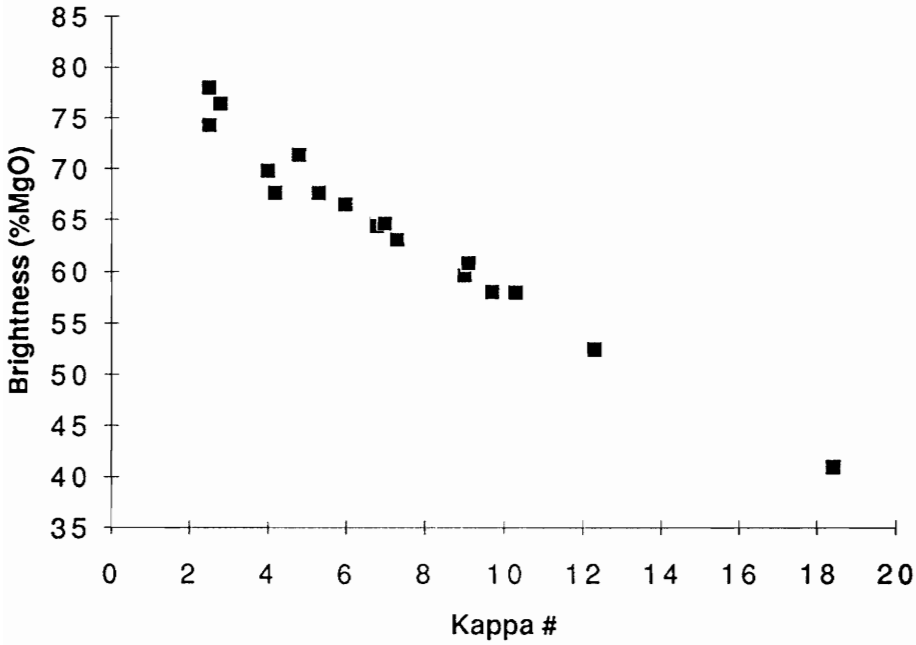


Figure 24. Brightness related to Kappa # for the peracetic acid trials.

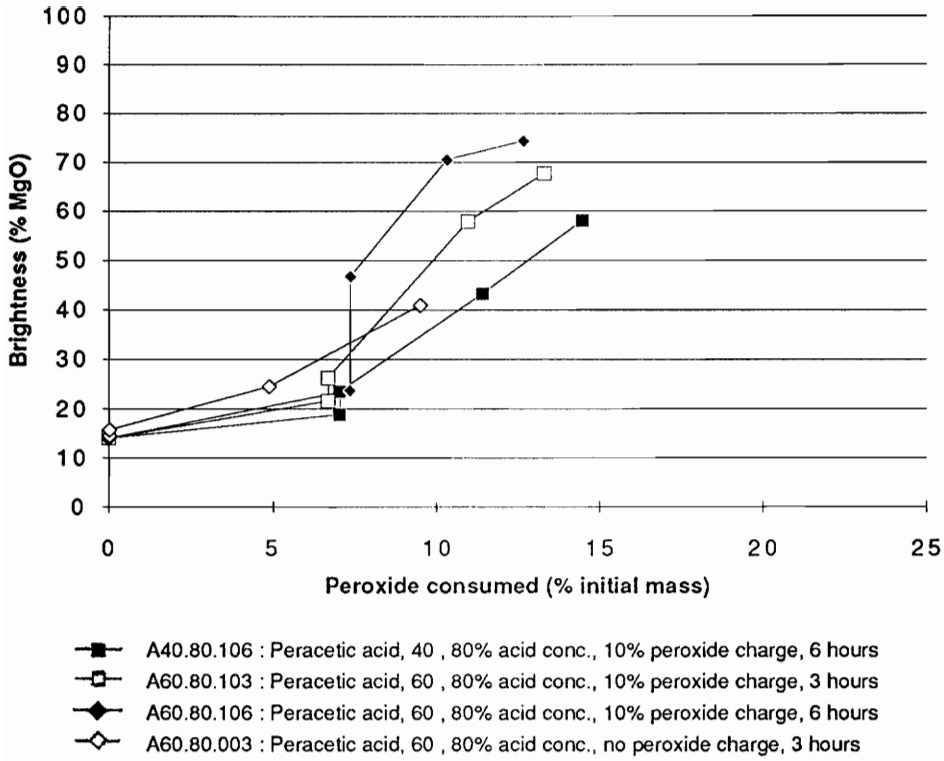


Figure 25. Comparison of samples charged with 10% peroxide on fiber initially and the control sample (no initial peroxide charge).

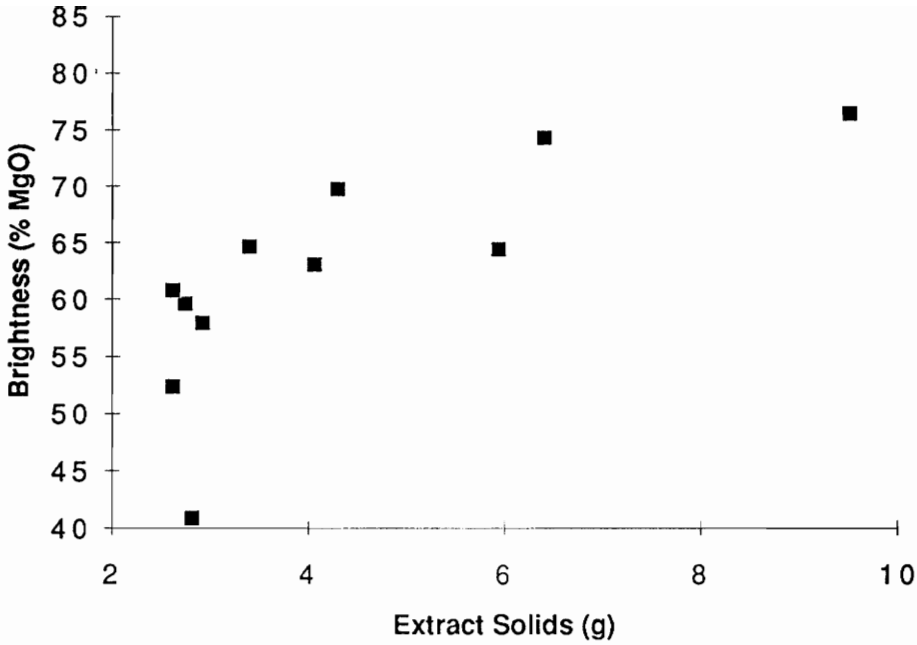


Figure 26. Final brightness (stage 4) vs. solids content of the alkaline extraction liquor (stage 2).

Temperature Effect

Table 6 is a tabulation of peroxide efficiency (%MgO per % H_2O_2 consumed) through the fourth stage. The temperature effect on overall efficiency can be seen by comparing matched samples. For example, sample A60.25.206 may be compared to sample A40.25.206. For these two the difference in efficiency is nearly 1 % MgO per % H_2O_2. This value is close to the average diference in efficiency for the two temperatures. Based on the tabulated data for overall efficiency, 60° is the more efficient temperature for the peracetic stage.

Final brightness data for all of the peracetic acid trials is tabulated along with other data in Table 7. The brightest 40° samples overlap the range of brightness for the 60° samples, but none of the 40° samples reached 70% brightness. Comparing matched samples the range in temperature effect on brightness is from approximately 10%(samples A60.25.206 and A40.25.206) to approximately 18 % (samples A40.80.106 and A60.80.106(2)). In terms of final brightness, 60° is a more effective temperature than 40°.

Duration Effect

For those samples in Table 6 where 3 and 6 hour trials were performed the six hour trials led to improved brightness (all times refer to the duration of the peracetic stage). At the extremes are the 19 hour 40° sample and the 23 hour 60° sample. Sample A60.80.1023 was the brightest sample of these experiments and A40.80.1019 was the brightest 40° sample that was run with 10% peroxide. Comparing brightness for samples that were run both three and six hours, the six hour run was usually about 5% brighter.

Table 6 also displays efficiency data (% gain in brightness per % consumption of peroxide) for the extended 40 and 60° trials. The 19 hour 40° trial was significantly more efficient than the other 40° trials. The 23 hour 60° trial was less efficient than several of the other 60° trials, however. Therefore, the 40° reactions could benefit from longer reaction times; whereas, the 60° trials demonstrated a high level of efficiency at 6 hour durations.

Table 6. Peroxide efficiency for the peracetic acid trials.

Sample*	Brightness after Stage 4**	Rate of Brightness Gain (%MgO / %H2O2)				
		Stages 1&2	Stage 3	Stage 4	Stages 3&4	Overall
A40.80.106	58.0	1.34	4.47	4.85	4.63	3.02
A40.80.203	64.4	0.85	6.06	3.30	4.95	1.97
A40.80.206	69.8	1.13	8.20	2.28	5.70	2.44
A40.25.106	52.4	1.04	4.75	3.16	4.03	2.59
A40.25.203	59.6	0.84	3.77	4.97	4.17	2.04
A40.25.206	60.8	0.68	5.91	2.77	4.72	2.00
A40.25.206(2)	57.9	0.60	5.43	3.03	4.39	1.89
A40.80.1019	67.6	2.25	5.82	2.67	4.60	3.48
A60.80.103	67.6	1.81	7.37	4.20	6.25	4.02
A60.80.106	74.3	4.42	7.99	1.62	5.19	4.74
A60.80.106i	73.5	4.42	10.78	4.47	8.90	5.72
A60.80.106(2)	76.3	4.81	7.00	1.96	5.13	4.95
A60.80.106(2)ww	73.9	1.80	7.75	5.35	6.81	4.31
A60.80.203	76.4	2.50	3.07	3.74	3.35	2.73
A60.50.106	67.0	3.45	4.39	4.26	4.34	3.89
A60.50.106ww	62.0	1.58	5.73	4.52	5.17	3.43
A60.25.103	63.1	2.28	5.89	2.84	4.58	3.54
A60.25.106	66.5	3.41	5.18	4.74	5.04	4.18
A60.25.106i	65.0	3.41	9.15	7.69	8.74	5.15
A60.25.203	64.6	1.44	4.08	3.34	3.76	2.17
A60.25.206	71.3	1.72	5.66	3.62	4.73	2.57
A60.25.206i	70.5	1.72	11.08	5.06	9.03	2.94
A60.80.1023	77.9	5.21	4.11	2.57	3.51	4.48
A60.80.003	40.9	x	1.80	3.54	2.65	4.30

* From left to right: first letter denotes acetic acid; next two digits give temperature of acid stage; next two digits give initial peroxide (% fiber) for acid stage; final digit(s) give duration (hrs.) of acid stage. "WW" refers to exhaustive water washing instead of alkaline extraction; "i" denotes 4-stage alkaline peroxide sequence. A number 2 in brackets, (2), indicates a duplicate trial.

** Stage 1= acid stage; stage 2= extraction; stages 3&4= alkaline peroxide.

Table 7. Comparison of data from 40 & 60 peracetic acid trials.

Sample**	Yield %	Acid stage Peroxide Consumption*	Total Peroxide Consumption*	Total Alkali Consumption*	Brightness Attained (% MgO)	Kappa #	Tappi T-230 Viscosity (mPa*s)
A40.80.106	87	7.0	14.5	17.3	58.0	9.7	2.65
A40.80.203	90	15.9	23.3	21.2	64.4	6.8	2.43
A40.80.206	83	16.2	22.8	21.2	69.8	4.0	2.47
A40.25.106	84	6.9	14.8	11.2	52.4	12.3	2.43
A40.25.203	85	16.0	22.3	11.0	59.6	9.0	2.42
A40.25.206	86	15.8	23.4	11.2	60.8	9.1	2.34
A40.25.206(2)	91	15.3	23.2	9.6	57.9	10.3	2.60
A40.80.1019	94	7.4	15.4	21.4	67.6	4.2	2.50
A60.80.103	81	6.7	13.3	18.9	67.6	5.3	2.50
A60.80.106	74	7.4	12.7	18.6	74.3	2.5	2.48
A60.80.106i	78	7.4	11.9	23.2	74.5		
A60.80.106(2)	87	6.9	12.6	16.8	76.3		2.44
A60.80.106(2)ww	86	6.9	13.9	2.6	73.9		
A60.80.203	84	16.5	22.8	20.0	76.4	2.8	2.36
A60.50.106	85	6.8	13.6	16.8	67.0		2.18
A60.50.106ww	86	6.8	14.0	2.6	62.0		
A60.25.103	87	6.3	13.9	16.0	63.1	7.3	2.25
A60.25.106	79	6.6	12.4	15.3	66.5	6.0	2.26
A60.25.106i	77	6.6	11.3	13.2	69.0		
A60.25.203	85	15.9	23.3	11.2	64.6	7.0	2.20
A60.25.206	83	16.0	22.3	11.1	71.3	4.8	2.16
A60.25.206i	81	16.0	20.8	13.2	71.3		
A60.80.1023	88	8.2	14.2	21.2	77.9	2.5	2.46
A60.80.003	96	0.0	9.5	21.4	40.9	18.4	2.64

* All values given as a percentage of starting mass.

**From left to right: first letter denotes acetic acid; next two digits give temperature of acid stage; next two digits give initial peroxide (% fiber) for acid stage; final digit(s) give duration (hrs.) of acid stage. Exhaustive water washing instead of alkaline extraction denoted "ww"; "i" denotes 4-stage alkaline peroxide sequence. A number 2 in brackets, (2), indicates a duplicate trial.

Acid Concentration Effect

Similarly, the acid concentration effect may be quantified. Figure 22 allows such comparisons. It can readily be seen that 80% acetic produced higher brightness than did 25% (for matched samples: A60.25.106 and A60.80.106; A60.25.203 and A60.80.203). Sample A60.50.106 is included in Table 7. Comparing samples A60.50.106, A60.25.106 and A60.80.106 (Table 7) it can be seen that the brightness attained through the intermediate acid strength is virtually the same as that for the weaker acid sample. The relationship between acid strength and brightness gain does not appear to be linear . The average gain in brightness due to increasing the acid concentration from 25% to 80% is 7%.

The overall efficiency for different acid concentrations does not show any uniform trends. (Refer to Table 6).

Peroxide Charge Effect

Comparing sample A40.25.106 to the average of samples A40.25.206 and A40.25.206(2), from Table 6, brightness increase is approximately 8%. The same comparison at 80% acid strength results in a difference greater than 10%. The difference between A60.80.103 and A60.80.203 is almost 9% whereas the difference for the analogous comparison at 25% acid concentration is 1.5%. These comparisons support the conclusion that the brightness effects of acid strength and peroxide dose are additive.

As already noted, the efficiency of 20% initial H_2O_2 charge on fiber is consistently poor relative to the efficiency for 10% initial charge (see Figure 22). Peroxide consumption is excessive when twenty percent peroxide is charged initially.

Alkaline Extraction vs. Water Washing

Samples A60.50.106, A60.50.106ww, A60.80.106(2), and A60.80.106(2)ww are samples that were matched to determine the effect of alkaline extraction as opposed to extensive water washing, ww. The extracted samples display higher efficiency in stages 1 and 2 ; whereas, the water washed samples display higher efficiency in stages 3 and 4. Overall, the alkali-extracted

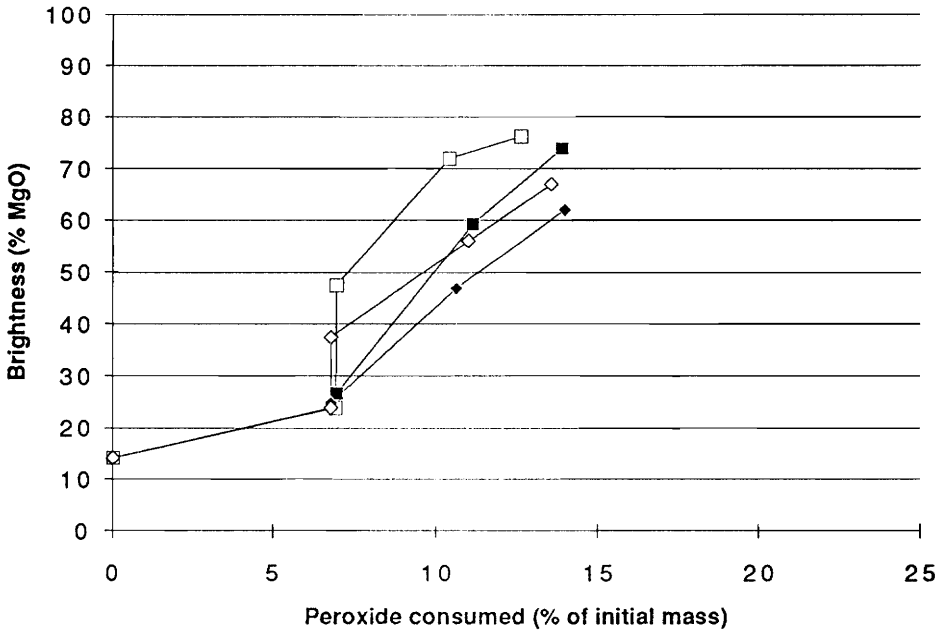
samples are more efficient: alkali-soluble lignin may be consuming peroxide in the case of the water washed samples.

The effects of alkaline extraction as opposed to water washing are depicted in Figure 27. Alkaline extracted samples achieved higher brightness with lower peroxide consumption using less than half the amount of wash water but at the expense of greater sodium hydroxide consumption. However, both gains were modest.

Multi-stage Sequences

Overall, the most efficient peroxide consumption was achieved by samples A60.80.106i, and A60.25.106i. (Overall efficiency is tabulated in Table 6). Both of these samples exceeded 5% gain in brightness per percent of peroxide consumed, and both were bleached with the multi-stage alkaline peroxide sequence, the final stages are not included in this tabulation, where the efficiency declined quite a bit; this decline can be seen in Figure 28. Note that final brightness was unaffected by the multi-stage sequence.

In summary, brightness correlates well with lignin content as measured by Kappa number. Brightness levels of 90% (complete delignification) appear to be attainable for steam exploded yellow poplar through the combination of peralkanoic acid followed by alkaline peroxide. The bleaching sequence may be broken into three phases: lignin activation, followed by alkaline dissolution (delignification), followed by alkaline peroxide bleaching. A temperature of 60° increased final brightness 5-12% when compared to matched 40° samples and also resulted in higher efficiency. An increase in acid concentration from 25% to 80% similarly resulted in average gains of 7% in brightness. Samples reacted for six hours achieved 5% higher brightness than those reacted for three hours. The effects on brightness of increased peroxide dose are increased by increased acid concentration (an interaction between these two was observed).



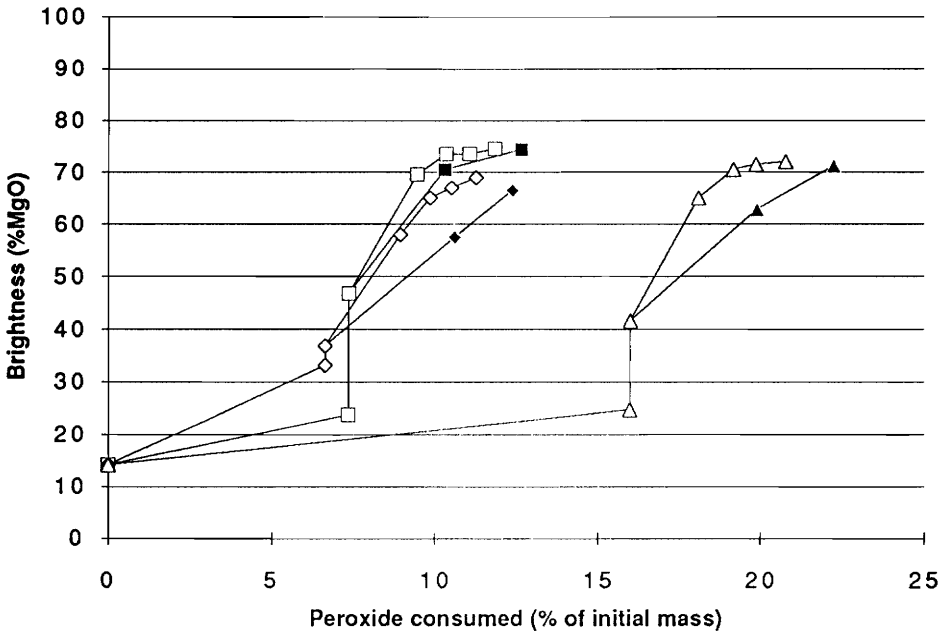
A60.80.106(2)ww: Peracetic acid, 60 , 80% acid conc., 10% peroxide charge, 6 hours, water washed

A60.80.106(2) : Peracetic acid, 60 , 80% acid conc., 10% peroxide charge, 6 hours, alkali extracted

A60.50.106ww : Peracetic acid, 60 , 50% acid conc., 10% peroxide charge, 6 hours, water washed

A60.50.106 : Peracetic acid, 60 , 50% acid conc., 10% peroxide charge, 6 hours, alkali extracted

Figure 27. Brightness vs. peroxide consumption for water washing, compared to alkaline extraction.



A60.80.106 : Peracetic acid, 60 , 80% acid conc., 10% peroxide charge, 6 hours, 2 alkaline peroxide stages

A60.80.106i : Peracetic acid, 60 , 80% acid conc., 10% peroxide charge, 6 hours, 4 alkaline peroxide stages

A60.25.106 : Peracetic acid, 60 , 25% acid conc., 10% peroxide charge, 6 hours, 2 alkaline peroxide stages

A60.25.106i : Peracetic acid, 60 , 25% acid conc., 10% peroxide charge, 6 hours, 4 alkaline peroxide stages

A60.25.206 : Peracetic acid, 60 , 25% acid conc., 20% peroxide charge, 6 hours, 2 alkaline peroxide stages

A60.25.206i : Peracetic acid, 60 , 25% acid conc., 20% peroxide charge, 6 hours, 4 alkaline peroxide stages

Figure 28. Brightness vs. peroxide consumption comparison between 2-stage and 4-stage alkaline peroxide sequences for peracetic acid trials.

7.5.4 Molecular Weight

Table 8 gives GPC molecular weight data from a large scale bleaching sequence which included an initial peracetic stage, followed by an alkaline extraction, followed by two alkaline peroxide stages. Note that results from GPC experiments include data for M_n, M_z, intrinsic viscosity, and the Mark-Houwink-Sakurada coefficient, α, as well as M_w. The focus in this discussion will be DP_w, which is less sensitive to the lower molecular weight material than DP_n.

Figure 29 displays the DP_w data from this experiment. Initial peroxide charges were 10% for the acid stage and 7 and 3% on fiber, for the two alkaline stages. The peracetic stage was 19 hours long while the alkaline peroxide stages were 24 hours each. The alkaline extraction included a two hour period at 40° followed by a one hour period at 55°. All stages were conducted at l:w of 6:1. Figure 29 clearly shows that the acid stage caused the greatest relative loss in molecular weight: approximately two thirds of initial DP_w was lost . Note that only four repeat units were lost over the course of two extended alkaline peroxide stages. The loss in terms of DP_n can be calculated from Table 6 to be approximately 50%. The higher percentage loss for the weight average indicates that high molecular weight material was hydrolyzed.

Table 9 is a tabulation of data for fiber samples taken after the peracetic acid stage. Figure 30 displays DP_w data from this table for peracetic acid fiber samples in relation to time. Note that the loss in DP_w does not exceed 50% for any of the three profiles. The temperature effect , comparing A40.80.10 with A60.80.10, shows no difference in DP_w for samples taken at nine hours. For these two samples, the loss in DP_w after nine hours is approximately ten percent. The largest decline in DP_w is displayed for the lower acid concentration sample, A60.25.10. This reduction in molecular weight due to lower acid concentration is unexpected but has been documented before with respect to acetic acid pulping . This effect has been attributed to the poor swelling capability of acetic acid: water is a much better swelling agent for cellulose (63). The M_z data for these trials is included in Table 9. The M_z values for the 60° , 80% acetic acid, trial show a more rapid decline than those for the 40° trials, otherwise these trials are very similar with respect to molecular weight. The M_z data is sensitve to the largest molecular weights: 60° results in more hydrolysis

Table 8. GPC Data from 5kg trial with peracetic acid.

Samples	Mn	DPn	Mw	DPw	Mz	Mw/Mn	Intrinsic Visc	M-H Alpha
Yellow poplar (log Ro 4.25)	107800	208	352000	678	1690000	3.265	1.763	0.775
Peracetic Stage 1 (5 kg 19hr)	52500	101	115700	223	274000	2.204	0.906	0.907
Extraction Stage 2 (2 extractions)	49410	95	109400	211	299000	2.214	0.978	0.911
NaOH/Peroxide Stage 4	45920	88	107500	207	304000	2.341	0.899	0.912

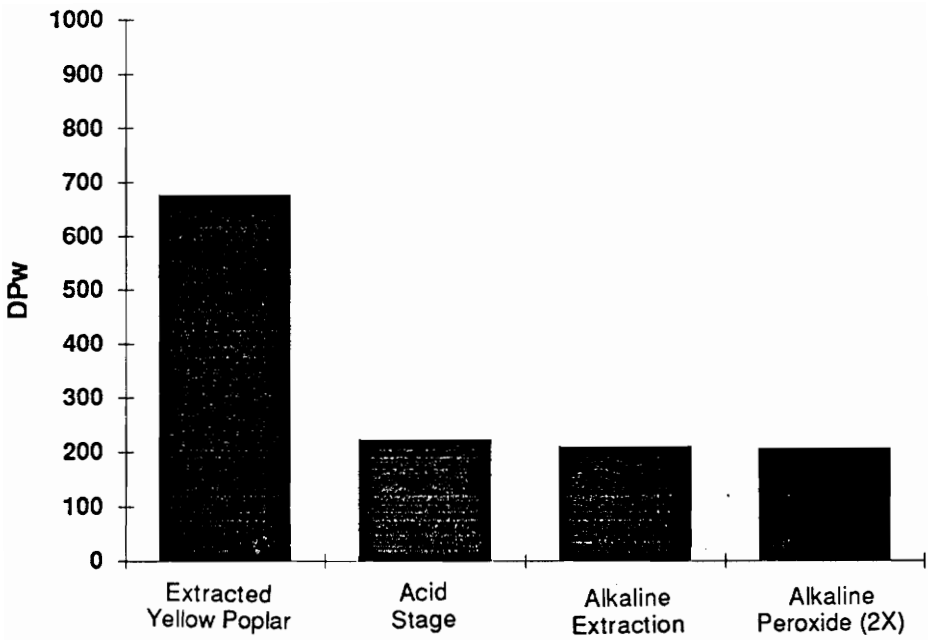
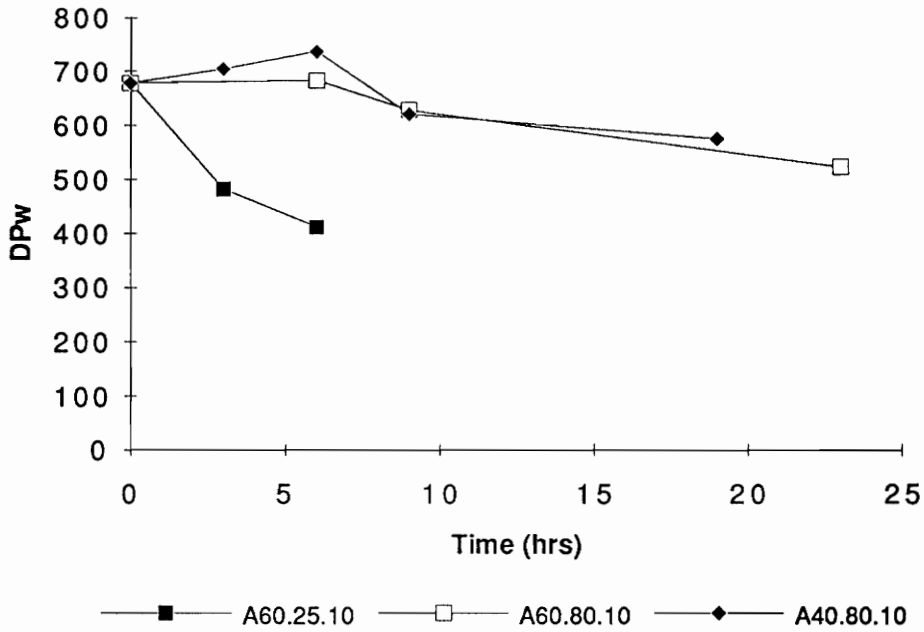


Figure 29. Molecular weight effect of the various stages of a 4-stage peracetic acid-based bleaching sequence. Data is presented for the large-scale (5kg) experiments. The alkaline peroxide segment reflects two stages.

Table 9. GPC Data from peracetic acid fiber samples (stage 1).

Samples	Mn	DPn	Mw	DPw	Mz	Mw/Mn	Intrinsic Visc	M-H Alpha
A40.80.103	132800	256	365600	704	1160000	2.753	1.340	0.764
A40.80.106	132500	255	382700	737	969000	2.888	1.196	0.692
A40.80.109	112300	216	322500	621	1076000	2.872	1.299	0.804
A40.80.1019	101600	196	298100	574	910000	2.934	1.298	0.786
A60.80.106	107600	207	354400	683	1110000	3.294	0.901	0.771
A60.80.109	117900	227	325800	628	911000	2.763	0.967	0.807
A60.80.1023	100300	193	271600	523	639000	2.708	1.052	0.839
A60.25.103	86210	166	250000	482	696000	2.900	1.137	0.770
A60.25.106	64000	123	213700	412	516000	3.339	0.916	0.816

Refer to Table 7 for the sample identification code.



A60.25.10 : Acetic acid, 60 , 25% acid conc., 10% peroxide charge
A60.80.10 : Acetic acid, 60 , 80% acid conc., 10% peroxide charge
A40.80.10 : Acetic acid, 40 , 80% acid conc., 10% peroxide charge

Figure 30. Molecular weight (DPw) of acid fiber samples as a function of reaction time. The 25% acetic acid sample displays significant molecular weight loss compared to the two 80% samples.

of the largest molecules. The 25% acetic acid trial shows significantly lower molecular weight for each average.

Comparing Figures 29 and 30 a large inconsistency may be noted. The DP_w loss displayed for the 5kg initial peracetic stage is about twice that for the smaller scale trials. The most probable cause for this may have been due to condensation which formed on the iron exhaust vents of the large cooking vessel. This condensate would have dripped into the reaction mixture, promoting the decomposition of peroxide to radical species. These would then be responsible for cellulose degradation. Alternatively, impurities may have been present initially that also were capable of catalyzing the production of peroxy radicals. Figure 29 should therefore be viewed as a diagram for potential degradation ; whereas, Figure 30 is more representative of expected response.

Table 10 is a compilation of GPC data for the final, bleached samples. The acid strength / DP_w relationship noted in the previous figures and tables may be tested against the data in this table. Comparing samples A60.80.103 with A60.25.103 the difference in DP_w is 10%. Comparing A40.80.206 with A40.25.206 the result is reversed for DP_w: the value is ten percent greater for the 25% acetic sample. Comparing A60.80.106(2)ww with A60.25.103 and A60.50.106 it can be seen that the intermediate acid concentration produced the higher DP_w value. The expected relationship between DP_w and acid strength is not supported by this data.

Extended reaction time in the peracetic stage might also be expected to result in decreased DP_w. Comparing samples A40.80.203 and A40.80.206 (Table 10) the DP_w values, 390 and 363 respectively, seem to support the hypothesis that increased time in the acid correlates with increased hydrolysis. The M_z values also follow the trend for these two samples. Samples A60.80.103 and A60.80.1023 contradict the previous pair of samples, however. Increased time in the peracetic acid may or may not result in increased hydrolysis.

Initial peroxide charge may also be compared based on the data in Table 10. For 40° samples the data reveal the expected relationship: DP_w decreases with increasing peroxide charge. Samples A60.80.106* and A60.80.103* display

Table 10. GPC Data from samples bleached with peracetic acid.

Samples	Mn	DPn	Mw	DPw	Mz	Mw/Mn	Intrinsic Visc (dL/g)
A40.80.106*	85350	164	241100	465	730000	2.825	1.477
A40.80.106	57650	111	221600	427	693000	3.844	1.579
A40.80.203	50960	98	202600	390	627000	3.976	1.158
A40.80.206*	73310	141	188200	363	544000	2.567	1.294
A40.25.206	61570	119	206400	398	630000	3.352	1.127
A60.80.103*	79220	153	199900	385	479000	2.523	1.237
A60.80.106*	79860	154	201250	388	491000	2.520	1.228
A60.80.106(2)A	62500	120	211200	407	637000	3.379	0.922
A60.80.106(2)ww	75410	145	232600	448	710500	3.084	1.029
A60.80.1023	63760	123	207500	400	610000	3.254	1.124
A60.80.203	56100	108	203700	392	590000	3.631	1.352
A60.25.103*	68530	132	158500	305	381000	2.313	1.170
A60.25.103	64890	125	200500	386	641000	3.090	1.184
A60.25.203	53040	102	196200	378	591000	3.699	1.090
A60.25.206	56550	109	172900	333	461000	3.057	1.022
A60.80.003	71580	138	278100	536	917000	3.885	1.347
A60.50.106A	87040	168	251800	485	892000	2.893	0.880
A60.50.106ww	76610	148	233100	449	718000	3.043	0.848

Refer to Table 7 for sample identification code.

a contradictory relationship, however. The data supports no conclusion regarding the effect of peroxide charge on molecular weight.

Similarly, comparing matched 40 and 60° samples from Table 10 reveals no consistent trend regarding the temperature effect. Alkaline extraction may be compared to water washing by comparing A60.80.106(2) and A60.80.106(2)ww. For this pair of samples a higher DP_w value was realized for the water-washed sample. However, this relationship was reversed for A60.50.106 and A60.50.106ww.

The nonsystematic variation in the molecular weight data suggest that random molecular weight losses are occurring or that some factor may be "smoothing" out the data. The presence of peroxide radicals may account for the randomness. The variability of the initial substrate may have also been a key factor. The "smoothing" effect may have been due to the alkaline stages, which were shown in the performic acid data to result in higher M_w through "stripping" of the lower molecular weight material.

Table 11 presents M_n and M_w data in relation to initial molecular weight for the steam exploded yellow poplar. The peracetic samples displayed a range of M_w loss of from 28 to 55%. The performic data displayed a similar range: 35 to 55% M_w loss. The average M_w loss for all of the peracetic acid samples was 41%. The brightest peracetic samples recorded losses in M_w of between 40 to 43%. The average for the performic samples was 46%. The molecular weight loss correlates to peroxide charge for the performic acid samples. The molecular weight loss for the performic and peracetic trials was comparable.

The possibility that molecular weight was sacrificed to gain brightness (delignification) is explored in Figure 31. The spread of data points suggest that no trend of this sort is occurring: both high brightness and high molecular weight are attainable.

The Tappi values for the bleached fiber are listed in Table 6. These values have been plotted against Dpw (Fig.32) as determined through GPC. The spread of the data suggest that the Tappi method is insensitive to the small changes which were present. The general trends of the two data sets seem similar, however.

Table 11. Molecular weight loss.

Samples	% Loss Mn	% Loss Mw
A60.80.106	27	43
A60.80.106(2)A	42	40
A60.80.106(2)ww	30	34
A60.80.1023	41	41
A60.80.203	37	42
A60.25.103	38	49
A60.25.203	51	44
A60.25.206	48	51
A60.80.003	34	21
A60.50.106A	19	28
A60.50.106A	29	34
A40.80.106	34	34
A40.80.203	53	42
A40.80.206	32	47
A40.25.206	43	41
F80.85.023	19	35
F80.85.053	30	47
F80.85.103	39	55

Refer to Table 7 for identification code.

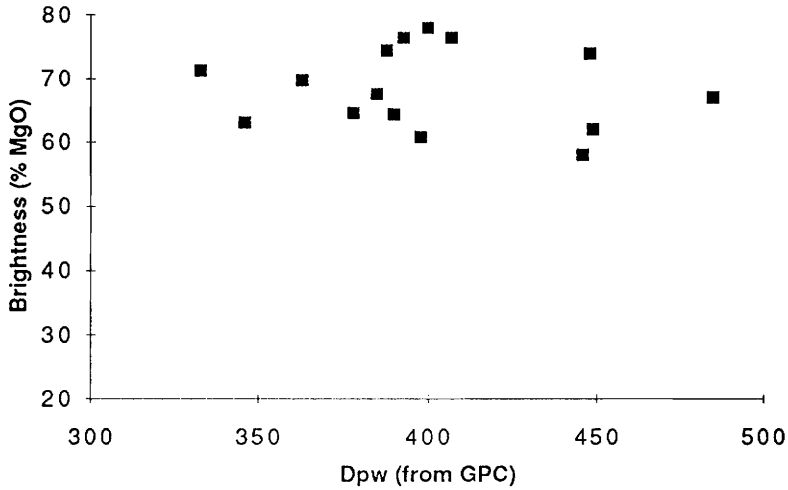


Figure 31. Brightness vs. DPw. No trade-off exists between these parameters.

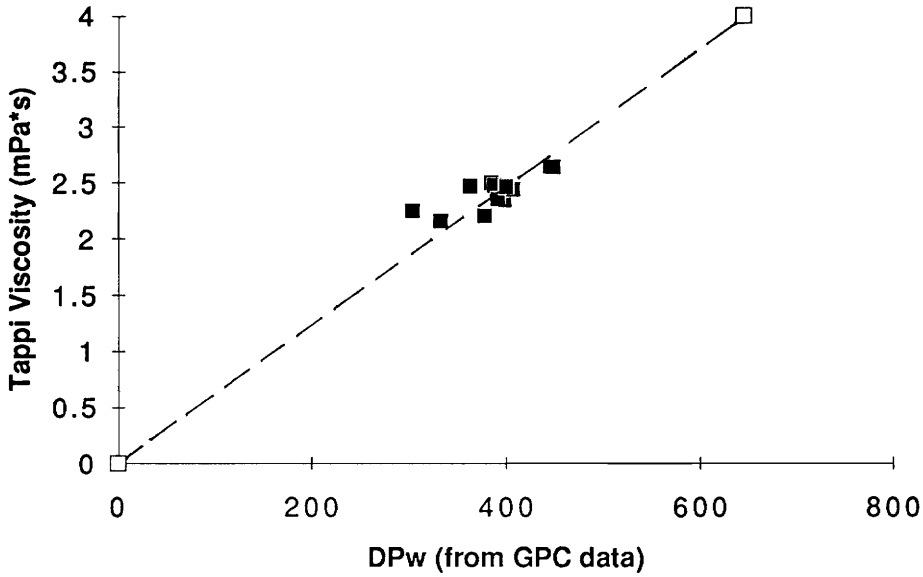


Figure 32. Tappi viscosity (Tappi#T230) vs. DPw from GPC data. (Regression line forced through zero.)

In summary, the molecular weight data for samples taken following the peracetic acid stage supported the conclusion that acid concentration (water percentage) was the primary parameter that influenced molecular weight loss. Molecular weight data for *bleached samples* showed inconclusive variation, however. On average, 42% loss of initial M_w could be expected by bleaching steam exploded yellow poplar with peralkanoic acid and alkaline peroxide.

7.5.5 Carbohydrate Analysis

Seven samples were analyzed for glucose and hemicellulose percentage as well as Klason lignin. These data are presented in Table 12. The Klason values are high as compared to the Kappa# values (some of these have been approximated based on the brightness data). Poppius et. al. (10) found that a factor of 0.17 should be used to convert Kappa to Klason (in %). Based on this factor, the Klason values should all be below 1%. Incomplete hydrolysis would be a good explanation for this discrepancy except that the glucose degradation product, hydroxymethyl furfural, is present in measurable quantity. All of the tabulated carbohydrate values are lower than those reported for the preliminary trials: this difference is attributed to a change in operating procedure. Allowing for furfural and the high Klason values a corrected glucose percentage of 93% appears to be obtainable from two different peracetic acid trials. For microcrystalline cellulose the total carbohydrate concentration is of interest. Allowing for the decomposition products this value exceeded 95%. Although this level is somewhat less than the specified 97% it was felt that this level of purity is attainable given refinements in technique.

Sample A60.80.106(b) was produced from the "improved" bleaching sequence which involved four alkaline peroxide stages. Sample A60.80.106(a) was taken following the first alkaline peroxide stage from the same sequence. An increase in glucose percentage can be seen indicating that though brightness gains may taper off, recoverable glucose may increase in response to alkaline peroxide. Klason lignin is also seen to decrease indicating that a smaller fraction of the insoluble portion is carbohydrate.

The effects due to acid concentration and peroxide concentration are inconclusive from the tabulated data. Sample A60.80.203 is significantly lower than the others in terms of glucose, however. This fact shows the importance of

allowing six hours for the acid stage as opposed to three hours. (Compare A60.25.206 with A60.80.203 and compare A60.80.106(2) with A60.25.206). The temperature effect supports 60° as a more effective temperature than 40° (compare A40.80.106 to A60.80.106(2)).

The xylose-to-glucose ratio displayed a narrow range of values with an average of 1.5%. This ratio is more important for acetylation grades than for microcrystalline grades; however, this is a very low percentage for retained xylose and is indicative of the overall success of the techniques employed.

Table 12. Carbohydrate analysis data.

Sample	Glucose (%)	Hydroxymethyl Furfural (%)	Xylose:Glucose Ratio (%)	2-Furfural (%)	Klason (%)	Brightness (% MgO)	Kappa #
A60.80.106(a)	89.1	1.2	1.5	0.4	1.8	69.5	4.5
A60.80.106(b)	93.1	1.2	1.7	0.3	1.4	74.5	2.5
A60.80.203	78.7	1.0	1.5	0.3	2.2	76.4	2.8
A60.25.206	92.8	1.3	1.4	0.4	0.6	71.3	4.8
A60.50.106A	87.2	1.2	1.4	0.3	1.9	67.0	5.0
A40.80.106	89.8	1.1	1.6	0.4	1.9	58.0	9.7
A60.80.003	94.1	1.4	2.2	0.5	4.6	40.9	18.4

Refer to Table 7 for the sample identification code.

8.0 Conclusions and Recommendations

1. Peralkanoic purification of cellulose from steam exploded yellow poplar is a promising method for producing microcrystalline cellulose that compares well to commercially available grades.

2. The brightness data support the hypothesis that before lignin can be effectively removed from the cellulose it must be chemically modified or fragmented. This change in structure is made evident in the peracetic stage by the change in color of the fiber mass; indicating the formation of quinonoid structures. The chemical activation of the lignin allows it to dissolve in subsequent alkaline extractions; this is evidenced by the tremendous gains in brightness during the extraction stage.

3. The parameter that has the greatest influence on final brightness and overall efficiency is temperature of the peracetic stage.

4. Brightness levels of 90% were achieved with performic acid at 80° and 85% concentration. Brightness levels of 75% were achieved with peracetic acid at 60° and 80% concentration. Kappa number was found to correlate well with brightness for the peracetic acid samples.

5. Multi-stage alkaline peroxide treatment proved to be more efficient than a two stage sequence (though slightly more NaOH was consumed).

6. Molecular weight appears to decrease with decreasing alkanoic acid strength.

7. The carbohydrate analysis revealed that 93% glucose is obtainable. The purity may be increased with alkaline peroxide treatments. Total carbohydrate may be expected to exceed 95%. The xylose-to-glucose ratio was 1.5%.

8. Of the peracetic acid conditions explored, the best results were realized with an initial acid strength of 80%, an initial acid stage peroxide concentration of 10% on fiber, a reaction time of 6 hours, and a reaction temperature of 60° followed by a 4 stage alkaline peroxide sequence.

Areas for Further Research

Temperature effect on brightness (delignification) was more pronounced in terms of percent gain than its detrimental effects on molecular weight. Higher temperature resulted in a higher percentage of recoverable glucose. Therefore, higher temperatures may be more desirable for peracetic bleaching. Further experiments at 80° and above are advised.

This study was specifically aimed at producing micro-crystalline cellulose without the use of any sulfur- or chlorine- containing reagents. The literature supports the use of H_2SO_4 as a catalyst for producing peracetic acid, however. Some experimentation with this catalyst is warranted.

References

1. Springer, Allan M. Industrial Environmental Control: Pulp and Paper Industry. John Wiley & Sons. New York. 1986. pp.309-323; 325-328.
2. Vollhardt, K. Peter C. Organic Chemistry. W.H.Freeman and Company New York. 1987. pp.1106-1107.
3. Schroeter, Martin C. Possible lignin reactions in the organocell pulping process. Tappi Oct.(1991). pp.197-200.
4. Glasser, Wolfgang G. Lignin. Pulp and Paper Chemistry and Chemical Technology, 3rd ed, vol.1. ed. James P. Casey. John Wiley & Sons. New York. 1980. pp.78-79.
5. Marchessault, R.H. Steam explosion: a refining process for lignocellulosics. Steam Explosion Techniques: Fundamentals and Industrial Applications. ed. B.Focher, A.Marzetti, V.Crescenzi. Gordon and Breach Science Publishers. Philadelphia. 1991. pp.1-19.
6. Overend, R.P.;E.Chornet. Fractionation of lignocellulosics by steam-aqueous pretreatments. Phil. Trans. R. Soc. Lond. A321, (1987). pp.523-536.
7. Glasser, W.G. Research with Biopolymers from Steam-Exploded Biomass. Paper presented at symposium in Melbourne, Australia. 1991.
8. Kokta,B.V. Steam explosion pulping. Steam Explosion Techniques... ed. B.Focher et al. pp.163-205.
9. Byrd, Medwick V.; Josef S.Gratzl; Rudra P.Singh. Delignification and bleaching of chemical pulps with ozone: a literature review. Tappi March(1992) pp.207-213.
10. Poppius-Levlin, K; I.Tuominen; J.Sundquist. Personal correspondence.
11. Sjostrom, Eero. Wood Chemistry : Fundamentals and Applications. Academic Press, Inc. New York. 1981. pp.78;51-55.
12. Fengel, D.; G.Wegener. Wood Chemistry Ultrastructure Reactions De Gruyter. Berlin. 1989. pp.143-148;pp.90-97;pp.167-174; pp.234-238;pp.55-59.
13. K.Sarkanen. Lignin. Handbook of Pulp and Paper Technology. ed. Kenneth W.Britt. Van Nostrand Reinhold. New York. 1970. pp.33-37.

14. Dence, C.W.; A.J. Nonni. The reactions of alkaline hydrogen peroxide with lignin model dimers, part 3. Holzforschung vol.42 no.1 (1988). pp.37-46.
15. Schwald, W.; H.H.Brownell; J.N.Saddler. Assessment of pretreatment conditions for fast and complete hydrolysis of biomass. Steam Explosion Techniques...ed. B.Focher, A Marzetti, V.Crescenzi. Gordon and Breach Science Publishers. Philadelphia. 1991. pp.307-330.
16. Robert, Danielle; Michel Bardet; Catherine Lapierre; Goran Gelerstedt. Structural changes in aspen lignin during steam explosion treatment. Cel. Chem. & Tech. 22 (1988). pp.221-230.
17. Bobleter,D.; G.Bonn; W.Prutsch. Steam explosion hydrothermolysis-organosolv: a comparison. Steam Explosion Techniques...ed. B.Focher et al. pp.59-82.
18. Excoffier, G.; A.Peguy; M.Rinaudo; M.R.Vignon. Evolution of lignocellulosic components during steam explosion and potential applications. Steam Explosion Techniques...ed. B.Focher et al. pp.83-95.
19. Dekker, R.F.H. Steam explosion: an effective pretreatment method for use in the bioconversion of lignocellulosic materials. Steam Explosion Techniques... ed. B.Focher et al. pp.277-305.
20. Singh, Rudra P. Bleaching -- chlorination. Handbook of Pulp and Paper Technology. ed. Kenneth W. Britt. Van Nostrand Reinhold Co. 1970. pp.249-262.
21. Gierer, Josef. The chemistry of delignification: part 1. Holzforschung. 36(1982)no.1, pp.43-51.
22. Gierer, Josef. The chemistry of delignification: part 2. Holzforschung. 36(1982)no.2, pp.55-64.
23. Gierer, Josef. Basic principles of bleaching part 1: cationic and radical processes. Holzforschung. 44(1990) no.5, pp.387-394.
24. Gierer, Josef. Basic principles of bleaching part 2: anionic processes. Holzforschung. 44(1990) no.6, pp.395-400.
25. Rapson, W.Howard. Bleaching -- chlorine dioxide. Handbook of Pulp and Paper Technology. ed. Kenneth W. Britt, 1970. pp.275-286.
26. V. Loras. Bleaching of chemical pulps. Pulp and Paper Chemistry and Technology vol.1, 3rd Edition. ed. James P.Casey. John Wiley & Sons. New York. (1980) .pp.663-702.

27. Fouquet, A.; F.Messier; D.Colgan; A.Grondin. Investigation for the presence of chlorinated dibenzo-p-dioxins and dibenzofurans in bleaching processes from pulp and paper industries. Chemosphere, 20(1990) nos.10-12. pp.1707-1714.
28. Hise, R.T.; H.T. Wright; H.E.Swanson. Formation of chlorinated dioxins andfurans from lignin and lignin model compounds. Chemosphere,20(1990) nos.10-12. pp.1723-1730.
29. Chung, A.; D.Halliburton. Measures to control chlorinated dioxin and furan formation and releases at Canadian bleached chemical pulp mills. Chemosphere, 20(1990) nos.10-12. pp.1739-1746.
30. Gierer, Josef; Finn Imsgard. The reactions of lignin with oxygen and hydrogen peroxide in alkaline media. Chemistry of Delignification with Oxygen, Ozone, and Peroxides. Symposium: Raleigh, N.C. 1975. Uni publishers co. ltd. Tokyo. 1980. pp.137-149.
31. Kringstad, Knut P.; Brengt O.Lindgren; Stefan E. Sundin. Studies on hydroxyl and perhydroxyl radicals. Symposium: Raleigh. 1975. pp. 25-32.
32. Starnes, W.H. Mechanisms of autoxidation in neutral or alkaline media. Symposium: Raleigh. 1975. pp.3-24.
33. Liebergott, Norman; Barbara van Lierop; Anastasios Skothos. A survey of ozone in bleaching pulps, part 1. Tappi, 75(1992) no.1, pp.145-152.
34. Liebergott, Norman; Barbara van Lierop; Anastasios Skothos. A survey of ozone in bleaching pulps, part 2. Tappi, 75(1992) no.2 pp.117-124.
35. Fenell, F.L. 4-7 Peroxide bleaching. The Handbook of Pulp and Paper Technology. ed. Kenneth W.Britt..pp.315-321.
36. Lachenal, D.; C. de Choudens; P. MOnzie. Hydrogen peroxide as a delignifying agent. Tappi, 63(1980) no.4. pp.119-122.
37. Moldenius, S. The stoichiometry of peroxide bleaching of mechanical pulps. Svensk Papperstidning, 85 (1982) no.15. pp.R116-R120.
38. Dafaye, J.; A.Gadelle. Magnesium salts in the alkaline-oxygen

degradation of cellulose. Pulp & Paper Canada, 75(1974), no.11. pp.50-53.

39. Parthasarathy, V.R., R.Klein; V.S.M.Sundaram; H.Jameel; J.S.Gratzl. Hydrogen-peroxide-reinforced delignification of southern pine kraft pulp and short sequence bleaching. Tappi, 75(1990) no.7. pp.177-187.
40. Battista, O.A. Cellulose, micrcrystalline. Encyclopedia of Polymer Science and Engineering. vol. 3. ed.-in-chief J.I. Koshwitz. John Wiley and Sons. New York. 1985. pp.85-89.
41. Annon. Cellulose, microcrystalline. Monograph. Food Chemicals Codex, Third edition. National Academy Press. Washington, D.C. 1981. p.79.
42. Anon. Cellulose. Ulmann's Encyclopedia of Industrial Chemistry, vol. A5. Fifth edition. Executive editor Wolfgang Gerhartz. VCH publishing. Federal Rep of Germany. 1986. p.390.
43. Browning,B.L. Methods of Wood Chemistry. vol 1 and vol.2 Interscience. New York. 1967.
44. Schultz, Tor P.; Wolfgang G. Glasser. Quantitative structural analysis of lignin by diffuse reflectance fourier transform infrared spectrometry. Holzforschung, 40 (1986), suppl. pp.37-44.
45. Faix, Oskar. Practical uses of ftir spectroscopy in wood science and technology. Mikrochim Acta [Wien] no.1 (1988). pp.21-25.
46. Berben,Sally A.; John P.Rademacher; et. al. Estimation of lignin in wood pulp by diffuse reflectance fourier-transform infrared spectrometry. Tappi, 70(1987) no.11. pp.129-133.
47. Braithwaite,A. F.J.Smith. Chromatographic Methods, fourth ed. Chapman and Hall. New York 1985.
48. Paice,M.G.; L.Jurasek; M.Desrochers. Simplified analysis of wood sugars. Tappi, July, 65(1982), no.7 . pp.103-106.
49. Wentz, Frank E.; A.Dale Marcy; Michael J.Gray. Analysis of wood sugars in pulp and paper industry samples by HPLC. J.Chromatography Sci. vol.20, Aug. (1982). pp.349-352.
50. U.S. Forest Prods. Lab. Determination of Wood Sugars. publication no.67-045. Madison, Wis. (no date). pp.1-66.

51. Evans, Robert; Adrian F.A.Wallis. Comparison of cellulose molecular weights determined by high performance size exclusion chromatography and viscometry. 4th Int. Sym. on Wood and Pulping Chem. Apr 27-30. Paris 1987 vol 1. pp.201-205.
52. Batzer, H.; F.Lohse. Introduction to Macromolecular Chemistry. 2nd Edition. John Wiley & Sons. New York. 1979. pp.147-192.
53. Ott, Lyman. An Introduction to Statistical and Data Analysis, 3rd ed. PWS-Kent Publishing. Boston. 1988.
54. Kaar,William E.,Lawrence G. Cool. The complete analysis of wood polysaccharides using HPLC. Journal of Wood Chemistry and Technology, 11(1991), no.4 . pp.447-463.
55. Kaar,William, David L. Brink. Summative analysis of nine common north American hardwoods. J. Wood Chemistry and Technology, 11(1991), no.4. pp.479-494.
56. Bryce, J.RG. . Alkaline pulping. Pulp and Paper Chemistry and Chemical Technology , ed. James P. Casey. John Wiley & Sons. New York. 1980. pp.402.
57. Rydholm, Sven A. Pulping Processes. Interscience Publishers. New York. 1965. pp.992-1003.
58. Poppius K.; L.Laamanen; J.Sundquist. Bleached pulp by peroxy acid/ alkaline peroxide delignification. Paperi ja puu , 2(1986). pp87-92.
59. Sabatier, J.; N.Fernandez; N.Romero. Kinetics of peroxide bagasse lignin reaction. Cellulose Chemistry and Technology, 20(1986). pp. 217-224.
60. Pugliese, Sebastian C. III; Thomas J. McDonough. Kraft pulp chlorination: a new mechanistic description. Tappi, 72(1989), no.3. pp.159-167.
61. Chang, Raymond. Physical Chemistry with Applications to Biological Systems, 2nd ed. Macmillan Publishing Co., Inc. New York. 1981.
62. Gustafson, Richard R. The role of diffusion during initial delignification of alkaline pulping. Tappi, 71(1988), no.4. pp. 145-147.
63. Young, R.A.; J.L.Davis; E.-B. Wiesmann. Organic acid pulping of wood. Part 2. Acetic acid pulping of aspen. Holzforschung, 40(1986), no.2. pp. 99-108.

VITA

Stephen Cameron Van Winkle was born September 26, 1960, in a Maryland suburb of Washington, D.C.. He is the second oldest of six children. He grew up in the Baltimore/Washington metropolitan area and attended high school at Baltimore Polytechnic Institute.

In 1978, Stephen entered Virginia Tech, in Blacksburg, Virginia, as a student in the School of Forestry. He completed his Bachelor of Science degree in Wood Products in 1986, after working while attending classes part-time.

In 1989 he returned to Virginia Tech's Forect Products Department to pursue full-time a Master of Science degree in wood chemistry. He received an assistentship through this department.

He has worked in building materials retailing, truss manufacture, restaurant work, and a host of odd jobs. Currently he is working as a chemist in the Pilot Plant of the Biobased Materials Center, located at the Thomas M. Brooks Center of the Forest Products Department at Virginia Tech.

In 1987 he married Na Liu. They have one child, Benjamin, who was born October 20, 1991.