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## **Lignin:**

### Kappa number

The kappa number test was used to estimate the amount of lignin by measuring the oxidant demand of the pulp. Kappa numbers were performed on air-dried pulp samples, which were dried on a heated balance to acquire their oven-dried weight. The pulp was then treated with potassium permanganate (KMnO<sub>4</sub>) in accordance with TAPPI Classical Method T 236 cm-85 “Kappa Number of Pulp.” Three separate titrations are performed on each pulp sample to establish a confidence interval for the specimen. Typical experimental standard deviation for our kraft brownstock pulps was 0.24.

### Acid-Insoluble Lignin

Acid-insoluble lignin content was measured in accordance with TAPPI standard T 222 om-98 “Acid-insoluble Lignin in Wood and Pulp.” The moisture content of the sample is determined for air-dried wood/pulp and was used to weigh a known weight of wood/pulp. Concentrated sulfuric acid was utilized to hydrolyze and solubilize the carbohydrates in wood and pulp samples. The acid-insoluble lignin was filtered, dried, and weighed. The acid-insoluble lignin content of the wood and pulp samples in this project was an average of two measurements. Typical experimental standard deviations for the brownstock pulps varied up to 0.2%. Klason lignin, % = 0.15 x Kappa number

### Lignin Molecular Weight Distribution Analysis

Dry lignin samples (50 mg/mL) were acetylated with acetic anhydride/pyridine (1:1, v/v) at room temperature with stirring for 24 hours. After stirring for 24 hours, ethanol was added to the reaction mixture and the mixture was concentrated to dryness under reduced pressure. The residual oil was diluted with ethanol and re-evaporated under reduced pressure to remove trace reagents. The acetylated lignin was then dissolved in chloroform and then added drop-wise to anhydrous diethyl ether with stirring. The precipitated

lignin was recovered. The precipitate was washed three times with diethyl ether and then dried for 24 hours.

GPC analysis of the acetylated lignin samples were performed using HP 1090 Liquid chromatography system containing an ultraviolet photodiode array detector and HP 1047A refractive index detector. Acetylated lignin samples were weighed out to a concentration of 0.40 mg/mL in THF and mixed for 24 hours to solubilize the samples. GPC analyses were carried out with an UV detector set at 270 nm on a two-column sequence of Waters™ stragel columns (HR 1 and HR 3) standardized with polystyrene standards and eluted at 1.00 mL/min. Agilent ChemStation A.10.01 and GPC software A.02.02 were used to collect data and determine molecular weight profiles which are summarized in Table 1.

Table 1. GPC Analysis of acetylated lignin samples.

	Lignin Samples		
MW Analysis	Sample 1	Sample 2	Sample 3
$M_n$	2948	1352	2057
$M_w$	29472	10005	7371
D	10.0	7.40	3.58

$M_n$ : Number average molecular weight;  $M_w$ : Weight average molecular weight

D: Polydispersity,  $M_w/M_n$

## **Cellulose - Hemicellulose:**

### *α, β, γ Cellulose*

Alpha-, beta-, and gamma- celluloses were determined according to TAPPI Test method T203. An air-dried sample was weighed to an equal of 1.50 g of oven-dried sample to the nearest 0.10 mg. The pulp sample was extracted consecutively with 17.5 % and 9.45 % NaOH solutions at 25 °C. The soluble fraction, consisting of beta- and gamma-celluloses, is determined volumetrically by oxidation with potassium dichromate, and the alpha-cellulose, is the insoluble fraction, derived by difference.

### *Pulp Carbohydrates*

The relative carbohydrate composition of wood and pulp samples was conducted using three different experimental protocols.

### *Determination by gas-liquid chromatography*

The first of these methods was accomplished in accordance with TAPPI Standard T 249 cm-85 “Carbohydrate composition of extractive-free wood and wood pulp by gas-liquid chromatography.” The five principal monosaccharides determined from this procedure including glucan, mannan, arabinan, xylan, and galactan. The samples were first thoroughly washed with deionized water and air-dried prior to Soxhlet extraction with acetone for 24 hours. Samples were weighed out to the nearest 0.1 mg and the moisture content was determined. The target sample weight was  $0.35 \pm 0.01$  g. The sample was placed in a 15 mL conical glass centrifuge tube and exactly 3 mL of 72% sulfuric acid was added with stirring. The centrifuge tube was placed in a 30°C water bath for one hour with occasional stirring. The contents of the centrifuge tube were quantitatively transferred to a 250 mL beaker with deionized water. The beaker was placed in an autoclave for 1 hour at 15 psi (103 kPa). The sample is then cooled to room temperature using an ice bath. Exactly 10.0 mL of reagent grade Inositol (internal standard solution containing 1.000g/100 mL) was added with mixing and the solution was transferred to a 50 mL beaker. Several drops of bromophenol blue indicator were added and a barium

hydroxide solution was added while mixing with a magnetic stirring bar. Barium hydroxide was added until the color of the solution changes from yellow to blue-violet. The contents of the 50 mL beaker were again transferred quantitatively to a 50 mL centrifuge and the solution was centrifuged until the supernatant is clear. The clear solution was then decanted into a 100 mL round bottom flask. Sodium borohydride (80 mg) was added to the sample, and mixed occasionally for 1.5 to 2 hours. Excess borohydride was then removed by adding glacial acetic acid drop-wise until gas evolution ceases. The solution was concentrated on a flash evaporator with the water bath set at  $\leq 40^{\circ}\text{C}$ . Approximately 10 mL of methanol was added to the syrup and evaporated to dryness several times. The residue was heated in an oven at  $105^{\circ}\text{C}$  to ensure complete removal of the water. The residue was then acetylated by adding 7.5 mL of acetic anhydride and 0.5 mL sulfuric acid and placing the sample in a water bath maintained at  $50\text{-}60^{\circ}\text{C}$  for 1 hour. The sample was allowed to cool and then extracted successively with 25, 15, and 10 mL portions of methylene chloride. The combined methylene chloride extracts were concentrated using a flash evaporator with the water bath set at  $75^{\circ}\text{C}$ . Approximately 1 mL of water was added to the residue and evaporated to dryness on the flash evaporator. The residue was dissolved in 2 mL methylene chloride. The dissolved solution of alditol acetates (0.5  $\mu\text{L}$ ) was injected into the gas chromatograph and the peak areas were determined for each of the five sugars and the internal standard. The percent of each component as a polysaccharide was calculated according to the

equation 
$$\text{Percent} = \frac{A \times W_s \times C \times 100}{A_s \times W \times k}$$

$A$  is the chromatographic area of the component peak;

$A_s$  is the chromatographic area of the internal standard peak;

$W_s$  is the weight of internal standard in milligrams;

$W$  is the oven-dry weight of the sample in milligrams;

$C$  is the conversion factor for monosaccharide to polysaccharide (0.88 for pentoses and 0.90 for hexoses);

$k$  is the calibration factor for each individual component.

Determination by pyrolysis GC/MS

The second method utilized involves enzymatically hydrolysis of kraft pulps with commercial cellulase, mannanase, and xylanase for 48 hours at 55°C in addition to 1 hour of acidic hydrolysis with 1 M trifluoroacetic acid at 100°C. The respective monosaccharides were detected by pyrolysis gas chromatography/mass spectrometry as described by Syverud, K.; Ingeborg, L. and Vaaler, D. (Characterization of Carbohydrates in Chemical Pulps by Pyrolysis Gas Chromatography/Mass Spectrometry. *Journal of Analytical and Applied Pyrolysis* **67** p. 381-391. (2003)). Briefly, the pyrolysis was performed with a filament pulse pyrolyzer. The pulp samples were placed on the pyrolysis filament and a drop of water was added to improve the contact between the sample and the filament. The water was removed by warm before the filament was mounted in the pyrolyzer. The sample was then further dried in the pyrolysis chamber for 2 minutes prior to pyrolysis. During pyrolysis, the pyrolysis chamber (maintained at 175°C) was purged with helium gas at a flow rate of 22 ml min<sup>-1</sup> in order to transport the pyrolysis products quickly into the GC column. Pyrolysis was set to 2 s, and temperature rise time to 8 ms.

The pyrolyzer was connected to an HP-6890 GC system and the gas flow was split to allow 1/33 to enter the GC column. The injector temperature was 250°C. The separation was performed on a 30m x 0.25 mm i.d. fused silica capillary column (film thickness 1 µm) denoted DB 1701 from J&W Scientific. Carrier gas velocity was constant at 0.8 mL/min. Temperature settings were as follows: 100°C, hold 2 min, increase 4°C per minute to 265°C, hold 5 min.

The mass spectrometer operated in the electron impact (EI) mode with ionization energy of 70 eV. The ion source temperature was 230°C. The scan speed was 5.27 scans s<sup>-1</sup>, and the mass range 35-300 amu. Between each run the sample probe was removed and the

column oven temperature was increased to 280°C for 20 minutes in order to remove the sample components completely from the column.

The carbohydrate composition was determined according to the equation below where *Glc*, *Man*, *Xyl*, *Ara*, and *Gal* are the relative amounts (in % by weight) of each monosaccharide in the hydrosylate, corrected for the addition of one molecule of water per anhydrosacchride unit during hydrolysis.

$$\text{Glucomannan} = \text{Gal} + \frac{4}{3}\text{Man}$$

$$\text{Cellulose} = \text{Glc} - \frac{1}{3}\text{Man}$$

$$\text{Xylan} = \text{Xyl} + \text{Ara}$$

Equation 1. Calculation to determine the relative carbohydrate composition when employing the method by Syverud.

*Determination by High Performance Anion-Exchange Chromatography with Pulsed Amperometric Detection (HPAEC-PAD).*

Sample preparation of pulp and acid hydrolysis for carbohydrate analysis is based on method described in TAPPI test method T-249. The monomeric sugar content of the hydrolysed pulp was determined by HPAEC-PAD analysis. Typical results are summarized in Tables 2 and 3. Complete chemical constituents are summarized in Table 4.

Table 2. The carbohydrate content of bleached kraft and unbleached TMP fibers.

Pulp	Arabinan (%)	Galactan (%)	Glucan (%)	Xylan (%)	Mannan (%)	Total Carbohydrate (%)
Kraft	0.51	0.24	80.50	8.88	6.39	96.50
TMP	0.57	1.28	48.64	4.31	9.60	64.40

Table 3. Monosaccharide content for series of SW kraft brownstock pulps.

Kraft Pulps ID	Glucan	Xylan	Mannan	Arabinan	Galactan	Total carbohydrate content *
M/K 2	81.93%	7.54%	5.75%	0.66%	0.56%	96.44%
M/K 3	84.28%	5.95%	6.16%	0.48%	0.45%	97.32%
M/K 4	86.24%	4.53%	6.26%	0.35%	0.37%	97.75%
M/K 5	77.25%	9.20%	5.19%	0.96%	0.63%	93.23%
M/K 6	84.97%	7.12%	5.58%	0.62%	0.50%	98.79%

\* It is expressed by the summation of monomeric sugar content including glucan, xylan, mannan, galactan, and arabinan.

Table 1. Species/pulping variation for unbleached cell wall composition

Component	% Wood Component		% Kraft Pulp Component	
	Pine	Birch	Pine	Birch
Cellulose	38-40	40-41	35	34
Hemicellulose	25-30	30-35	10	17
Lignin	27-29	20-22	2-3	1.5-2
Extractives	4-6	2-4	0.25	<0.5

Hexenuronic Acid Content

Kraft brownstock pulps were analyzed for hexenuronic acids (HexA) using the method developed by Chai X.-S.; Zhu, J.Y. and Li, J. see “A Simple and Rapid Method to Determine Hexenuronic Acid Groups in Chemical Pulps” *Journal of Pulp and Paper Science* **27** (5). p. 165-170. (2001). Briefly, a known weight of oven-dried pulp (0.05 o.d. grams) was weighed and placed in a vial containing 10 mL of a hydrolysis solution. The hydrolysis solution contained 0.6% mercuric chloride and 0.7% sodium acetate. The vial was sealed, mixed well, and placed in a hot water bath (60-70°C) for 30 minutes. After cooling, the solution UV absorption at 260 nm and 290 was measured and recorded. The hexenuronic acid content of the pulp was calculated with the equation below.

$$C_{HexA} = 0.287 \times \frac{(A_{260} - 1.2A_{290}) \times V}{w}$$

Calculation to determine the hexenuronic acid (HexA) content in pulp.

HexA concentration in  $\mu\text{mol/g}$  o.d. pulp;

$A_{260}$  and  $A_{290}$  are the absorbances at 260 and 290 nm, respectively;

V is the volume of hydrolysis solution; and w is the oven-dried weight of pulp.

Typical standard deviations for replicates were 0.96  $\mu\text{mol/g}$  pulp.

Carboxylic Acid Group Content

Kraft brownstock pulps were analyzed for carboxylic acid groups using the method developed by Chai, X.-S.; Hou, Q.X.; Zhu, J.Y.; Chen, S.-L.; Wang, S.F. and Lucia, L.A.; Carboxyl Groups in Wood Fibers. 1. Determination of Carboxyl Groups by Headspace Gas Chromatography. *Industrial & Engineering Chemistry Research* **42** (22). p. 5440-5444. (2003). Briefly, the fiber samples were first pretreated at 1% consistency using a 0.1000 mol/L hydrochloric acid solution for 1 hour at room temperature, magnetically stirring at a constant speed. The fiber sample was then dewatered in a Büchner funnel, washed thoroughly with Nanopure water, and air-dried. A known weight of oven-dried pulp (0.05 o.d. grams) was weighed and placed in a headspace testing vial. Subsequently, four milliliters of a 0.005 mol/L standard bicarbonate solution mixed with 0.1 mol/L NaCl was added to the same headspace testing vial. The vial was flushed with nitrogen for 15 seconds, mixed thoroughly, sealed with a septum, and placed in a headspace sampler tray for HS-GC measurements. All measurements were performed on an HP-7694 Automatic Headspace sampler and Model HP-6890 capillary gas chromatograph equipped with a thermal conductivity detector. GC conditions were as follows: capillary column with ID = 0.53 mm and a length of 30 m (Model GS-Q J&W Scientific Inc. Folsom, CA, USA) at 30°C, carrier gas helium flow rate of 3.1 mL/min. Headspace sampler operating conditions were as follows: oven temperature of 60°C, vial pressurized by helium with pressurization time of 0.2 min., loop equilibration time of 0.05 min., vial equilibration time of 10 min. with strong shaking, and loop fill time of 1.0 min. The GC was run in splitless mode. The method used is based on the reaction of a protonated carboxylic acid group with bicarbonate resulting in the formation of carbon dioxide and water. The amount of carbon dioxide liberated can be used to quantify the bulk acid groups of a known quantity of pulp. The carboxylic acid content of the pulp was calculated by the relationship presented below:

$$C_{COOH} = 0.046 \times \frac{(A_{sample} - A_{blank})}{w}$$

$C_{COOH}$  is the carboxyl group concentration in  $\mu\text{mol/g}$  o.d. pulp;

$A_{\text{sample}}$  is the area under the GC peak for the analyzed sample;

$A_{\text{blank}}$  is area under the GC peak for the standard bicarbonate solution;

w is the oven-dried weight of pulp.

Total Charge: Conductometric Titration

To perform the conductometric titration, the pulps were stirred with 300 mL of 0.1000 M hydrochloric acid to liberate the fibers and convert the pulp to the protonated form. Then the pulp was washed with deionized water, dispersed in 250 mL of 0.001 M sodium chloride (NaCl), and 1.5 mL of 0.1000 M HCl was added. Then, the solution was titrated with a standardized 0.0500 M NaOH (NaHCO<sub>3</sub>) solution as conductivities were measured.

The total acid groups were extrapolated from plots of the titration data as described by Figure 1. Initially, conductometric titration curves indicate a rapid decrease which represents the neutralization of strong acid groups. The first equivalence point represents weaker carboxylic acids beginning to dissociate, and the second equivalence point represents increases in conductivity due to excess NaOH.

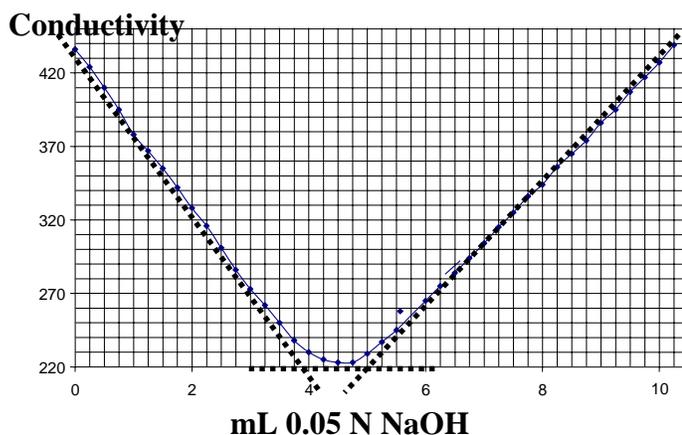
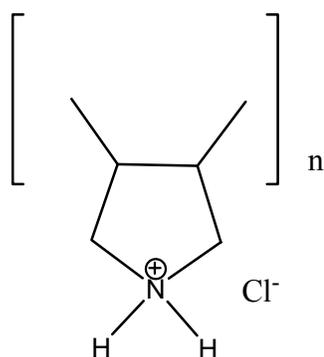


Figure 1. Conductometric pulp titration curve.

Surface Charge - Polyelectrolyte Titration

Polyelectrolyte titrations were done to differentiate between the surface and bulk carboxylic acid contents of treated and untreated fibers. A high molecular weight (450,000 – 500,000) cationic poly-DADMAC (poly-(diallyldimethylammonium chloride)), described in Figure 2, was used. The polymer was filtered with a poly(ether sulfone) (PES) Nalgene centrifuge filter at 1000 rpm for 25 minutes to ensure that no low



molecular weight polymer was used. These filters eliminate polymer with molecular weights near and below 100,000. Since the largest pores found in TMP and BKP typically range from 22 - 105 Å, this eliminated the danger of measuring acid groups beyond the fiber surface.

Figure 2. Poly-DADMAC

Prior to titrating the pulp, five 1.0 oven-dry gram samples of pulp were stirred for an hour with 250 mL of 0.1 molar hydrochloric acid, and washed with 1,500 ml deionized water by filtration. The fibers were then converted to the sodium form using 0.005 N NaHCO<sub>3</sub>, and the pulp was stirred for twenty minutes, then again washed with deionized water. Various concentrations (0.00001 – 0.0007 N) of a Nalco high molecular weight poly-DADMAC diluted with Nano-pure water was added in 100 ml aliquots, the fibers were stirred gently for 40 minutes, then the filtrates were collected. The filtrates were titrated with 0.001 N potassium poly(vinyl sulfate) (PVSK) in the presence of ortho-toluidine blue (OTB) until the color changed from blue to purple/pink. Then the volume of titrant was recorded within +/- 0.01 ml. The plots of adsorbed poly-DADMAC versus the equilibrium concentrations were extrapolated to the y-intercept to determine the amount of poly-DADMAC adsorbed by fibers as described in Figure 3.

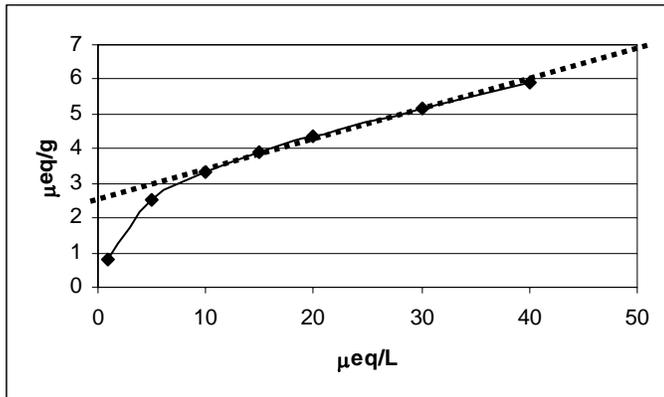


Figure 3. Typical polyelectrolyte titration data plot.

Table 5 provides a summary of typical bulk charge of mechanical and chemical pulps.

Table 5. Typical acid group content of various pulps.

Pulp	Sulfonic Acid Groups (μeq/g)	Total Acidic Groups (μeq/g)
Unbleached TMP		80-110
Bleached TMP (Peroxide)		150-250
Unbleached CTMP	40-70	120-180
Peroxide Bleached CTMP	40-70	190-320
Unbleached Sulfite (K<32)	<100-120	<150-180
Unbleached Pine Kraft (K=25.9)		85
Unbleached Kraft (K<32)		<60-80
ECF Bleached Softwood Kraft [ODEDED]		32
ECF Bleached Hardwood Kraft [D(EOP)DD]		55
TCF Bleached Softwood Kraft [OOQPO]		70
TCF Bleached Hardwood Bleached Kraft		120

K: kappa #

CED Viscosity

Pulp viscosity values were determined in accordance with TAPPI Standard T 230 om-94 “Viscosity of Pulp (capillary viscometer method).” The moisture content was determined for air-dried pulp and was used to weigh 0.2500 g o.d. of pulp. The weighed pulp was solvated with cupriethylenediamine and passed through Cannon-Fenske 150 viscometers at 25°C. The viscometers were carefully cleaned with nitric acid water and acetone and dried between measurements. Two separate viscometer readings were performed for each sample and each sample was run twice (total of four viscometer readings). The standard deviation for the brownstock pulps was 0.40 for four replicates of one pulp while the standard deviation of the same pulping conditions was 0.47 cP. The viscosity was converted to the degree of polymerization ( see Morton, J.H.; Viscosity/DP Relationships for Cellulose Dissolved in Cuprammonium and Cupriethylene Diamine Solvents. In *Proceedings of the Chemistry and Processing of Wood and Plant Fibrous Materials, Cellucon 1994*. Bangor, U.K. p. 151-158. (1996)) as follows:

$$D.P. = -449.6 + 598.4 \ln[\eta] + 118.02(\ln[\eta])^2$$

where D.P. is the degree of polymerization and  $\eta$  is the viscosity in cP measured according to TAPPI T 230 om-89.

## **OPTICAL PROPERTIES**

### ISO Brightness

ISO brightness measurements were made on pulp handsheets in accordance with TAPPI Standard T 525 om-92 “Diffuse Brightness of Pulp ( $d/O^\circ$ ).” The handsheets were made at a basis weight of 200 g/m<sup>2</sup> using TAPPI Standard T 205 sp-95 “Forming Handsheets for Physical Test of Pulp.” The pH of the slurry and the water in the handsheet mold are adjusted to a pH of  $6.5 \pm 0.5$ . The typical brightness standard deviation for five replicates of one pulp was 0.14 while for replicates of the same pulping conditions it was 0.18 brightness units.

### Determining $k$ , $s$ , and $k/s$

Diffuse reflectance measurements of handsheets were carried out on a Perkin-Elmer Lambda 900 UV/vis spectrometer equipped with a diffuse reflectance and transmittance accessory. The accessory is essentially an optical bench that includes double-beam transfer optics and a six-inch integrating sphere. Background corrections were recorded using a Labsphere SRS-99-020 standard made of Spectralon<sup>®</sup> and having a reflectance factor of 99%. The diffuse reflectance measurements were made using handsheets that were cut to 8 cm x 8 cm squares and placed in the sample holder perpendicular to the light source.

### Chromophore Index

The Kubelka-Munk remission function ( $k/s$ ) data were taken over the entire visible spectrum (400 to 700 nm) and entered into the Number Crunching Statistical Software (NCSS 2001).

## **EXTRACTIVES**

### *Metals: Inductively Coupled Plasma (ICP) – Atomic Emission Spectroscopy*

The determination of trace metals in wood and pulps was accomplished using Inductively Coupled Plasma (ICP) Emission Spectroscopy. This technique requires the preparation of acid digests from representative sample specimens to enable the instrumental analysis of metallic analytes. A summary of the digestion method, from US EPA SW-846 Method 3050A, is as follows:

1. An oven-dried (105°C) sample of wood or pulp (0.5000 -2.0000 g) was accurately weighed in a clean, labeled, pre-digested glass griffin beaker and covered with a watch glass.
2. The sample was transferred to a hot plate in a fume hood. To the beaker, 5.00 mL of 1:1 HNO<sub>3</sub> was added, swirled, and recovered with the watch glass.
3. The sample was heated slowly for 10 to 15 minutes to a gentle reflux. After 10 to 15 minutes the beaker was removed from the hot plate and allowed to cool.
4. 2.50 mL of concentrated HNO<sub>3</sub> was added to the beaker. The watch glass was placed back on the beaker.
5. The beaker was returned to the hot plate to reflux for 30 minutes. The volume was not allowed to drop below 5 mL. After 30 minutes, the beaker was removed from the hot plate and allowed to cool.
6. Repeat steps 4 and 5.
7. To the cooled beaker, 1.00 mL of deionized water and 1.50 mL of 30% H<sub>2</sub>O<sub>2</sub> was added. The watch glass was placed back on the beaker.
8. Return the beaker to the hot plate on a reduced heat. The samples begin to effervesce. Heat until the effervescence subsides then remove beaker to cool.
9. To the beaker, add 0.50 mL of 30% H<sub>2</sub>O<sub>2</sub>, return the watch glass and return to hot plate and heat until effervescence subsides.

10. Repeat step 9 until the general appearance of the digest was unchanged, or a total of 5.00 mL of 30% H<sub>2</sub>O<sub>2</sub> was added.
11. To the beaker, 2.50 mL of concentrated HCl was added along with 5 mL of deionized water. Return the beaker to the hot plate and heat for 15 minutes and then remove to cool.
12. Once cool, rinse the under surface of the watch glass into the sample beaker with deionized water. Filter the digest through a pre-rinsed Whatman 41 filter paper into a 50 mL graduated cylinder. Rinse the sides of the beaker with deionized water to ensure quantitative transfer of the sample digest. Do not exceed a final volume of 50 mL.
13. Bring the final volume of the filtrate up to 50 mL with deionized water.
14. Transfer the digests to appropriately labeled, pretreated sample bottles and submit for ICP analysis.

Analysis of the sample digests is accomplished using a Perkin Elmer Optima 3000 DV ICP Emission Spectrometer. This instrument, equipped with an autosampler and integral computer workstation is configured to detect up to 30 elements simultaneously in less than 5 mL of sample digest solution. The principle analysis is the detection of characteristic ultraviolet and visible light emission from metallic elements injected in a high temperature argon plasma torch. To improve instrument performance, a yttrium internal standard was added to each sample, standard, and blank to compensate for small variations in sample flow rate, sample viscosity, acid concentration, and other instrumental and chemical parameters. Quantification of the sample analytes was based on the measurement of specific wavelength intensities and comparison against multi-point calibration standards for each element. The method employed is from US EPA SW-846 Method 6010A and typical results are shown in Table 6.

Table 6. Typical metals content of bleached kraft and unbleached TMP long fibers.

Element	Concentration in Bleached Kraft Pulp (mgkg <sup>-1</sup> )	Concentration in TMP (mgkg <sup>-1</sup> )
Cr	0.12	0.16
Mn	0.092	2.07
Fe	1.28	7.75
Co	0.096	0.22
Ni	1.865	2.55
Cu	517.5	679.50
Zn	24.05	35.60
Al	3.30	59.91
B	0.29	4.93
Si	20.90	25.70
P	8.85	19.85
S	37.30	57.75
Se	1.63	5.335
As	1.24	2.79
Mo	0.23	0.52
Cd	0.07	0.15
Sn	0.00	1.42
Sb	0.76	1.66
Pb	137.00	94.85
Tl	1.65	3.71
Sr	0.04	0.45
Ba	0.11	0.81
Be	0.01	0.0067
Na	7.71	9.93
Mg	1.22	3.32
K	8.73	12.41
Ca	14.20	54.5
Ti	0.11	0.10
V	0.03	0.058

Elemental Analysis

Carbon, hydrogen, oxygen, and sulfur analyses of the lignin samples were performed on oven-dried samples (24 hours 105°C). The samples were combusted and analyzed for carbon, hydrogen, and sulfur by elemental analysis.

Ash Content

The ash content of the residual lignin samples was analyzed in accordance with TAPPI Standard T 211 om-93 “Ash in Wood, Pulp, Paper, and Paperboard: Combustion at 525°C”. Approximately 100 mg was ignited in a muffle furnace at 525°C. A separate test sample was used to find the moisture content of the specimen. The resulting weights of ash and moisture level in the sample are used to calculate the percentage ash present at 525°C on a moisture-free sample basis by the relationship shown below.

$$Ash, \% = \frac{A \times 100}{B}$$

Calculation to determine the ash content in a wood, pulp, paper, paperboard, or lignin.

*A* is the weight of ash in grams

*B* is the weight of the moisture-free test sample in grams.

Typical values ranged from 0.71-2.7%.

Residual Extractives: Soxhlet Extraction

Residual extractives were removed from pulp via solvent extraction for 24 hours in a Soxhlet extraction apparatus as described in Tappi Provisional Method T 280 pm-99, see Table 7.

Table 7. Extractives removed from softwood and hardwood wood chips by extraction with acetone, dichloromethane, and benzene-ethanol.

	Softwood	Hardwood
Solvent, Sample Count	% Extractives	% Extractives
Acetone	2.23	0.69
(n = 7)	+/- 0.12	+/- 0.05
Dichloromethane	1.46	0.27
(n = 7)	+/- 0.07	+/- 0.01
Benzene-ethanol	1.47	0.26
(n = 7)	+/- 0.07	+/- 0.03

The procedure for Soxhlet extraction of the pulp begins with allowing the pulp or paper sheet to air dry. Next, the pulp or paper sheet is placed either into cellulose filters which are placed into the extractors, or cellulose Whatman filter paper is placed across the opening of the capillary of the extraction tube (so that pulp does not enter the capillary) and pulp is placed over the Whatman filter paper. The extraction tube is placed over a three-necked flask which is 60% full of acetone (or alternative solvent) and a small handful of poly(tetrafluoro ethylene) boiling chips as shown in Figure 4. The solvent is refluxed at a rate of cycle repetitions in this study was 5 to 6 per hour, and extractions were performed for 24 - 48 hours. The solvent was then concentrated to a dry residue

ragauskas@hotmail.com

and gravimetrically analyzed and GC-MS analyzed for determination of individual components.



Figure 4. Soxhlet extraction apparatus.

## **FIBER – PAPER PROPERTIES**

### Handsheets Making

Pulp handsheet needed for physical testing were prepared based on a modification of T205, in which the Carver Model C Press was used to press the sheets to 0, 35, 212, 424, and 619 psi for the analysis of dry tensile. The sheets at 0 psi were made following TAPPI test method T205 and couched without further pressing (see Figure 4). All sheets were restraint-dried in brass rings at Tappi standard conditions in accordance with T402.



Figure 4. Handsheet making apparatus.

Fiber Quality Analyzer

The fiber quality analyzer (FQA) was used to optically characterize the pulp. The FQA uses uniform, diffuse light at an infrared wavelength to illuminate an 80 mm<sup>2</sup> viewing area. Since fibrous materials contain crystalline cellulose, the light can be polarized. A charged coupling device (CCD) camera is used to capture the light that has been polarized, thus capturing images of the fibers. The fiber contour length, percent fines, and curl are simultaneously analyzed. The curl index is based on a ratio of the contour length to the projected length.

Table 8. FQA fines, fiber length and curl index of Southern Pine TMP/Bleached Kraft.

Pulp	Fines (%)	Average fiber length/mm	Curl index
TMP	0.15 +/- 0.028	2.74 +/- 0.0071	0.0335 +/- 0.00071
Bleached kraft	0.0233 +/- 0.0058	3.82 +/- 0.060	0.11 +/- 0.0043

Freeness

Freeness testing gives an indication of the ability of a pulp to drain and is relative to the level of pulp refining. This allows comparison of the degree of refining of pulps, if separate pulps are compared. This is important, since the level of refining is critical to strength properties. Freeness of pulps was characterized using by method TAPPI method T227. One liter of the 0.30% consistency pulp was rapidly poured into the freeness tester, and the volume discharged from the side orifice was recorded in milliliters.

Paper Strength Properties

Paper physical tests were performed on all samples where treatments were advanced to handsheet formation.

#### Tensile Testing

Tensile testing was performed on a Kinston tester and on a Lorentz and Wetter (Alperton) tester according to TAPPI-T 494. The Kinston was connected to data analysis system running Test works software. Wet tensile testing was performed according to Tappi T-456 with a 5 min span between wetting the sample and testing.

#### Tear testing

Tear testing was performed according to TAPPI T-414 on an Elmendorf tearing tester .

#### Zero span

Zero span testing was performed on a Pullman zero-span testing apparatus according to TAPPI T-403.

#### Burst

Bursting strength was tested according to TAPPI T-403 on a Mullen bursting tester.

#### Z-Directional Tensile Testing (ZDT)

ZDT was performed on a TMI tester according to TAPPI T-411 using double-sided tape from Scotch<sup>™</sup>.

#### Tensile Energy Absorption (TEA)

TEA is measured as the area under the stress-strain curve over the range of no strain through the strain at which the sample breaks under the load.

#### Wet Strength Properties

The wet strength properties, wet tensile, wet strain, and wet TEA, were performed on the Model 1122 Instron tensile tester at Tappi standard conditions. The 15.0 mm wide, 4.0 inch long strips were submerged in water for 5 minutes, and the wet tensile testing was performed using a 2.0 kg load cell.

#### **AFM Studies**

AFM analysis was done over 5 micron by 5 micron areas in tapping mode. A silicon nitride cantilever tip was used in a Digital Instruments 3100 Scanning Probe Microscope. For each sample, height images were collected at three points along each of eight fibers. Root-mean square roughness calculations were done on the height images. These values were averaged to provide the roughness measurements in nm<sup>2</sup> for each sample.

#### **Surface Energy**

Dynamic contact angle (DCA) analysis by the Wilhelmy plate method and inverse gas chromatography (IGC) are methods which are not affected by the absorbency or surface roughness of the fiber web. These methods provide information about the dispersive and non-dispersive components of substrate's surface using probes with polar and dispersive characteristics.

#### Dynamic Contact Angle (DCA) Analysis

In DCA experiments, the single fibers are mounted and submerged into the test liquid (typically distilled water or methylene iodide), then retreated as the advancing and receding forces are recording along the length of the fiber. This allows the advancing

contact angles of these liquids on the fiber surface to be determined, and then used to calculate the polar and dispersive components of surface energy via the harmonic mean method.

The Wilhelmy plate technique was used to determine the dynamic contact angles of distilled water and methylene iodide on the surface of treated and untreated BKP and TMP fibers. Single fibers were carefully mounted to an adhesive tape, mounted in a clip, and placed on a CAHN DCA-332 dynamic contact angle instrument (Figure 5). The CAHN DCA-332 was used at a stage speed of  $20 \mu\text{msec}^{-1}$  to measure the advancing forces required to push the fiber into the test liquid and the receding forces required to pull the fiber from the test liquid along the length of the fiber. Ten single fibers for each treatment condition were randomly selected from the surface of treated and reference sheets, and then analyzed. The average advancing contact angle of fibers in methylene iodide and distilled water, along with the surface tension properties of each test liquid, were used to determine the components of surface energy of each fiber via the harmonic mean method.

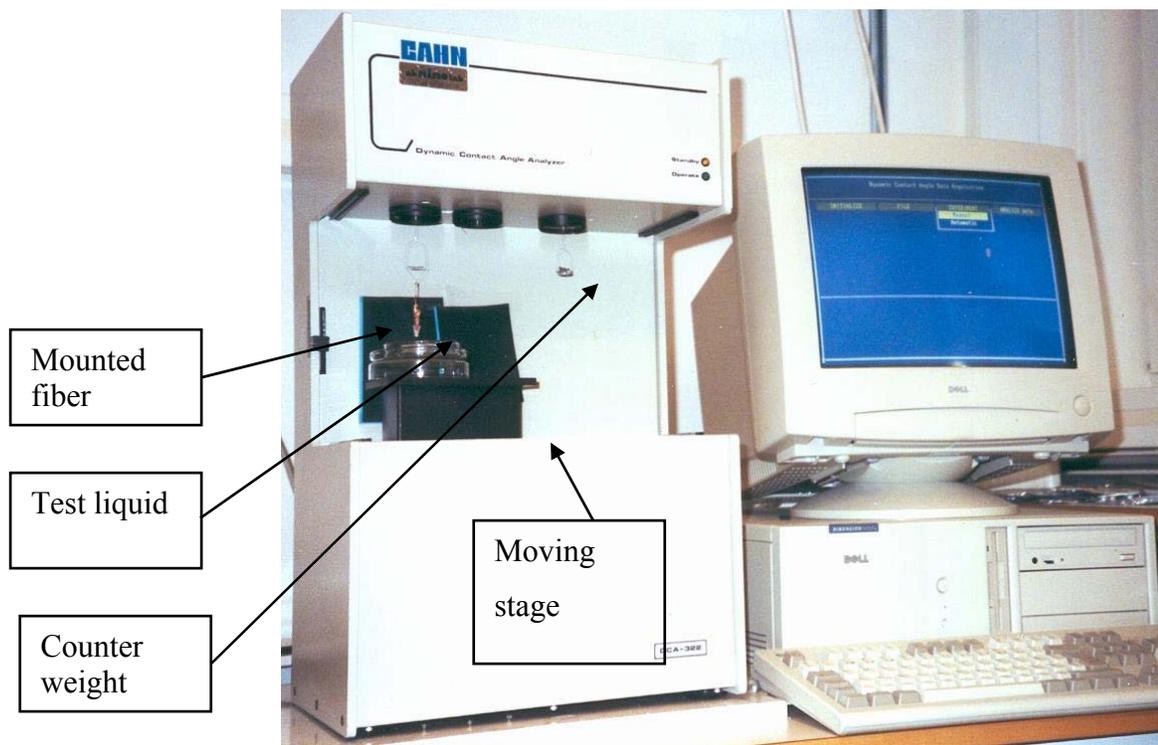


Figure 5. CAHN DCA-332 instrument used for evaluation of single-fiber contact angle.

Table 9. Polar and dispersive components of surface tension for test liquids used in dynamic contact angle analysis.

Surface Tension ( $\gamma$ )	Total ( $\gamma_t$ )	Polar ( $\gamma_p$ )	Dispersive ( $\gamma_d$ )
Water	72.8	50.7	22.1
Methylene iodide	50.8	6.7	44.1

#### Inverse Gas Chromatography (IGC)

The IGC analysis was performed in on a Hewlett-Packard 5890 gas chromatograph with a flame ionization detector. Approximately 1.00 g of bleached kraft pulp or TMP paper was torn into approximately 1.00 mm by 1.00 mm squares and packed into the Teflon columns (Figure 6). The columns were 0.50 m long with an outer diameter of 0.25 inches and an internal diameter of 0.125 inches. The columns were equilibrated at 50, 60 and 70°C overnight. Alkane probe molecules (hexane, heptane, octane, nonane, decane and undecane) were injected at temperatures of 50, 60 and 70°C and applied using helium as the carrier gas, with a flow rate of 15 ml/minute. The temperature of the injector was 150°C. Retention times were determined based upon averages of five injections at each temperature relative to methane as an unretained probe molecule. Injection volumes of 1 to 5  $\mu$ L of each probe were used, as retention times of injected probes are independent of injection volumes in the range of 1 to 10  $\mu$ L.

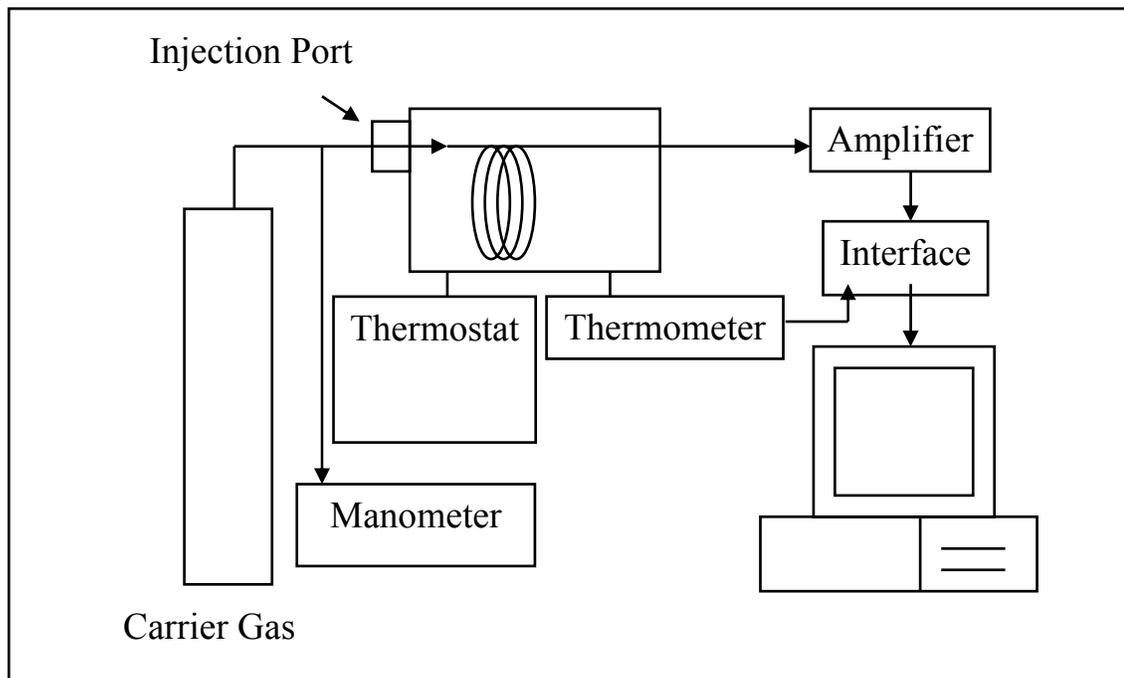


Figure 6. Inverse gas chromatography apparatus.

Scanning Electron Microscopy (SEM)

A JEOL JSM-35C Scanning Electron Microscope was used to characterize reference samples. 4.0 cm by 4.0 cm samples were cut from handsheets, acetone extracted for 48 hours, dried in the vacuum oven at 35°C or 24 hours, cut to approximately 0.75 by 0.75 cm, mounted on a stub, then sputter-coated with a gold/palladium alloy in the Anatech Limited Hummer V sputter coater for 3.0 – 3.5 minutes. A 15 kV electron beam was used to analyze all samples. Image analysis of the images collected on the JOEL JSM-35C was done using NIH Image Version 1.61 software on a McIntosh Quadra 650 computer, operating system 7.6.1 to collect images at 1280 by 960 pixels.

The samples were cut from handsheets, acetone extracted for 48 hours, mounted on a stub, then sputter-coated with a gold/palladium alloy in the Anatech Limited Hummer V sputter coater. A 25 mm working distance and 10 kV accelerating potential for the

electron beam was used to analyze all samples. The image analysis was performed using Princeton Gamma Tech (PGT) Spirit version 1.05 software at 1024 pixels resolution.