

# Influence of Kraft Pulping on Carboxylate Content of Softwood Kraft Pulp

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This study characterizes changes in fiber charge, which is the carboxylate content of fibers, for two sets of kraft pulps: (1) conventional laboratory cooked loblolly pine kraft pulps and (2) conventional pulping (CK) versus low solids pulping (LS) pulps. Laboratory kraft pulping of loblolly pine was carried out to study the influence of pulping conditions, including effective alkali (EA), sulfidity, and pulping temperature, on fiber charge. The results indicated that, when pulping to the same H-factor, low EA charge and low pulping temperature are favorable for increasing bulk carboxylic acid group content of fibers. Sulfidity did not have an obvious effect on bulk or surface carboxylic acid group content of fibers. Surface charge was not significantly affected by pulping temperature. Bulk fiber charge has a linear relationship with water retention value. Roughnesses of holocellulose fiber handsheets were determined by atomic force microscopy (AFM). No apparent relationship between roughness and surface charge of holocellulose fibers was found, but unrefined holocellulose fibers exhibited at least 26% lower root-mean square (RMS) roughness values compared to refined holocellulose fibers. Another set of kraft pulps distinguished by conventional pulping and low solids pulping were investigated to determine the effect of H-factor and pulping protocol on fiber charge. When bulk fiber charge was plotted against kappa number, pulps from low solids pulping had a higher slope value than the conventional pulping pulps. The charge on holocellulose fibers approaches a constant value as pulping advances for both types of pulping processes.

## Introduction

There is a renewed interest in the relationship between fiber chemistry and fiber properties due to chemical pulping processes. The charge on fibers has been established as a key parameter in papermaking, because many of the interactions between soluble and particulate fractions of the papermaking furnish are charged and their performance is based on electronic interactions.<sup>1–3</sup> In addition, fiber charge influences fiber swelling, flexibility, fiber–fiber bonding, and light scattering properties of paper.<sup>4–9</sup> The acidic functional groups associated with wood consist of (i) carboxylic acid groups with an approximate  $pK_a$  value of 4.5; (ii) phenolic hydroxyl groups with an approximate  $pK_a$  of 10.2; and (iii) weakly acidic hydroxyl groups present in polysaccharides with a  $pK_a$  of roughly 13.7.<sup>10</sup> With the exception of pulps that contain significant levels of sulfonate groups, carboxylic acid groups are the only functional groups that give rise to the generation of charged sites on the fibers under typical papermaking conditions.

During kraft pulping of wood, a significant proportion of the initial 4-*O*-methylglucuronic acid side groups (MeGlcA) of xylan are converted to hexenuronic acids (HexA) which can contribute to the fiber charge of kraft brownstock.<sup>11,12</sup> Pulping conditions and green liquor pretreatment, prior to pulping, strongly affect the formation and stability of HexA.<sup>13–15</sup> Alkaline pulping also results in the formation of new polysaccharide carboxyl groups, generated from the peeling reaction which is stopped by the formation of metasaccharinic acid or other alkali-stable carboxyl groups.<sup>16</sup> The residual lignin in kraft pulps is

well-known to contain carboxylic acid groups.<sup>17</sup> The bleaching of kraft pulps is directed at removing residual lignin, hexenuronic acids, and other chromophoric compounds. The Kraft pulping process and bleaching processes including oxygen delignification, peroxide bleaching, and ozone bleaching not only remove these components but also generate new carboxylic acids.<sup>18–22</sup>

Over the last few decades, kraft pulping technology has significantly evolved to achieve extended delignification, enhanced yield, lower chemical use, reduced energy, and increased production rates employing batch and continuous digesters.<sup>23</sup> Low solids pulping is an example of a modern continuous pulping technology. The main feature of the low solids pulping method is the extraction of dissolved organic substances before bulk delignification. These organic substances detrimentally impact pulp viscosity, brownstock brightness values, bleachability, final bleached pulp brightness ceilings, and pulp tear strength.<sup>23</sup> The effect of the modified pulping protocols on fiber charge has not yet been well-established. Bhardwaj et al. investigated the fiber charge of low solids kraft pulps with high kappa number from 40 to 128.<sup>18</sup> By conductometric titration, the fiber charge was found to vary from 6 to 12 mmol/100 g o.d. pulp, at a kappa number range of 40 to 128, respectively.<sup>18</sup> A recent report by Liu et al. reported the effect of green-liquor (GL) pretreatment of U.S. southern pine wood chips prior to kraft pulping on carboxyl groups of pulps.<sup>24</sup> It was found that the carboxyl groups of linerboard pulps with 30% (GL/[GL+H<sub>2</sub>O]) green liquor pretreatment was the highest (214  $\mu\text{mol}/(\text{g of pulp})$ ), which was 2%, 9%, and 16% higher than that with 20%, 40%, and 50% green liquor pretreatment, respectively.<sup>24</sup> Studies by Buchert et al. reported that the residual lignin of *Pinus sylvestris* kraft pulp accounted for 32% of the total acids in the conventional pulp; whereas, in the Superbatch pulp, the percentage was estimated to be 45%, because of nearly complete degradation of HexA during pulping.<sup>25</sup>

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**Table 1. Pulping Parameters and the Results of Laboratory Kraft Pulping of Loblolly Pine Cooked in an M/K Batch Digester**

kraft pulping ID/ pulp abbreviation	M/K1	M/K2	M/K3	M/K4	M/K5	M/K6	M/K7	M/K8	M/K9
% EA	12	16	20	24	12	16	20	24	12
% sulfidity	30	30	30	30	50	50	50	50	50
H-factor	1000	1000	1000	1000	1000	1000	1000	1000	1000
maximum pulping temp/°C	170	170	170	170	170	170	170	170	160
L/W	4	4	4	4	4	4	4	4	4
kappa number	61.7 ± 0.5	31.6 ± 0.5	22.1 ± 0.5	17.2 ± 0.5	44.4 ± 0.5	26.6 ± 0.5	18.5 ± 0.5	14.2 ± 0.5	46.6 ± 0.5
intrinsic viscosity (mL/g)	1084 ± 10	1024 ± 10	858 ± 10	684 ± 10	1245 ± 10	1029 ± 10	835 ± 10	686 ± 10	1321 ± 10

**Table 2. Conventional and Low Solids Pulping Conditions and Pulp Properties after Pulping**

cook ID	conventional pulping kraft pulps (CK)				low solids pulping kraft pulps (LS)				
	CK-1	CK-2	CK-3	CK-4	LS-1	LS-2	LS-3	LS-4	LS-5
EA charge									
impregnation, % on wood NaOH	20.5	20.5	20.5	20.5	10.0	10.0	10.0	10.0	10.0
displacement 1, g/L NaOH	NA	NA	NA	NA	89.6	92.9	92.9	92.8	92.8
displacement 2, g/L NaOH	NA	NA	NA	NA	45.4	45.4	45.4	45.0	45.0
WL sulfidity, %AA	30.0	29.8	29.8	30.0	29.8	29.8	29.8	30.0	30.0
intrinsic viscosity, mL/g	669 ± 10	864 ± 10	1068 ± 10	1120 ± 10	794 ± 10	833 ± 10	923 ± 10	1140 ± 10	1289 ± 10
pulping temperature/°C	171.0	170.0	168.0	166.0	170.0	169.0	166.3	166.6	166.3
H-factor	4000	1999	1201	995	4489	4126	3362	2442	2008

This study is directed at determining how fiber charge is influenced by varying kraft pulping conditions, including effective alkali (EA), sulfidity, and pulping temperatures for batch pulping. The effect of the low solids continuous kraft pulping technology on fiber charge was also compared with conventional kraft pulping. The primary parameters examined in the latter study were H-factor and pulping protocol.

### Experimental Section

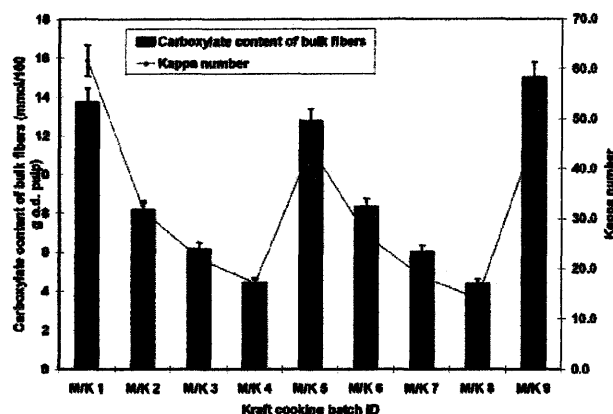
**Materials.** All chemicals used in this study were purchased from Aldrich, JT Baker, and Fisher as analytical grade, except NaOH and Na<sub>2</sub>S used for kraft pulping. The latter two reagents were industrial grade. Deionized water was utilized throughout the study. Two individual loblolly pine (*Pinus taeda*) trees visibly free of disease and compression wood and approximately 25 years old were employed in this study. The debarked logs were chipped, mixed, and screened, with accepts being 2–8 mm in thickness. The chips were stored in a cold room at 4 °C, prior to use.

**Kraft Pulps.** Two series of kraft cooks were accomplished in this study. The first study prepared a series of kraft pulps employing an M/K batch digester. The kraft pulping conditions and pulp kappa and viscosity values are summarized in Table 1.

The second series of softwood kraft pulps were prepared using a conventional batch digester (CK) and laboratory simulation of low solids (LS) kraft pulping, conditions,<sup>26</sup> and these results are presented in Table 2.

**Analytical Methods.** The kappa number of the pulps was measured according to TAPPI standard method T236 os-76.<sup>27</sup> The intrinsic viscosity ( $\eta$ ) was measured according to ASTM standard D1795-62. Both of these tests were performed in duplicate, and the typical errors were  $\pm 0.5$  for kappa number and  $\pm 10$  for intrinsic viscosity of the average numbers. Tensile strength (Tappi standard T494)<sup>27</sup> and burst strength (Tappi standard T403)<sup>27</sup> were measured to investigate the paper physical properties with an error less than  $\pm 5\%$ . The fiber quality analyzer (FQA) was used to optically characterize the fiber curl and kink properties.

**Carboxylic Acid Group Content of Fibers.** Bulk carboxylic acid group content was measured by using conductometric titration methodology.<sup>1</sup> Air-dried fibers equivalent to 1.500 g of oven-dried fibers were added to 300.00 mL of 0.10 N HCl



**Figure 1.** Carboxylate content of kraft pulps prepared with varying EA, S, and maximum pulping temperature employing M/K digester at constant H-factor of 1000 and liquid/wood of 4:1 of loblolly pine.

and stirred for 1 h. The pulp was then filtered and washed with 2000 mL of deionized water until the effluent water conductivity was  $< 5 \mu\text{V}$ . The washed pulp was treated with a 0.001 N NaCl (250.00 mL) and 0.10 N HCl solution (1.50 mL), stirred, and conductrimetrically titrated with 0.05 N NaOH under a nitrogen atmosphere. The experiments were performed in duplicate to check the reproducibility of these values, and the results are reported in Figures 1 and 2.

**Carboxylic Acid Group Content of Holocellulose Fibers.** Holocellulose pulps were prepared following the literature method.<sup>28</sup> In brief, air-dried kraft fibers equivalent to 1.500 g of oven-dried fibers was dispersed into 125.00 mL of deionized water, followed by the addition of glacial acetic acid (1.00 mL, 0.017 mol) and NaClO<sub>2</sub> (1.00 gr, 0.011 mol). The slurry was heated to 70 °C and mixed for 1 h. Thereafter, a second addition of glacial acetic acid (1.00 mL, 0.017 mol) and NaClO<sub>2</sub> (1.00 gr, 0.011 mol) was employed, and the slurry was treated for an additional hour. The fully delignified pulp sample was then cooled to room temperature and stored at 3 °C for overnight. The sample was filtered and thoroughly washed with 2000 mL of deionized water. The washed fibers were analyzed for carboxylic acid group content as described above.

**Polyelectrolyte Adsorption Method for Surface Charge of Fibers.** Surface fiber charge was measured using the polyelectrolyte adsorption method.<sup>29,30</sup> Prior to determining the

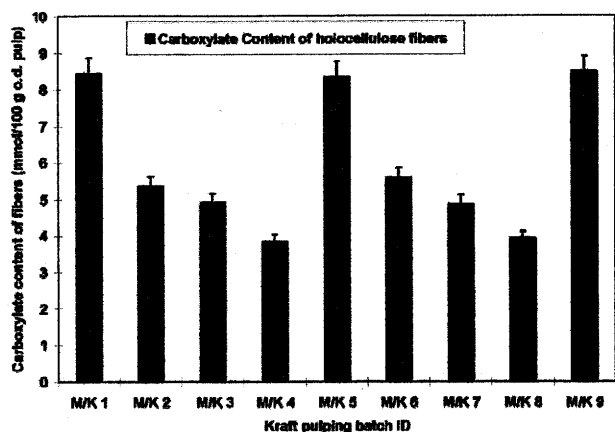


Figure 2. Carboxylate content of holocellulose fibers from kraft pulps prepared with varying EA, S, and maximum pulping temperature employing M/K digester at constant H-factor of 1000 and liquid/wood of 4:1 of loblolly pine.

surface charge of a given pulp sample, a series of control tests were prepared. Different volumes (12.50, 18.75, 25.00, and 31.25 mL) of chitosan solution (1.00 g/L) were diluted with deionized water to the final solution weight of 300.00 g. After mixing for 40 min, 25.00 mL of diluted solutions were titrated with  $2.00 \times 10^{-4}$  N potassium poly(vinyl sulfate) (PVSK). This titration procedure was performed in triplicate, and analysis showed a linear relationship between the volume of chitosan and the amount of PVSK.

Subsequently, air-dried pulp samples ( $4 \times 1.500$  g) were dispersed in 0.01 N HCl (300.00 mL) for 1 h and then washed with deionized water (at least 2000 mL). The washed pulp samples were placed into a 0.005 N  $\text{NaHCO}_3$  (250.00 mL) solution. The pH of the slurries was adjusted to 9.00 by addition of 0.05 N NaOH. After stirring for 20 min, the pulp slurries were filtered and washed with deionized water (at least 2000 mL). Different volumes (12.50, 18.75, 25.00, and 31.25 mL) of chitosan solution were added with the washed pulp samples separately and diluted to 301.50 g with deionized water. After mixing for 40 min, the slurries were filtered and the filtrates of unabsorbed chitosan were collected for titration. Each filtrate (25.00 mL) was pipetted into a flask and titrated with PVSK. Each titration was performed in triplicate. The amount of chitosan adsorbed on the fibers was determined for each of the different volumes of chitosan solution added. By plotting the moles of chitosan adsorbed on fibers (surface acid,  $\mu\text{mol/g}$ ) versus the chitosan concentration added, the surface charge of fibers can be calculated. The results are summarized in Figure 3; titration errors were evaluated using standard deviation at 95% confidential level.

**Carbohydrate Analysis by High-Performance Anion-Exchange Chromatography with Pulsed Amperometric Detection (HPAEC-PAD).** The sample preparation of pulp and acid hydrolysis for carbohydrate analysis is based on the method described in Tappi T-249.<sup>27</sup> The monomeric sugar content of the hydrolyzed pulp was determined by HPAEC-PAD analysis.<sup>31</sup> The results are summarized in Table 2.

**Water Retention Value (WRV).** Pulp water retention values were evaluated according to Tappi Useful Method 256: Water Retention Value. This methodology involves a pulp mat formed by draining a dilute pulp slurry on a fine mesh screen in a centrifuge cup. The pulp mat was prepared at a fixed basis weight of  $555 \pm 55$  g/m<sup>2</sup>. The pulp pad is then centrifuged at 900 g for 30 min. The wet pad, after centrifuging, is weighed, dried at 105 °C, and then reweighed. The WRV is calculated

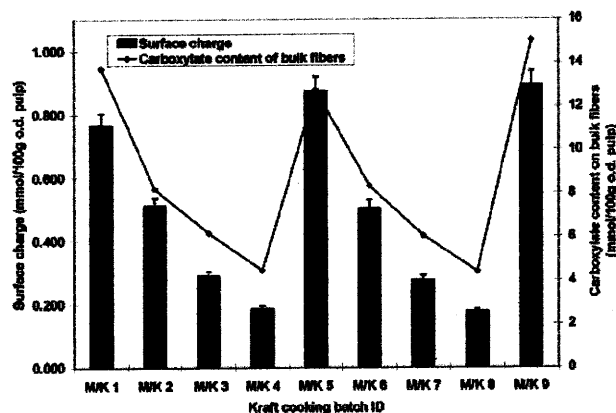


Figure 3. Surface charge of kraft pulps prepared with varying EA, S, and maximum pulping temperature employing M/K digester at constant H-factor of 1000 and liquid/wood of 4:1 of loblolly pine.

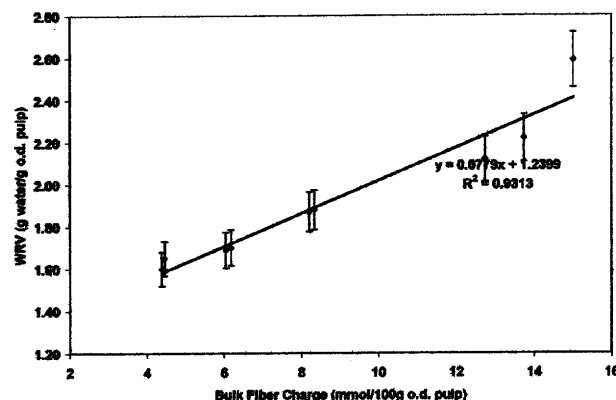


Figure 4. Relationship between bulk fiber charge and water retention value of original M/K1-M/K9 kraft pulps.

as the amount of water by weight retained in the pad after centrifuging per o.d. weight of fibers (eq 1).

$$\text{WRV} = \frac{W_w - W_d}{W_d} \times 100\% \quad (1)$$

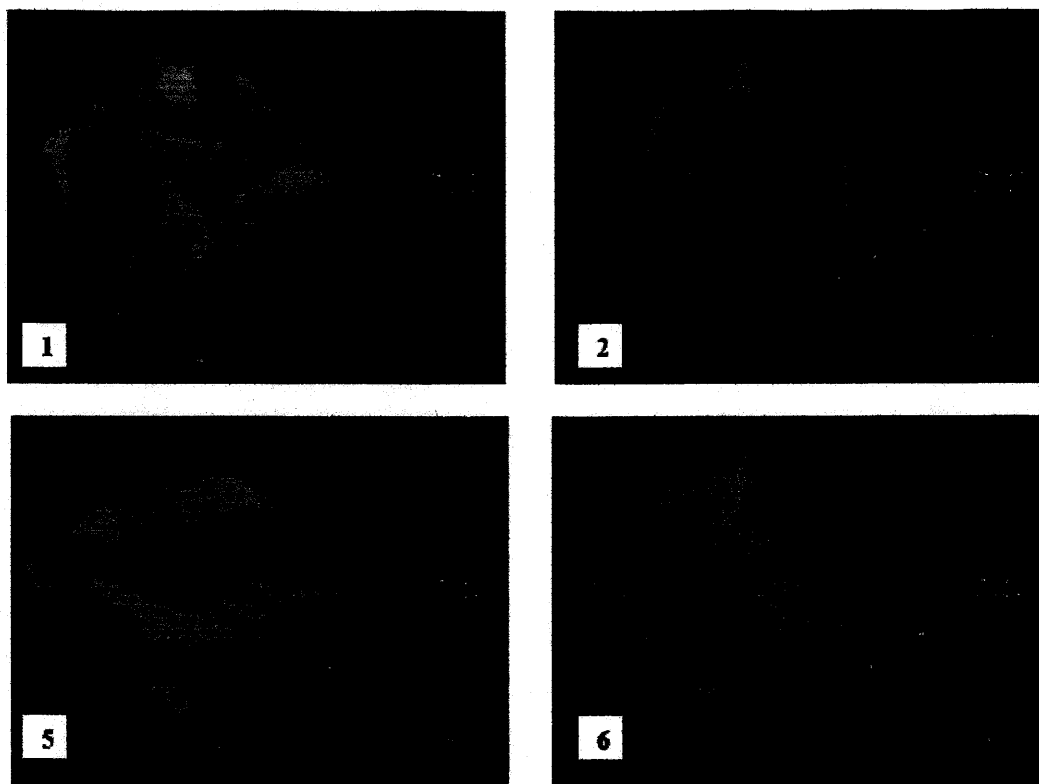
$W_w$  is the weight of the wet sample after centrifuging, and  $W_d$  is that of the dry sample. The tests were done in quadruplicate, and standard deviation of 95% confidential level was used for the experimental error evaluation. The results are presented in Figure 4.

**Atomic Force Microscopy (AFM).** A silicon nitrile cantilever tip was used with a Digital Instruments 3100 scanning probe microscope to evaluate the surface morphology of fibers. The AFM phase images are presented in Figures 5 and 6.

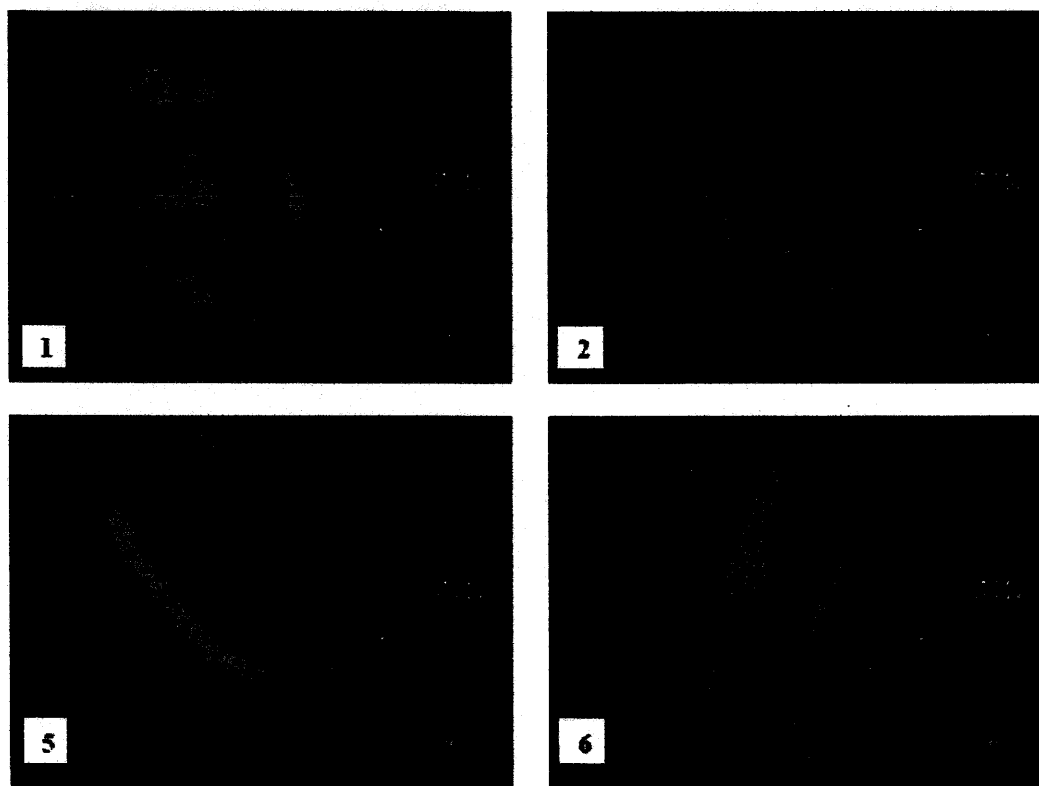
For each sample, height images were collected at two positions along each of five fibers. These values were averaged to provide the roughness measurements in nm<sup>2</sup> for each sample by using eq 2.<sup>32</sup>

$$R_{\text{rms}} = R(F \sum_{i=1}^N (Z_i - Z_{\text{ave}})^2 / N) \quad (2)$$

where  $N$  is the number of points in the area examined,  $Z_i$  is the current height value, and  $Z_{\text{ave}}$  is the average height value.  $R_{\text{rms}}$  is the root-mean square of the standard deviation for the height ( $Z$ ) data. The standard deviation (SD) values of roughness determined by AFM are presented in Figure 7, where refined



**Figure 5.** Atomic force microscopy (AFM) phase images of holocellulose fibers. 1, 2, 5, and 6 are holocellulose fibers from M/K1, M/K2, M/K5, and M/K6 kraft pulps, respectively.



**Figure 6.** Atomic force microscopy (AFM) phase images of holocellulose fibers treated by 2000 rev PFI refining. 1, 2, 5, and 6 are holocellulose fibers from M/K1, M/K2, M/K5, and M/K6 kraft pulps, respectively.

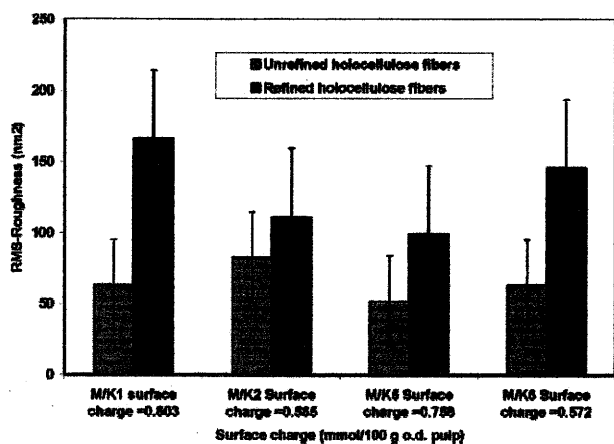


Figure 7. Comparison between holocellulose fibers RMS-roughness measured by AFM and surface charge on holocellulose fibers of M/K1, M/K2, M/K5, and M/K6 kraft pulps.

samples have standard deviation values between 29 and 48 and unrefined samples have standard deviation values between 24 and 34.

## Results and Discussion

The effect of kraft pulping conditions on fiber charge was investigated by preparing a series of laboratory prepared conventional loblolly pine kraft pulps. The experimental parameters varied included effective alkali, sulfidity, and pulping temperature. The pulp identifications (IDs) for the samples described in Table 1 were assigned M/K1–M/K9. The primary pulping factors investigated were effective alkali and sulfidity. A preliminary study for the effect of maximum pulping temperature on fiber charge was accomplished by comparing kraft pulp M/K5 versus M/K9. M/K5 was prepared at 170 °C, and M/K9 was prepared at 160 °C. Basic fiber properties including kappa number and viscosity are summarized in Table 1. The results of intrinsic viscosity values shown in Table 1 indicate that the viscosity decreases with increasing effective alkali when kraft pulping is performed at the same sulfidity, H-factor, and maximum pulping temperature. This result is in agreement with Dyer and Ragauskas' prior studies.<sup>33</sup>

**Effect of Effective Alkali, Sulfidity, and Pulping Temperature on Carboxylic Acid Group Content of Bulk Fibers and Holocellulose Fibers.** The results for bulk carboxylic acid group content for kraft pulps are presented in Figure 1. EA increases in the order M/K1 to 4 and in the order MK/5 to 8. The latter set of four samples has higher sulfidity. Condition M/K9 has a lower maximum pulping temperature but is otherwise similar to condition M/K5 as summarized, in Table 1.

These results indicate that, the higher the EA for a batch kraft cook, the lower is the carboxylic acid content of the resulting pulp when pulping is accomplished at the same H-factor and pulping temperature (170 °C). This result is in accordance with other researchers' studies.<sup>15,24,25</sup> It has been reported that a higher alkalinity in extended pulping serves to minimize the reprecipitation of the hemicellulose onto the fibers' surface is also decreased.<sup>34</sup> Hence, the results of this study, which indicate that a lower effective alkali charge during pulping leads to kraft pulps with a higher fiber charge, are consistent with literature findings. In contrast, pulping sulfidity did not appear to have an obvious effect on carboxylic acid group content of bulk fibers, except under low EA (12%) conditions. Analysis of the results from

M/K9 and M/K5 indicate that a lower temperature possibly favors the retention of carboxylic acid group content in the pulp.

The differences in carboxylate content of kraft pulps reported in Figure 1 are due to differences in the carboxylate content of fiber polysaccharides and lignin. In elementally chlorine-free (ECF) bleached pulps, fiber charge originates primarily from carboxylate groups attached to saturated polysaccharides. It is now well-established that most hexenuronic acids in pulp are oxidatively removed during ECF bleaching.<sup>35</sup> To evaluate the content of fiber charge associated with bleached polysaccharides, the kraft pulps in Table 1 were holocellulose pulped. Figure 2 shows the carboxylate content of holocellulose pulps. The difference between carboxylate groups content of bulk kraft pulp fibers and that of holocellulose pulps is attributed to the charge associated with lignin and hexenuronic acid groups present in the kraft pulps. These results demonstrate that ~56–86% of the carboxylic acid groups of the kraft pulps can be attributed to saturated pulp carbohydrates. The key pulping parameters influencing fiber charge on saturated polysaccharides include effective alkali and pulping temperature. Although holocellulose pulping is not employed industrially, it is relevant to ECF bleaching protocols. The results in Figure 2 indicate that the kraft pulps with higher fiber charge maintain higher fiber charge after holocellulose bleaching when compared against kraft pulps having lower fiber charge.

**Effect of Effective Alkali, Sulfidity, and Pulping Temperature on Surface Charge on Bulk Fibers.** Figure 3 summarizes the effect of EA profiles on surface charge. At the same H-factor and pulping temperature (170 °C), a high EA in the digester yields a low surface charge. In contrast, no significant difference in fiber surface charge was observed when 30% or 50% sulfidity was employed for pulping. The only exception to this observation was noted when the pulping conditions employed a low EA charge (12%), as previously observed for bulk fiber charge. As for the pulping temperature effect, the M/K9 pulp prepared with a maximum pulping temperature of 160 °C resulted in a slightly higher (2%) surface charge compared to M/K5 pulp (i.e., same conditions except pulping temperature). These results suggested that a lower EA is favorable for increasing overall surface charge, while sulfidity is not a key parameter for controlling surface charge during kraft pulping. After comparing surface charge with bulk fiber charge, it suggests that surface charge accounts for ~4–7% of the bulk fiber charge.

**Relationship between Carboxylate Content of Bulk Fibers and Water Retention Value (WRV) of Pulps.** Water retention value (WRV) is useful for evaluating the performance of pulps in dewatering on a paper machine and for some paper applications.<sup>36</sup> It can also provide a relative indication of the swelling capability of the pulps. As fibers swell, they are more easily beaten and defibrillated, thus exposing greater surface area for bonding to occur. It is commonly acknowledged that enhanced fiber swelling relates to increased concentration of acid groups in the pulp.<sup>6–9</sup> This has been attributed to two effects. One is Donnan equilibrium theory,<sup>37</sup> which was applied to cellulosic membrane.<sup>38,39</sup> The other is the electrostatic repulsion between the negatively charged carboxylate anions of fibers.<sup>6,40</sup> Figure 4 summarizes the relationship between bulk fiber charge and water retention value of pulps. It is shown that there is a linear relationship coefficient of determination,  $R^2$ , of 0.93.

Prior studies have demonstrated that WRVs clearly increase by introduction of carboxyl groups into pulps via carboxymethylation under alkaline conditions.<sup>5,29,41,42</sup> Kitaoka et al. studied the chemical modification of pulp fibers by TEMPO-mediated oxidation; their results have shown that WRVs of pulps

**Table 3. Fiber Charge and Monosaccharide Content Kraft Pulps Underwent Pulping Condition M/K1–M/K9**

kraft pulps ID	fiber charge of holocellulose (mmol/100 g o.d. pulp)	glucan	xylan	mannan	arabinan	galactan	total carbohydrate content <sup>a</sup>	fiber charge of holocellulose fibers vs carbohydrate content
M/K1	8.44	74.80%	7.99%	4.80%	0.88%	0.86%	89.33%	9.45
M/K2	5.35	81.93%	7.54%	5.75%	0.66%	0.56%	96.44%	5.55
M/K3	4.91	84.28%	5.95%	6.16%	0.48%	0.45%	97.32%	5.05
M/K4	3.85	86.24%	4.53%	6.26%	0.35%	0.37%	97.75%	3.94
M/K5	8.35	77.25%	9.20%	5.19%	0.96%	0.63%	93.23%	8.96
M/K6	5.58	84.97%	7.12%	5.58%	0.62%	0.50%	98.79%	5.65
M/K7	4.88	85.35%	6.46%	6.24%	0.50%	0.42%	98.97%	4.93
M/K8	3.91	87.18%	5.07%	6.72%	0.38%	0.33%	99.68%	3.92
M/K9	8.49	77.41%	9.92%	5.14%	1.10%	0.67%	94.24%	9.01

<sup>a</sup> It is expressed by the summation of monomeric sugar content including glucan, xylan, mannan, galactan, and arabinan.

**Table 4. Paper Physical Strength and FQA Results of Holocellulose Fibers from M/K1, M/K2, M/K5, and M/K6 Kraft Pulps**

holocellulose sample of M/K kraft pulps	fiber charge of holocellulose fibers after refining (mmol/100 g o.d. pulp)	tensile Index of holocellulose fibers after refining (Nm/g)	burst Index of holocellulose fibers after refining (kPa·m <sup>2</sup> /g)	curl of of holocellulose fibers after refining	kink of holocellulose fibers after refining (L/mm)
#M/K 1	8.44 ± 0.09	58.87 ± 1.66	7.21 ± 0.21	0.064 ± 0.006	0.82
#M/K 2	5.35 ± 0.09	54.03 ± 1.08	6.94 ± 0.18	0.066 ± 0.006	0.90
#M/K 5	8.35 ± 0.09	57.79 ± 1.54	7.33 ± 0.22	0.061 ± 0.006	0.78
#M/K 6	5.58 ± 0.09	54.14 ± 0.97	6.78 ± 0.18	0.068 ± 0.006	0.86

were roughly constant, even though these pulps had carboxyl contents from 0.06 to 0.47 mmol/g.<sup>43</sup>

**Carboxylate Content of Holocellulose Fibers versus Total Carbohydrate Content of Pulp Fibers.** To determine carboxylic acid group content per unit carbohydrate, including cellulose and hemicellulose of fibers, monomeric sugar content was determined by HPAEC–PAD. The results are shown in Table 3. The results show that mannan was relatively resistant to removal by increasing EA charge during kraft pulping. Total carbohydrate content expressed by the sum of the monomeric sugar content increased with increasing EA charge. On the basis of Table 3, it is indicated that fiber charge of unit holocellulose appeared highest at the lowest EA charge. It can be concluded that EA charge is the most important factor controlling carboxylic acid groups of holocellulose or kraft pulp fibers during kraft pulping.

**Paper Physical Testing and PFI Refining of Holocellulose Pulps.** To further investigate the effect of acidic group on fully bleached paper physical strength, the strength properties of holocellulose pulped M/K1, M/K2, M/K5, and M/K6 were determined. Since it is well-known that curl and kink detrimentally impact physical strength properties, the holocellulose pulps were Paper and Fibre Research Institute (PFI) refined to obtain similar curl and kink values. Bulk fiber charge analysis of the pre- and postPFI refined pulps indicated that the refining process did not change bulk fiber charge when the fibers are refined at 2000 revolutions (rev). This result is consistent with recent reports that beating does not alter total fiber charge.<sup>44</sup> Table 4 summarizes the results of paper physical strength and fiber quality of holocellulose fibers after PFI refining with 2000 rev. The results of fiber quality analysis (FQA) show that holocellulose fibers have similar curl and kink values after PFI treatment of 2000 revolutions. From Table 4, it can be seen that a higher fiber charge corresponds to enhanced tensile strength and burst strength of paper prepared from holocellulose fibers with similar curl and kink values. Nonetheless, both burst strength and tensile strength depend on other factors, such as interfiber bond strength, web structure, and inherent fiber strength. By comparing the results of holocellulose pulps M/K6 and M/K5, it shows that a 50% increase in fiber charge of holocellulose fibers enhances tensile and burst index by 7% and 8%, respectively.

AFM is used to evaluate surface morphology and properties of a large number of materials which also include wood, fibers, and cellulose.<sup>32,45–47</sup> Handsheets of unrefined and refined holocellulose fibers from M/K1, M/K2, M/K5, and M/K6 kraft pulps were analyzed by AFM. Figures 5 and 6 show AFM phase images of the holocellulose fibers.

On the basis of the AFM phase images of samples, there are no striking differences in the surface topographies between high fiber charge (holocellulose fibers M/K1 and M/K5) and low fiber charge (holocellulose fibers M/K2 and M/K6). Figure 7 presents the root-mean square (RMS) roughness values for holocellulose fibers M/K1, M/K2, M/K5, and M/K6. As expected, the unrefined samples exhibited at least 26% lower RMS values when compared to refined samples. However, no marked differences in RMS were noted between the high-surface-charge samples and low-surface-charge samples. On the basis of the research by Pang and Gray,<sup>48</sup> it was found that the force acting on the AFM tip as it approaches a pulp-fiber surface can be measured using the AFM tip as a probe. Higher fibrillation of a pulp surface corresponds to high force acting on the tip as it approaches the pulp surface. Mechanical action causes fibrillation of the fiber surface, which can be detected from the tip-fiber force–distance curves.<sup>48</sup> PFI refining increased the fibrillation of fiber surfaces, which might lead to a higher roughness value of the refined pulp surface compared to that of the unrefined pulp fiber surface.

**Investigation of Batch Versus Continuous Low Solids Pulping on Fiber Charge.** A series of lab-produced kraft pulps were prepared by employing conventional pulping (CK) and simulated continuous low solids (LS) pulping from kappa number 14.7 to 39.9. Kraft pulping parameters and pulp properties are summarized in Table 2. The primary parameters investigated in this study were H-factor and pulping protocols. The remaining pulping parameters were kept constant within experimental control capabilities.

From Table 2, it is apparent that the viscosities of low solids kraft pulps were higher than the viscosities of conventional kraft pulps, when pulping was conducted under the same conditions. This is in accordance with literature results.<sup>23</sup> Figure 8 presents kappa number plotted against bulk fiber charge for all the pulps shown in Table 2.

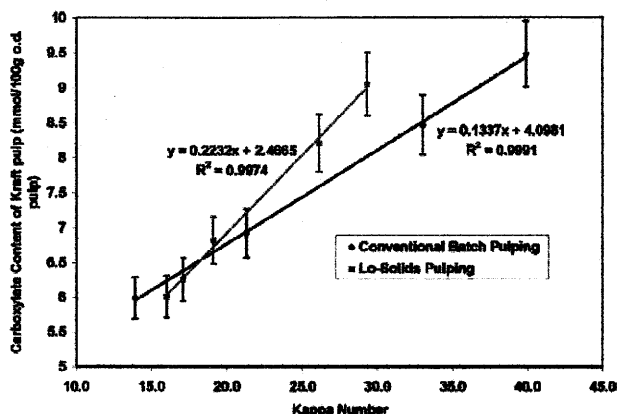


Figure 8. Comparison between carboxylate content and kappa number of conventional and low solids pulping loblolly kraft pulps that underwent 20.5% EA and 170 °C maximum temperature pulping.

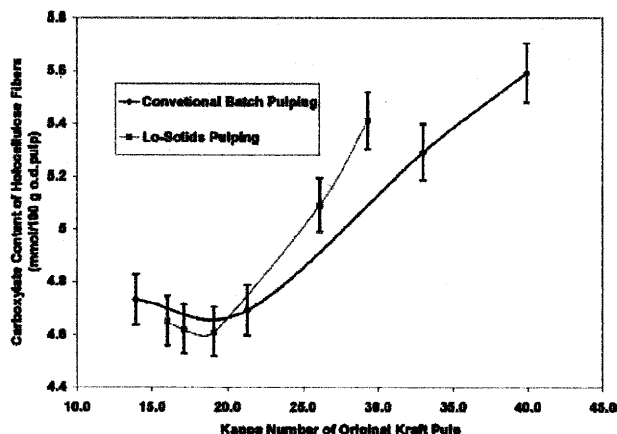


Figure 9. Holocellulose fiber charge vs kappa number of conventional and low solids pulping kraft pulps prepared from loblolly woodchips with 20.5% EA and 170 °C maximum cooking temperature.

It appears in Figure 8 that there is a linear relationship between kappa number and fiber charge. Although no linear relationship between fiber charge and kappa number of low solids pulping pulps was found in Bhardwaj et al.'s study,<sup>18</sup> fiber charge was found to be positively proportional to kappa number, which is widely accepted in numbers of studies of kraft pulps.<sup>15,18,21,22,24,25</sup>

Also from Figure 8, the fiber charge of low solids pulping pulps had a higher slope value than that of the conventional pulping pulps. The two trend lines intersect at a kappa number of 18.2. This suggests that LS pulps with a kappa number > 18.2 have a higher fiber charge than CK pulps. On the contrary, LS pulps with a kappa number < 18.2 have a lower fiber charge than CK pulps. These data indicate that low solids pulps should not be pulped to a high H-factor if the desired effect is to produce high-fiber-charge pulps. This is the first time that fiber charge has been compared between conventional and low solids pulping.

Figures 9 and 10 present the fiber charge of holocellulose fibers against kappa number of original kraft pulps and pulping H-factor, respectively. From these data, it is apparent that the charge of holocellulose fibers reached a constant value as pulping advanced. This constant value for the LS pulps (4.62 mmol/100 g o.d. pulp) was somewhat lower than the value for the CK pulps (4.70 mmol/100 g o.d. pulp). From Figure 9, fiber charge of holocellulose LS pulps has higher values than that of CK pulps when the pulps have the same kappa number. This is

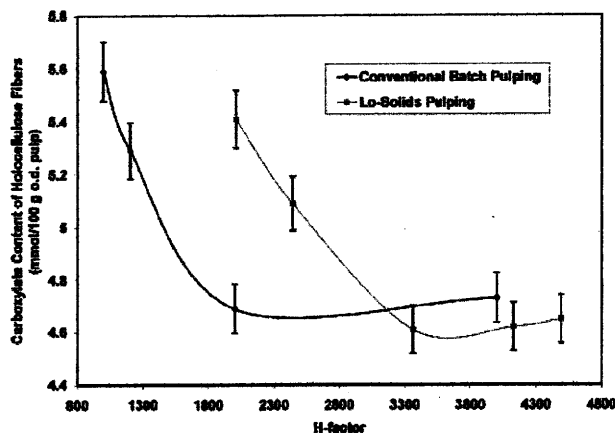


Figure 10. Holocellulose fiber charge versus pulping H-factor of conventional and low solids pulping kraft pulps prepared from loblolly woodchips with 20.5% EA and 170 °C maximum cooking temperature.

the first study to compare the charge of polysaccharides against H-factor. In Buchert et al.'s study of kraft pulps,<sup>25</sup> the results showed that the carboxyl content of kraft pulps tended to be constant with the extension of cooking time, which is an indication of the H-factor.

## Summary and Conclusions

The results of laboratory-pulping loblolly pine kraft pulps, which are generated in an M/K digester, show that EA charge is the key factor in controlling fiber charge when kraft pulping was performed at same H-factor. Low EA charge and low pulping temperature were favorable for increasing carboxylic acid group content of bulk fibers. Carboxylic acid group content of lignin and HexA contributes ~14–44% of the total carboxylic acid group content of bulk fibers, depending on the level of lignin content. The surface charge on fibers accounts for 4–7% of the bulk fiber charge. Higher fiber charge correlated with enhanced paper physical strength by measuring tensile strength and burst strength of holocellulose fibers handsheets, with different fiber charge. The roughness data measured by AFM does not show a correlation with surface charge of holocellulose fibers. The results of another set of lab-produced pulp, conventional pulping and low solids pulping, were investigated to determine the effect of pulping type on fiber charge. Kappa number was linearly related with fiber charge. The fiber charge of low solids pulps had a higher slope value than that of the conventional pulping pulps when bulk fiber charge and kappa number were plotted. The charge of holocellulose fibers reached a constant value as pulping advanced for both types of pulps. The fiber charge of holocellulose LS pulps has higher values than the CK pulps when cooked to the same kappa number.

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