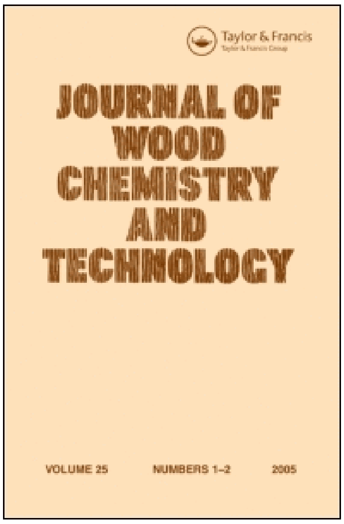

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article Dai, Qizhou , Jameel, Hasan , Chang, Hou-min and Kadla, John F.(2004) 'Bleachability of Kraft Pulps from Earlywood and Latewood of Fast-Growing Loblolly Pine', Journal of Wood Chemistry and Technology, 24: 4, 357 — 370

To link to this Article: DOI: 10.1081/WCT-200046256

URL: http://dx.doi.org/10.1081/WCT-200046256

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY
Vol. 24, No. 4, pp. 357–370, 2004

Bleachability of Kraft Pulps from Earlywood and Latewood of Fast-Growing Loblolly Pine

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ABSTRACT

The pulping and bleaching properties of earlywood and latewood of a fast-growing loblolly pine were studied. Under the same pulping condition, the kappa number of the latewood kraft pulp was higher than that of the earlywood. At around the same kappa number, the yield of the latewood was higher than that of the earlywood. The bleaching results showed that the latewood kraft pulp had lower bleachability

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DOI: 10.1081/WCT-200046256 0277-3813 (Print); 1532-2319 (Online)

than the earlywood kraft pulp, due to its thicker cell wall and slower leaching rate.

Key Words: Bleachability; Cell wall thickness; Coarseness; Earlywood; Kraft pulping; Latewood; Leaching; Mature wood; Softwood.

INTRODUCTION

Owing to increasing environmental pressure, concerns regarding the environmental impact of bleach plant effluent have resulted in the kraft pulping processes undergoing major modifications.[1–3] Recently, the factors that affect the bleachability of kraft pulps, such as the residual lignin structure[4,5] and extractives,[6,7] have been the topics of intensive research. However, the fiber morphology, as a factor of determining the bleachability of kraft pulps, has rarely been studied.

Because of the increasing demand and decreasing supply of raw fiber materials, an increasing portion of wood available to the pulp and paper industry will come from young, fast-growing plantation trees. Woods produced under intensive plantation forest will be different from those of traditionally managed forests. The fast-growing plantation trees will have an increase in the proportion of juvenile wood[8–11] and earlywood.[12] The characteristics of such wood and fiber will be different from older, natural stands of the same wood species. The ratio of juvenile wood to mature wood, and earlywood to latewood will thus affect the quality of wood and properties of wood and fiber products. Therefore, gaining a better understanding of juvenile wood, earlywood, and latewood properties will help evaluate the quality of fast-growing wood and its utilization.

That the fibers from earlywood and latewood have different properties has been studied for many years. Previous studies have focused on the chemical composition,[13–15] refining properties,[15,16] penetration properties,[17] and handsheet properties.[18] The bleaching properties of earlywood and latewood pulps have been rarely studied. It is well known that the chemical compositions of earlywood and latewood are different. For loblolly pine, the earlywood has a higher extractives content[13] and higher lignin content[13,14] than the latewood. A higher percentage of tracheid lignin in the earlywood exists in the middle lamella and cell corners when compared with latewood.[14] These factors may make earlywood harder to bleach than latewood. On the other hand, the latewood fiber wall is much thicker than that of the earlywood fiber.[19,20] As the bleaching process is a combination of chemical reaction kinetics and diffusion dynamics of bleaching chemicals, it is therefore possible that the thick cell wall will retard the penetration of the bleaching chemicals into the cell wall, or the diffusion of the lignin fragment out of the fiber wall, which may lower the bleachability of the latewood pulp.

In this study, a fast-growing loblolly pine tree was selected and the earlywood and latewood of the mature wood were carefully separated. The pulping and bleaching properties of the earlywood and latewood were determined.

EXPERIMENTAL

Raw Material

A 20-year-old fast-growing loblolly pine plantation tree grown near Raleigh, North Carolina, was used in this study. Wood was collected from a chest high level to 10-foot level based on radial symmetry and absence of compression wood. The mature wood was defined as that wood outside the inner eight rings. The outer 8–10 rings were used in this study.

Chip Preparation

The log was debarked and cut into 1 in. thick disks. The disks were cut into 0.5 in. wide small pieces. The small pieces were then immersed into water overnight before proceeding to separate the earlywood and latewood. The earlywood and latewood zones in a ring became more distinct after soaking. The earlywood and latewood were carefully separated using a sharp knife. The latewood chips were carefully cut, so that they were almost pure latewood. The earlywood chips were mixtures of earlywood and latewood. The chips were air-dried to ~15% moisture (wet basis) and stored in a refrigerator at 4°C. The properties of the earlywood and latewood chips are given in Table 1.

Table 1. Wood properties.

	Earlywood	Latewood
Purity	~20–30% Latewood	<5% Earlywood
Extractive contents	3.67%	1.66%
Neutral extractive contents	0.16%	0.08%

Pulping

The kraft cooks were done in a single 7L M&K digester. The cooking conditions are described in Table 2. The target kappa number was 30.

Two cooks were performed. In the first cook, equal amounts of earlywood and latewood chips were put into the digester. The earlywood chips and the latewood chips were separated by a coarse metal screen. They were therefore cooked under the same conditions. The pulps prepared from earlywood and latewood are labeled as early-1 and late-1, respectively. In the second cook, only latewood chips were put into the digester. The H-factor was adjusted so that the kappa number of the latewood pulp would match that of the early-1. The pulp prepared from the second cook is labeled as late-2.

Bleaching

Bleaching was conducted in either high-density polyethylene (HDPE) bags using chlorine dioxide (D) and alkali extraction (E) stages, or an oxygen oxidation bomb for an oxygen reinforced alkali extraction (E_{OP}) stage. All bleaching was carried out at 70°C. The bleaching sequence D(E_{OP})DED was used. The operating conditions used during bleaching are listed in Table 3.

Extraction and Fractionation

To determine the non-volatile extractive contents of the wood meals and pulps, samples of wood chips and pulps were dried in a vacuum oven at room temperature over night. The wood meals were prepared by grinding the wood chips in a Willey mill. The wood powder with size between a 40-mesh screen and a 60-mesh screen was accepted. Fifteen grams of wood meal or pulp was extracted with 9 : 1 acetone : H_2O for at least 10 hr using a soxhlet extraction apparatus. The solvent was removed under reduced pressure. For wood meals,

Table 2. Kraft cooking conditions.

Active alkali charge, as Na_2O	19%
Sulfidity	25%
Liquor volume	$L/W = 4.5$
Temperature increasing rate	100°C/hr
Maximum temperature	170°C
H-factor	To target kappa number

Table 3. Process conditions for bleaching.

Stages	Time (min)	Temperature (°C)	Consistency (%)	Chemical charge	Final pH
D_0	60	70	10	KF = 0.23	
E_{OP}	60	70	10	NaOH ~2%, H_2O_2 = 0.5%, O_2 = 30 psi, 15 min	10.3–10.9
D_1	180	70	10	ClO_2 = 0.7%, 1.0%, 1.3%	3.5–4.0
E	60	70	10	NaOH = 1.0%	10.3–10.9
D_2	180	70	10	ClO_2 = 0.5%	3.5–4.0

the extracts were hydrolyzed in a flask at 70°C for 4 hr with 80 mL 0.5 N KOH/95% ethanol solution. The solution was then diluted with 80 mL water and the pH of the solution was adjusted to 13.2 ± 0.2 with KOH. The diluted solution was extracted with 50 mL of hexane using a separatory funnel. The hexane extraction was performed three times and the extracts were combined. The extractives in the hexane phase were labeled as the neutral fraction. The aqueous phase was acidified to ~pH 2.5 using 1 N HCl and extracted three times with 50 mL of chloroform. The chloroform extracts were combined and labeled as the saponifiable fraction. The sum of the neutral fraction and the saponifiable fraction was the total extractive contents of the sample. For pulps, only the total extractive content (i.e., acetone extract) was determined.

Leaching

Leachability measures the diffusion rate of the bulky lignin out of the fiber wall. As the extractive molecules are smaller than lignin molecules, they are much easier to leach out. As well, some of the extractives have UV absorbances comparable to lignin. Therefore, the existence of extractives will affect the accuracy of the lignin leaching measurement. To exclude the effect of extractives, all the pulps were extracted by organic solvents before leaching measurements.

Leaching measurements were conducted in 1.0 L PVC bottles. In a typical experiment, 10 g of pulp was mixed with 1.0 N NaOH solution and the bottle was sealed. The bottle was put in a water bath under controlled temperature. The operating conditions are listed in Table 4.

Table 4. Process conditions for leaching.

Pulp	10 g
NaOH charge	0.01 M
Consistency	1%
Temperature	70°C
Starting pH	11.8

Solution samples, ~15 mL, were collected at set time intervals and analyzed for leachable compounds. The sample solution was cooled to room temperature and filtered to remove fines and insoluble material. The amount of lignin dissolved during the alkaline treatment was measured by UV spectroscopy (Agilent Technology) at 280 nm using a molecular extinction coefficient of 20 L/g cm.[21]

Fiber Analysis

Fiber properties including fiber length and coarseness were determined using a Fiber Quality Analyzer from OpTest Equipment Inc.

RESULTS AND DISCUSSION

Pulp Properties of Earlywood and Latewood

Generally, latewood from loblolly pine has a higher cellulose content[13,22] and lower lignin content[13,22–24] than the corresponding earlywood. The properties of kraft pulps from earlywood and latewood are listed in Table 5. At about the same kappa number, the yield of latewood was much higher than that of the earlywood. This result is consistent with former studies on kraft pulping of loblolly pine earlywood and latewood.[22] The difference in yield of the earlywood and the latewood was attributed to the different chemical compositions. As well, in latewood, the cellulose content is higher and has a greater resistance to degradative pulping reactions.[13] Likewise, xylan reprecipitation was also more evident in latewood than in earlywood.[22]

Under the same pulping conditions, the kappa number of latewood kraft pulps was higher than that of the earlywood kraft pulps. The difference in the delignification rate of earlywood and latewood was mainly due to their different fiber morphology. The cell wall of latewood is much thicker than that of

Table 5. Properties of kraft pulps from earlywood and latewood.

	Early-1	Late-1	Late-2
H-Factor	1600	1600	2100
Yield (%)	45.5	54.4	53.6
Kappa number	30.1	37.5	28.6
Kappa number after extraction	28.6	36.7	27.5
Extractive contents	0.38%	0.22%	0.19%
Brownstock bright (% ISO)	28.2	18.3	19.2
Coarseness (mg/m)	0.226 ± 0.012	0.330 ± 0.018	0.318 ± 0.004
Fiber length (mm)	3.37 ± 0.04	3.63 ± 0.04	3.60 ± 0.02

the earlywood. The thick cell wall retards the penetration of cooking liquor, which causes a non-uniform distribution of the cooking chemicals. The surface roughness of earlywood is usually greater than that of the latewood.[25] Besides, the surface tension of earlywood was higher. Thus, cooking liquor penetration in the latewood was much slower. In addition, because of the difference in lumen dimensions, the earlywood contained disproportionately more cooking chemicals than latewood.[26] This gave a tendency of overcharging the earlywood and increasing the rate of degradation of lignin and cellulose. Therefore, pulping earlywood resulted in a low kappa number and a low yield.

Kraft pulp from earlywood had a higher extractive contents than latewood, as found in earlier studies.[13,22] The coarseness of the latewood pulp was about 50% higher than that of the earlywood pulp, indicating the much thicker cell walls of the latewood pulp. The fiber length of the latewood pulp was about 10% greater than that of the earlywood pulp, again in agreement with an earlier study.[27]

At approximately the same kappa number, $\sim$28, the brightness of the latewood unbleached pulp was about 9% ISO lower than that of the earlywood unbleached pulp. According to Kubelka–Munk theory, the sheet brightness is approximately described as

$$R_\infty \approx 1 - \sqrt{\frac{2K}{S}}$$

where K is the absorption coefficient and S is the scattering coefficient.[28] K depends primarily on the degree of pulp bleaching. At the same kappa number, the earlywood and latewood fibers have approximately the same *K* value. The light scattering coefficient *S* arises from the specific surface area (area per unit mass). Studies have found that the light scattering coefficient *S* of fibers with thinner fiber walls was higher than those with thicker fiber walls.[29] Owing to the smaller cell wall thickness, the light scattering coefficient *S* of the earlywood fibers is expected to be higher.[28] Therefore, at the same kappa number, the brightness of the earlywood fiber is expected to be higher than that of the latewood fibers.

Leaching Properties of Earlywood and Latewood Pulps

Leaching studies measure the rate of bulky lignin diffusion out of the fiber cell wall. The leaching properties of Early-1 and Late-2 are shown in Fig. 1.

Owing to its thicker cell wall, the latewood pulp had a lower leaching rate than the earlywood pulp. The difference in leachability will affect the bleachability of the latewood pulp and the earlywood pulp.

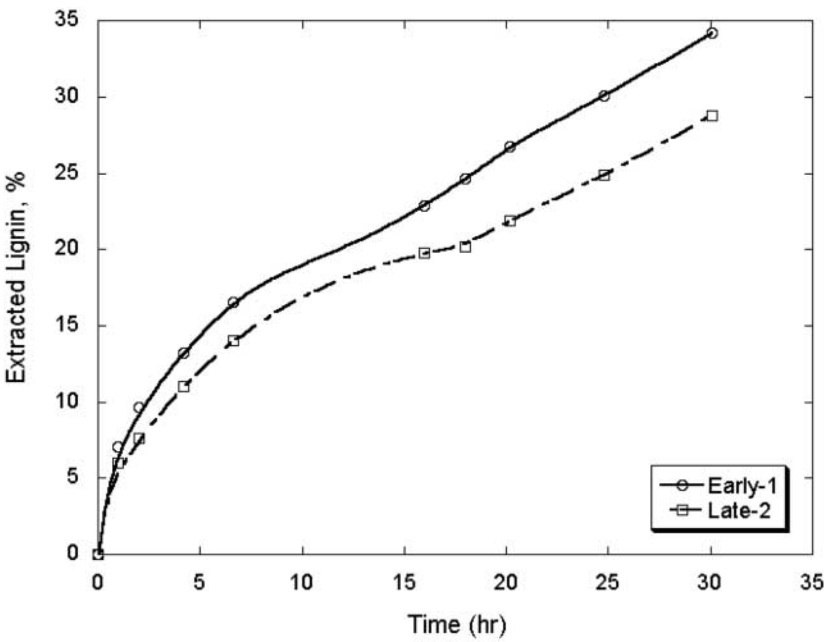

Figure 1. Leaching of extractive-free pulps.

Bleaching Properties of Earlywood and Latewood Pulps

The earlywood and latewood chips were from the same tree. Under the same pulping conditions and at the same kappa number, the earlywood and latewood pulps would presumably have more similar residual lignin structure than pulps from different trees of the same species or trees of different species. However, even in the same tree, after pulping, the residual lignin of earlywood pulp is likely structurally different from that of latewood pulp. It is known that earlywood possesses a lower amount of secondary wall lignin than latewood, i.e., more middle lamella and cell corner lignin.[14] In addition, Terashema and co-workers[30] have shown that the middle lamella region contains high levels of condensed *p*-hydroxyphenyl units. Further, residual kraft lignin has been suggested to come mainly from middle lamella lignin, having low phenolic and methoxyl contents.[31] Therefore, the structure of residual lignin from the earlywood pulp is likely more condensed than that from the latewood pulp in the same tree. Combined with the higher extractive content, it may be expected that the earlywood pulp is harder to bleach than latewood pulp

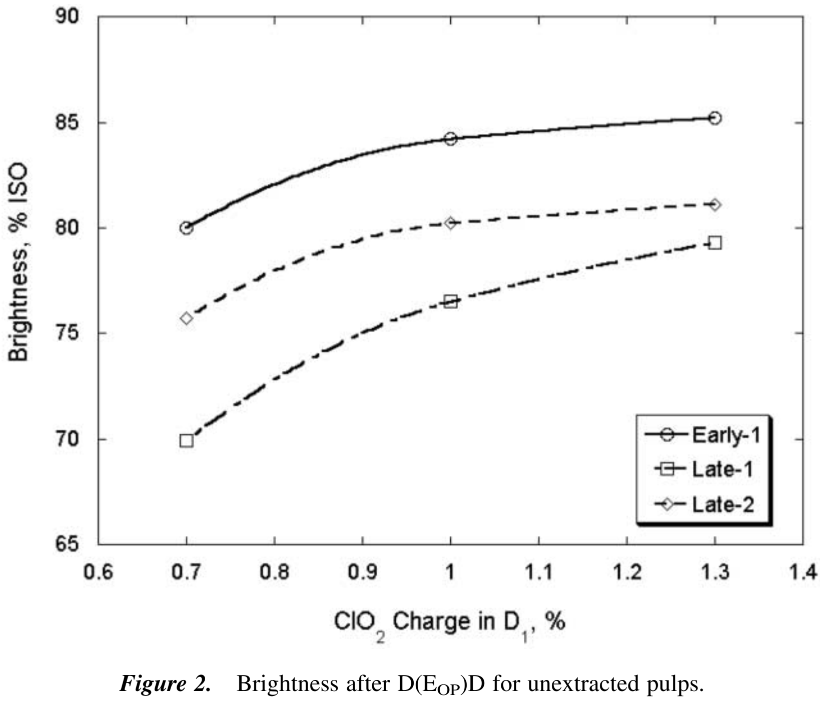

Figure 2. Brightness after D(E_{OP})D for unextracted pulps.

if their difference in coarseness is not taken into consideration. The brightnesses of earlywood and latewood pulps without organic solvent extraction are shown in Figs. 2 and 3.

After three stages [D(E_{OP})D] of bleaching, the brightness of the earlywood pulp was about 4% ISO higher than that of the latewood pulp. After five stages of bleaching, the brightness of the earlywood pulp was only about 2–3% ISO higher than that of the latewood pulp.

To exclude the difference in the extractive content, all the pulps were extracted with organic solvent before bleaching. The brightnesses of the earlywood and latewood pulps after organic solvent extraction are shown in Figs. 4 and 5.

After organic solvent extraction, the final brightness of latewood pulps was about the same. However, the final brightness of the earlywood pulps was increased at least by 1% ISO due to its higher extractive content.

In a previous study, it was found that the blocking effect of extractives in softwood pulp was very dominant due to its thick cell wall;[32] i.e., extractives on the fiber surface affected the diffusion of residual lignin out and/or the

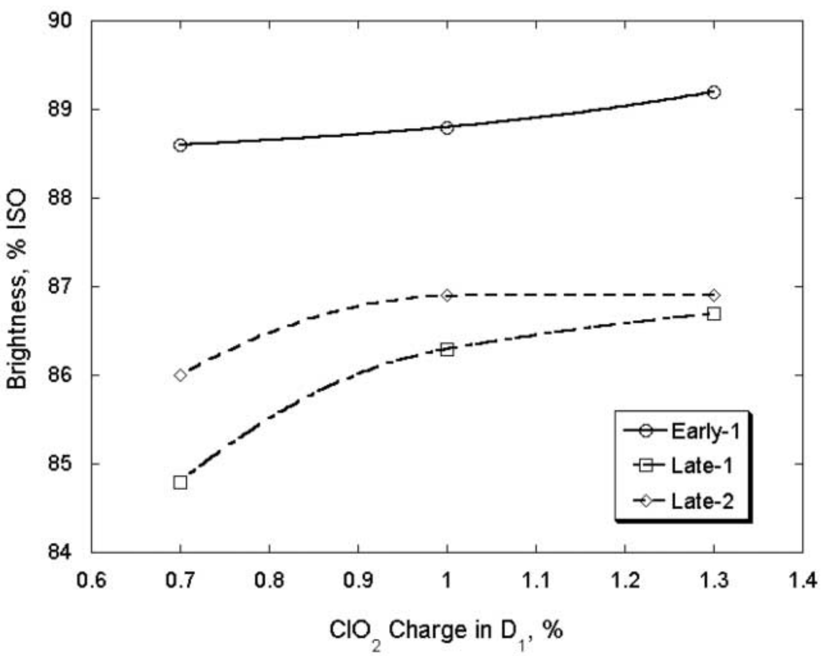

Figure 3. Final brightness after D(E_{OP})DED for unextracted pulps.

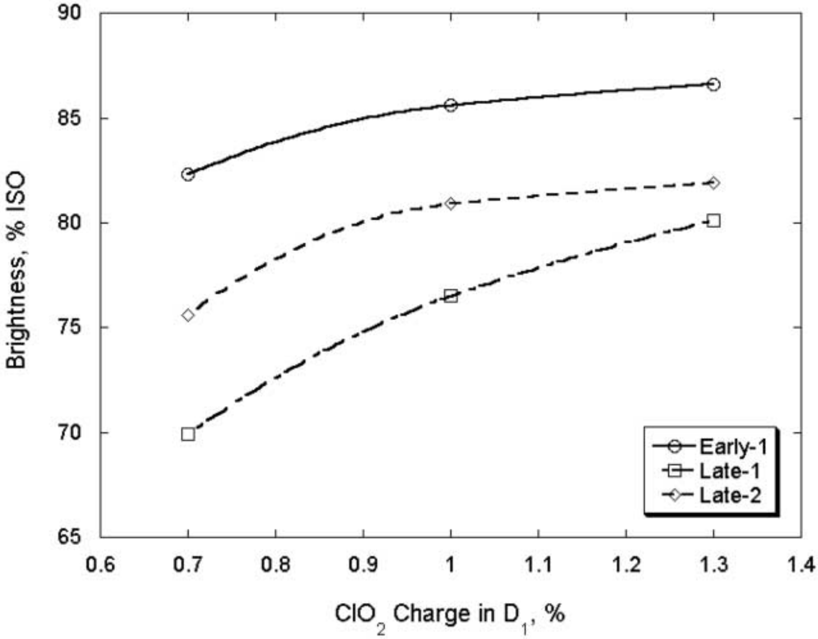

Figure 4. Brightness after D(E_{OP})D for extracted pulps.

penetration of bleaching chemicals into the fiber wall. However, for the latewood pulp from loblolly pine, with a cell wall ~50% thicker than that of the earlywood pulp, its bleachability is barely improved with the removal of extractives. The bleachability of the earlywood pulp though, with a thinner cell wall, is strongly affected by extractives. This result indicates that the cell wall thickness is likely a dominant factor in determining the bleachability of earlywood and latewood pulps, specifically as the earlywood pulp with its structurally different residual lignin and higher extractive content, is easier to bleach than the latewood pulp.

CONCLUSIONS

Fiber morphology affected the pulping and bleaching properties of a fast-growing loblolly pine. For earlywood and latewood, when they were cooked and bleached under the same conditions, the yield was higher for the latewood than for the earlywood. The kappa number of the earlywood kraft pulp was

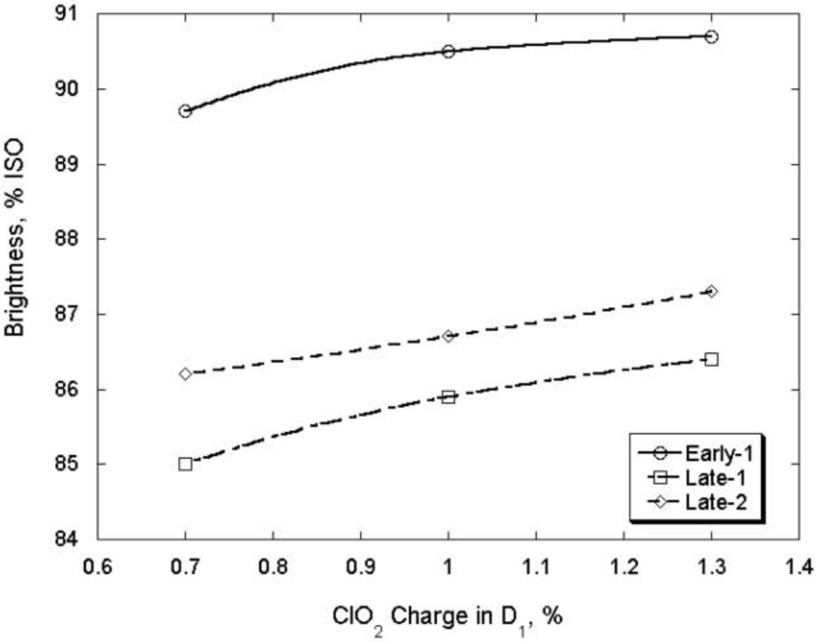

Figure 5. Final brightness after D(E_{OP})DED for extracted pulps.

lower than that of the latewood kraft pulp. The leachability of the earlywood kraft pulp was higher than that of the latewood kraft pulp. The bleachability of the earlywood kraft pulp was significantly higher than that of the latewood kraft pulp.

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