RDH pulping of southern hardwoods

BRENDA A. MATHEISON AND RICHARD R. GUSTAFSON

ABSTRACT

Southern hardwoods were kraft pulped using laboratory rapid-displacement heating (RDH) and conventional processes. RDH pulping achieved acceptable hardwood kappa numbers at lower H-factors than required by conventional batch pulping. The RDH pulps had lower yields at a given kappa number than a conventional batch pulp. However, RDH and conventional cooks produced the same amount of screen rejects at a given kappa number. Reduction of alkali concentration in the black liquor diminished the rate of delignification, but it did not change the pulp yield. Results for RDH pulping of five hardwood species showed significant interspecies variability with respect to pulping rate and selectivity. This suggests that mills using RDH to pulp hardwoods could experience significant swings in kappa number and yield with a change in the mix of wood species.

THE RAPID-DISPLACEMENT HEATING (RDH) system is a batch pulping process that recycles black liquor from a completed batch to pretreat the raw chips in the next batch. White liquor is charged to the digester after the pretreatment.

The black-liquor pretreatment heats the chips and drives out air, neutralizes wood acids, and fills the chips with high-sulfidity liquor *(1–4)*. The primary advantage of the RDH process is a decrease in digester steam consumption, with a reduction of 60–80% compared with conventional batch kraft pulping. The energy savings accrue from the shorter steaming time required to reach white-liquor cooking temperature *(2, 3, 5, 6)*. In addition, RDH pulping extends delignification, making it possible to produce pulps with lower kappa numbers than have been traditionally achieved. Lignin removal also is faster than in conventional batch kraft cooking. This improved pulping performance provides practical economic benefits in terms of increased production, savings in bleach-plant chemicals, and reduced bleach-plant effluent *(2, 3, 7)*. Additional operating advantages have been previously reported *(2–9)*.

Most of the published RDH pulping studies have focused on softwood species. However, several mills are currently using the RDH process to pulp hardwoods, and the RDH performance of hardwoods is of considerable interest. The use of hardwood as a fiber source for pulping is intensifying, and this trend will likely continue as softwood chip supplies become increasingly scarce.

This paper presents the results of a study investigating the pulping response of five southern U.S. hardwoods (white oak, red oak, red maple, sweetgum, and yellow poplar) to a laboratory RDH process. The effects of varying white-liquor cooking temperature, white-liquor effective-alkali charge, black-liquor effective-alkali charge, and wood species are evaluated.

EXPERIMENTAL

Wood chips

The chips used in this investigation were commercial southern U.S. hardwoods supplied by a mill owned by Willamette Industries (Marlboro, SC). The exact age of the chips was unknown, but the wood appeared green on arrival. The chips were air-dried for 3 weeks and screened to 2–10 mm thickness. Chips with a large portion of bark or knots were removed by hand. Air-dried chips were stored at room temperature in plastic bags until used.

White oak chips were used for the studies involving variation of pulping parameters. White oak, red oak, red maple, sweetgum, and yellow poplar were supplied for the species comparison study.

Pulping conditions

The RDH pulping experiments were carried out in a 10-L dual-vessel laboratory digester. Chips were placed into one of the 10-L vessels and treated with the following impregnation sequence: Vacuum was applied for 7 min followed by 10-psi steam for 7 min. Black liquor at room temperature was pulled into the digester by a second vacuum application and then heated with the chips to 120°C over 20 min. The digester was kept at 120°C for an additional 20 min to complete the warm-black-liquor phase of the RDH cook. The warm liquor was drained from the digester, and hot black liquor at 155°C was transferred into the digester using nitrogen gas pressure. (Liquor displacement was not used in the laboratory-scale equipment, since this would have led to mixing of pulping liquors between phases. Instead, the draining–filling liquor-transfer method was used because it provided careful control of the composition of the three pulping phases.) The digester was heated to 155°C over 10 min and was kept at temperature for 20 min to complete the hot-black-liquor phase. The hot black liquor was drained from the digester, and white liquor at 100°C was transferred into the digester using nitrogen gas pressure. The temperature of the digester was raised to the desired cooking temperature (usually 165°C) over 10 min and was held at

	Cooking temperature, °C	Liquor-to-wood ratio, L/kg	*H*-factor	Black-liquor effective alkali,[a] g NaOH/L	White-liquor effective alkali, % on o.d. wood (as Na_2O)	White-liquor sulfidity, %
Pulping of white oak at various conditions						
Conventional batch pulp	165	4.5:1	310–1400	...	14	30
RDH pulps						
Varied white-liquor effective alkali	165	4.5:1	500–1500	7	10,12,14,16	30
Varied black-liquor effective alkali	165	4.5:1	500–1800	2.5, 7,12	14	30
Varied temperature	160,165, 170	4.5:1	300–1400	7	14	30
RDH pulping of mixed species[b]	165	5.5:1	300–1400	7	14	30

[a] Warm and hot black liquors
[b] White oak, red oak, yellow poplar, sweetgum, and maple

I. Pulping conditions

temperature for the desired *H*-factor of the cook. The *H*-factor was accumulated over the warm black-liquor, hot black-liquor, and white-liquor phases. At the conclusion of the cook, the spent white liquor was drained from the digester, and fresh water at 100°C was transferred into the digester and circulated for 5 min. The wash water was drained from the digester and the chips removed.

The original white oak study was done with a 4.5:1 liquor-to-wood ratio. A 5.5:1 liquor-to-wood ratio was required for the species-comparison study to handle some of the lower-density wood used in these experiments. Table I summarizes the pulping conditions used in both studies.

Pulp preparation

The cooked wood chips were disintegrated in a 120-L laboratory slusher containing 80 L of fresh water for 2 min. The pulp was dewatered and screened on a 0.01-in. cut flat vibratory screen to remove rejects. Accept pulp was centrifuged, fluffed, and placed into plastic bags for refrigerated storage.

White and black liquors

The black liquors (warm and hot) were taken from a 50-L storage reservoir containing a mixture of white and black liquors from previous cooks. The entire portion of spent white liquor was recycled back to the reservoir (4.5–6.0 L, depending on the liquor-to-wood ratio used) along with the entire wash liquor (5.2–5.5 L). Spent hot black liquor was added as needed to restore the reservoir to 50 L. Black liquors were stored at room temperature with a nitrogen blanket to inhibit oxidation of the liquor.

White liquor was prepared using sodium hydroxide and sodium sulfide at 10–16% EA (effective alkali) and 30% sulfidity. Alkali content of the initial and final liquors was determined by titration with hydrochloric acid. Further details of the experimental procedure are provided by Matheison *(10)*.

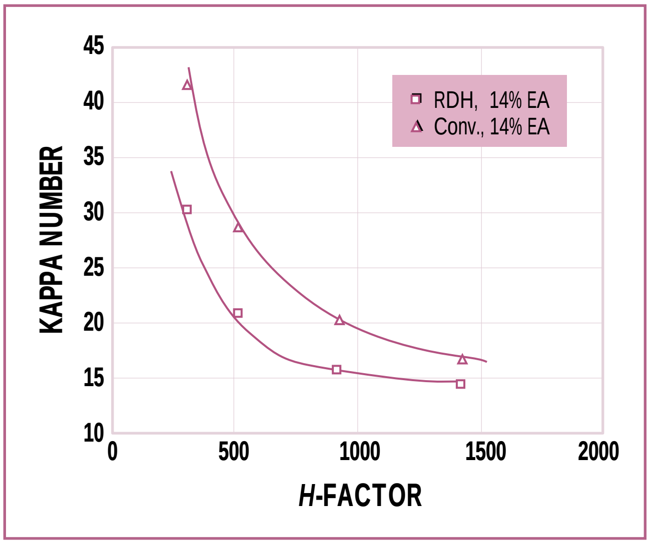
PULPING RESULTS

RDH pulping of white oak at various conditions

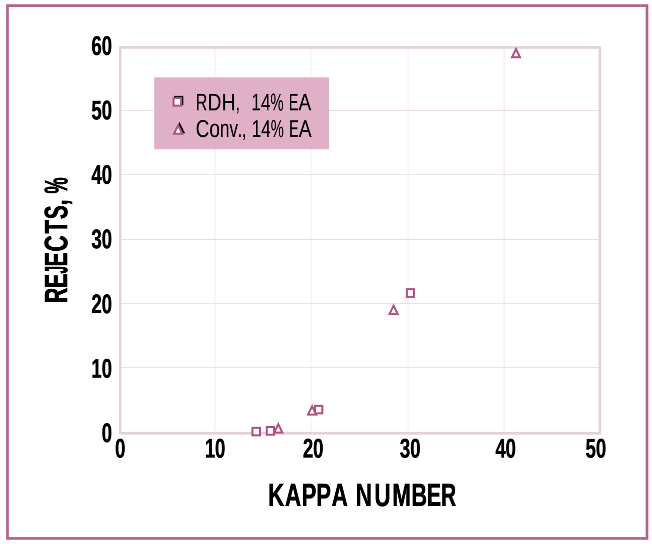
RDH and conventional pulping at 14% EA. Results for RDH and conventional pulping at 14% EA are presented in Figs. 1–3.

The RDH pulps reached lower kappa numbers at a given *H*-factor than those achieved in conventional batch cooks, as seen in Fig. 1. A contributor to this "RDH effect" of enhanced lignin removal is proposed to be the high hydrosulfide ion concentration present in the warm-black-liquor stage of the RDH process. Such a sulfidity profile in the early portion of a conventional softwood kraft cook has been shown to increase the bulk delignification rate and delay the onset of residual delignification *(11–13)*. An additional RDH advantage that enhances lignin removal is that the alkali concentration is maintained at a higher level during the cook phase than in conventional batch pulping. The enhanced white-liquor alkali concentration is due to the neutralization of wood acids by the alkali in the black-liquor phases.

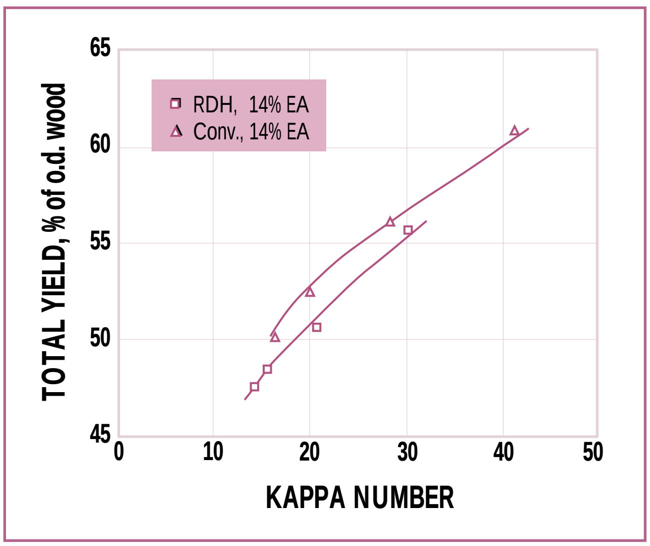
Figure 2 shows the relationship between kappa number and pulp rejects. The RDH and conventional pulps produce about the same



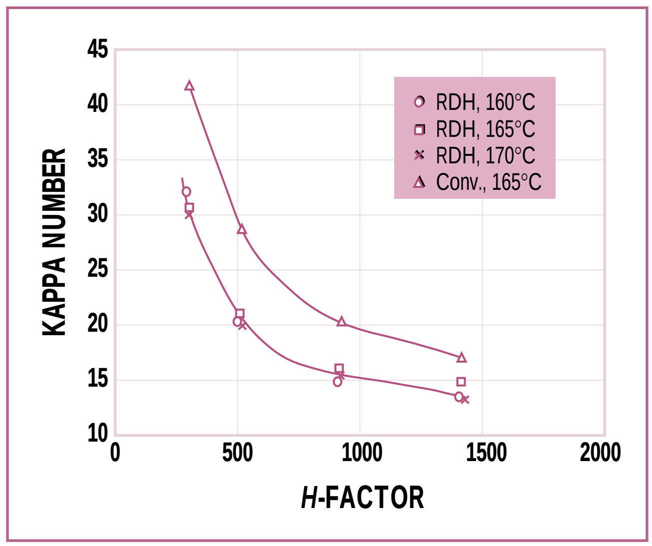
1. *Kappa number as a function of H-factor for RDH and conventional batch pulping of white oak*



2. *Pulp rejects as a function of kappa number for RDH and conventional batch pulping of white oak*



3. *Total pulp yield as a function of kappa number for RDH and conventional batch pulping of white oak*

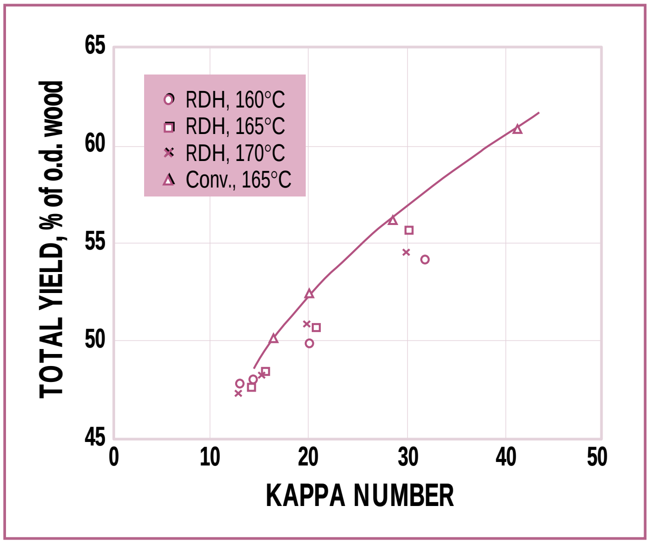


4. *Kappa number as a function of H-factor for RDH and conventional batch pulping of white oak at three levels of white-liquor cooking temperature*

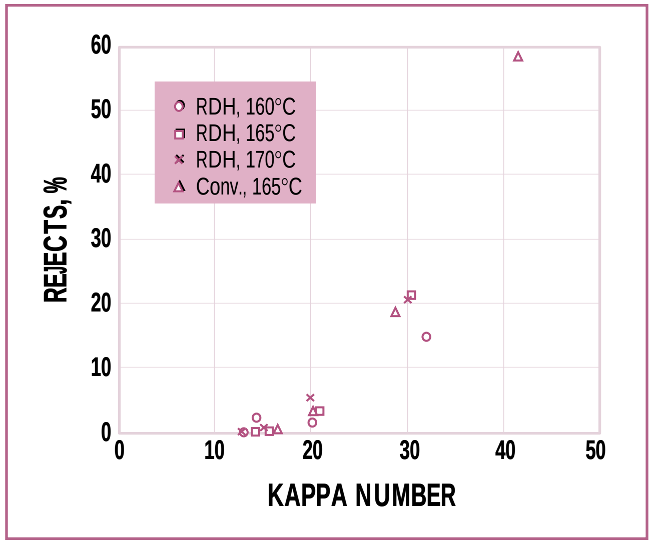
amount of rejects at a given extent of delignification.

Pulp yield at a given kappa number was lower for the RDH pulps than for the conventional batch cooks, as seen in Fig. 3. This contrasts with the results of equivalent *(6, 14, 15)* or higher RDH yields *(4, 16)* reported for softwoods. One possible explanation for this may be the increased dissolution of xylans in hardwood pulping. The white-liquor alkali concentration for an RDH cook is higher than that of a conventional cook, with the liquors removed during the cook prohibiting any xylan redeposition onto the fibers. Xylan redeposition in hardwood conventional cooks has been shown to contribute as much as 3% on pulp to the total pulp yield *(16)*. While xylans were not measured in this study, they may have played a role in the lower pulp yields for RDH pulping.

Effect of white-liquor cooking temperature. The effect of white-liquor cooking temperature was determined with a set of RDH cooks conducted with white oak chips at 14% EA charge (as Na_2O, % on wood) at 160°C, 165°C, and 170°C. Inlet residual alkali concentration of the



5. Total pulp yield as a function of kappa number for RDH and conventional batch pulping of white oak at three levels of white-liquor cooking temperature



6. Pulp rejects as a function of kappa number for RDH and conventional batch pulping of white oak at three levels of white-liquor cooking temperature

black liquors (warm and hot) was 7 g NaOH/L.

Figure 4 shows the kappa numbers obtained over a range of *H*-factor for the RDH pulps and a conventional kraft batch cook at 165°C. Again, the kappa numbers at a given *H*-factor were lower for the RDH pulps. The overlap of the RDH curves indicates that (a) the activation energy of 32,000 cal/mol used to calculate *H*-factor is satisfactory for describing the pulping system *(17)* and (b) the *H*-factor is an effective indicator for extent of cooking *(18)*.

The pulp yields at a given kappa number were lower for the RDH cooks at all three temperatures compared with the conventional cooks at 165°C, as seen in Fig. 5.

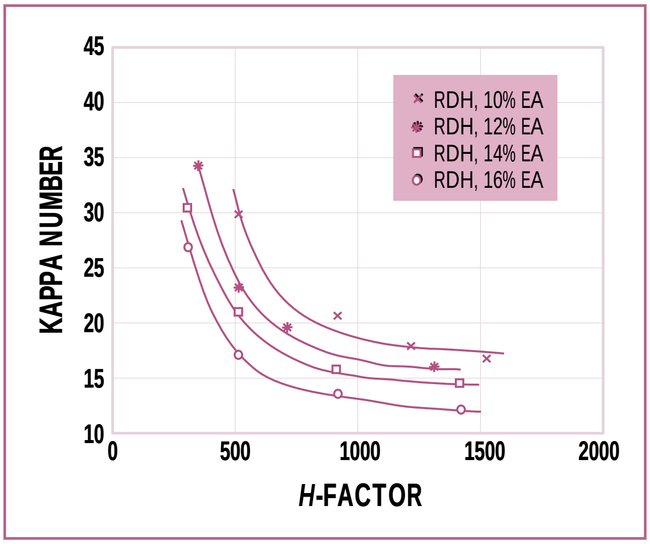
Pulping rejects as a function of kappa number were essentially independent of temperature and similar for the RDH and conventional cooks, as seen in Fig. 6. The results in Figs. 4–6 indicate that the RDH process produced comparable hardwood pulps over the temperature range of 160–170°C.

Effect of white-liquor effective alkali. The white-liquor charge was varied from 10–16% EA (as Na_2O, % on wood) using white oak chips and a cooking temperature of 165°C. The average black-liquor alkali concentrations (warm and hot black liquor) for these cooks was 7 g NaOH/L. This value was held reasonably constant from cook to cook by scheduling the order of the high and low effective-alkali pulping and by using a large reservoir for the warm and hot black liquors.

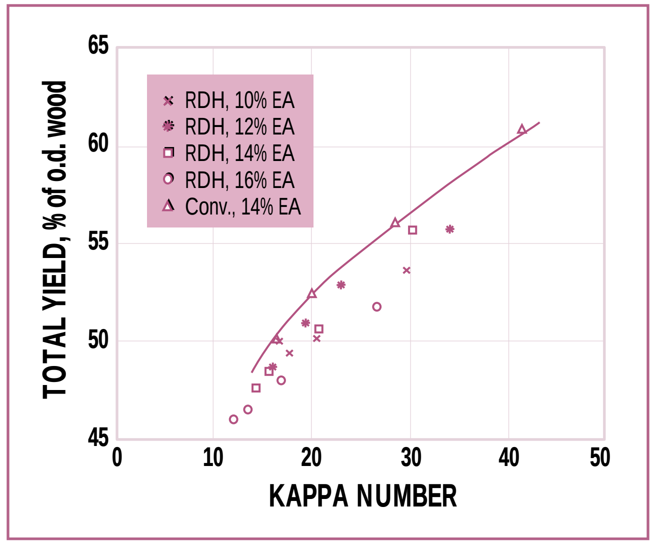
Figure 7 shows that as the charge of effective alkali was increased, the kappa number obtained at a given *H*-factor decreased, similar to the behavior commonly observed for conventional pulping. The data in Fig. 8 do not show a definitive trend for the relationship between pulp yield and kappa number for the RDH cooks at various levels of alkali charge. However, it does appear that the cooks at higher alkalinity have a slightly lower yield. Again, the RDH yields were all slightly lower than the conventional cook conducted with a white-liquor charge of 14% EA. The pulping rejects produced by the RDH cooks and conventional cooks were all roughly equivalent, as seen in Fig. 9.

At the end of the warm and hot black-liquor phases, the residual alkali concentrations for these cooks varied from 0.2 g NaOH/L to 0.9 g NaOH/L, with most of the cooks having a residual alkalinity in the range of 0.5 g NaOH/L . Total alkali depletion was not observed for the cooks with black-liquor charges (warm and hot) of 7 g NaOH/L.

Figure 10 shows the white-liquor residual alkali content for the RDH pulps in this series. It is clear from Fig. 10, along with Fig. 7, that low white-liquor effective-alkali charges (10–12%) can produce pulps with acceptable kappa numbers, albeit at long *H*-factors. However, low effective-alkali charges may yield black liquors with insufficient residual alkalinities for use in subsequent cooks. In determining the required value of white-liquor alkali charge, an alkali balance must be done over the entire pulping process. If the white-liquor alkali concentration is too high, residual alkali concentration will build up in the black liquor used to pretreat the chips. Conversely, a white-liquor alkali concentration



7. Kappa number as a function of H-factor for RDH pulping of white oak at four levels of white-liquor alkali charge



8. Total pulp yield as a function of kappa number for RDH and conventional batch pulping of white oak at four levels of white-liquor alkali charge

that is too low will lead to alkali depletion of the black liquors. The extent of RDH pulping effect is determined by the alkali content of the black liquors, as discussed in the following section. Consideration also should be given to the time required to reach the target kappa number, since it will take longer to achieve the target for lower levels of effective alkali.

Effect of black-liquor residual effective alkali. Pulping cooks were conducted with white oak chips in which the effective alkali concentrations of the warm and hot black liquors were varied, while white liquor was maintained at 14% EA (as Na_2O, % on wood). The following black-liquor alkali levels were used: 2.5 g NaOH/L, 7 g NaOH/L, and 12 g NaOH/L.

Figure 11 shows that for all three levels of black-liquor alkali, the delignification achieved at 14% EA during the RDH cooks at a given *H*-factor was greater than that attained for conventional kraft pulping. However, this RDH effect diminished as black-liquor residual alkali content was decreased, with the kappa numbers leveling off at higher *H*-factors.

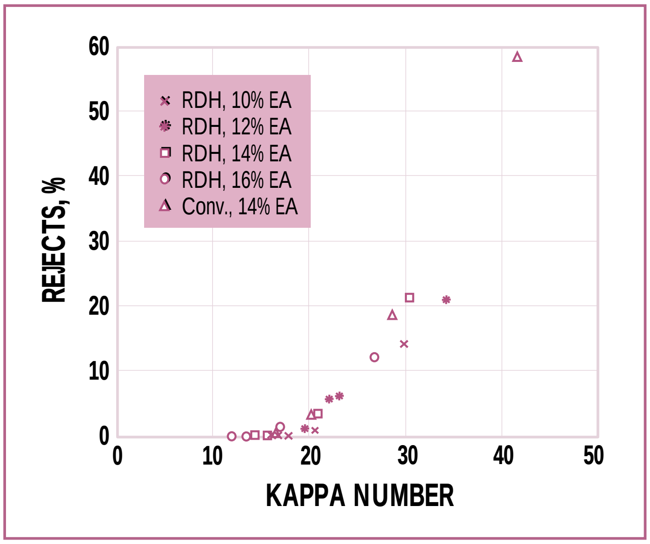
Conductometric titration of the black liquors at the conclusion of the warm and hot phases indicated that the liquors with 2.5 g/L alkali became depleted before the end of the respective black-liquor phases, with 0.0 g NaOH/L remaining. Trace amounts of alkali (0.2–0.9 g NaOH/L) were detected in the black liquors (warm and hot) retrieved from the cooks using alkali concentrations of 7 g/L. Residual alkali was distinctly present (0.8–1.9 g NaOH/L) in the liquors retrieved from cooks performed with 12 g NaOH/L in the black liquors.

The extent of alkali present in the early phases of the RDH cook determines the degree to which the accelerated delignification of the RDH process can proceed. Thus the amount of residual alkali in the black liquor is an important consideration. Nevertheless, a minimum initial black-liquor residual alkali content was not found below which the RDH effects were lost entirely for hardwood pulping. This differs from the findings of Pu *(14)* for loblolly pine, which show that an alkali concentration below 4 g/L effectively suspends the RDH delignification benefits. Depletion of alkali during the black-liquor cooking phases should also be avoided from the perspective of process stability. Low black-liquor alkalinity can have adverse repercussions on the kraft recovery system, where a neutral or acidic black liquor can cause precipitation in the evaporators.

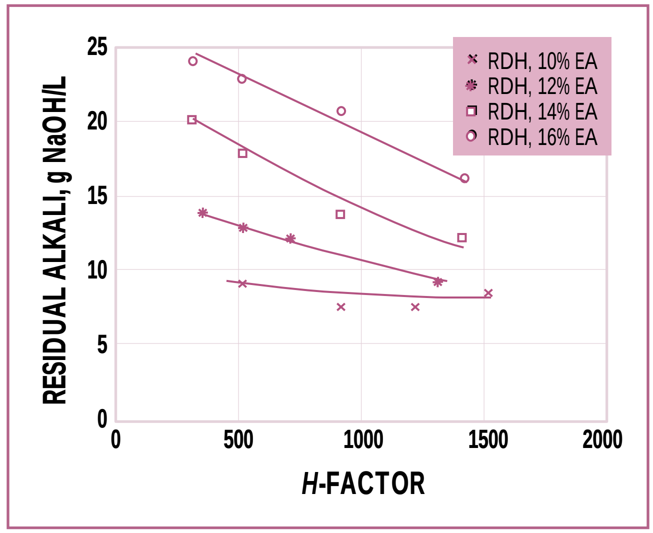
The pulp yields for all three sets of conditions were equivalent at a given kappa number, as seen in Fig. 12. Thus the selectivity for lignin removal remained approximately the same for the RDH cooks over the black-liquor alkali range of 2.5–12 g NaOH/L.

RDH pulping of five hardwood species at constant conditions

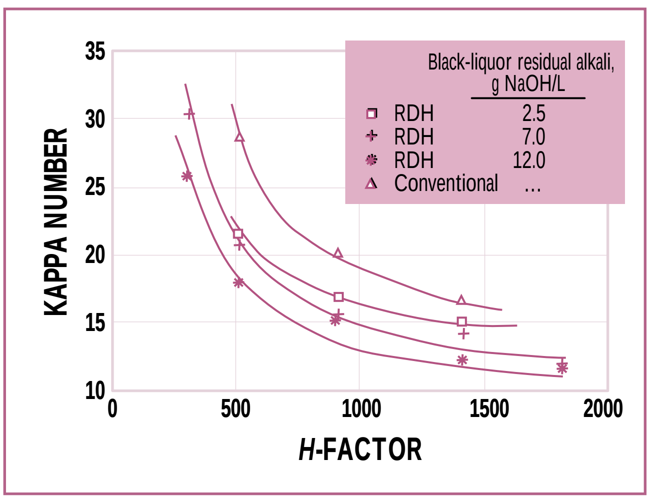
Five hardwood species commonly used for pulping in the southern United States—white oak, red oak, red maple, sweetgum, and yellow poplar—were pulped using the RDH process. The objectives were to quantify the response of these species to RDH pulping and to identify potential difficulties regarding their use in an RDH process. Hardwoods are known to exhibit a wide spectrum of pulping behaviors as a result of variations in wood structure



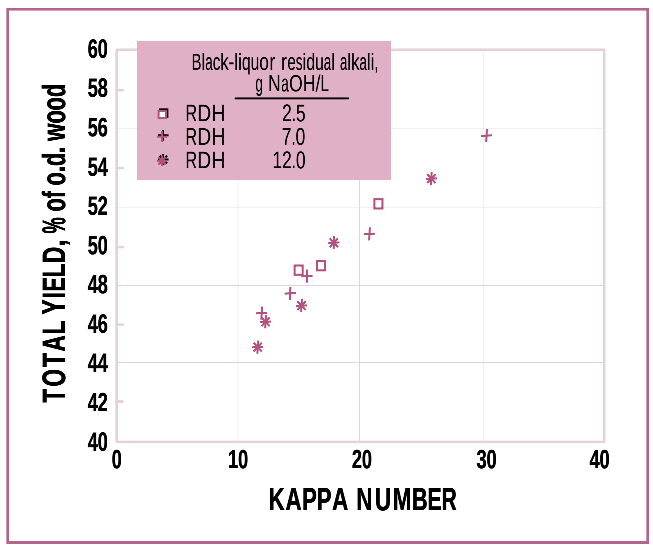
9. Pulp rejects as a function of kappa number for RDH and conventional batch pulping of white oak at four levels of white-liquor alkali charge



10. White-liquor residual alkali as a function of H-factor for RDH pulping of white oak at four levels of white-liquor alkali charge



11. Kappa number as a function of H-factor for RDH and conventional batch pulping of white oak at three levels of black-liquor effective alkali



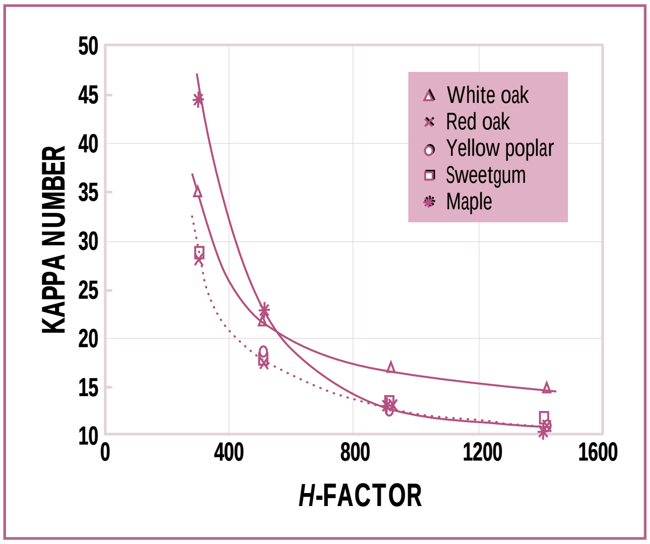
12. Total pulp yield as a function of kappa number for RDH pulping of white oak at three levels of black-liquor effective alkali

and chemical composition among species.

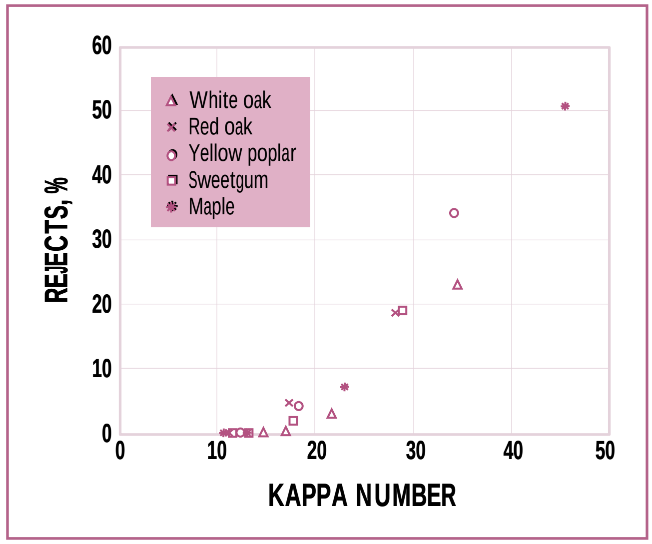
Figure 13 shows the kappa number vs. *H*-factor for RDH cooking of the different species. Similar delignification profiles were observed for yellow poplar, sweetgum, and red oak. The red maple and white oak each exhibited pulping behavior that deviated from the remaining species.

The red maple showed a delayed pulping response, with the kappa numbers very high at low *H*-factors (below 900) relative to those of the other species. At *H*-factors above 900, the red maple kappa numbers reached equal values with the yellow poplar, sweetgum, and red oak pulps. This delayed pulping behavior may partially be attributed to slower diffusion of pulping chemicals into the red maple chips. Red maple has a tight wood structure, with relatively few vessel elements present in a given surface area to aid chemical transport.

The white oak displayed consistently higher kappa numbers (approximately 3–5 units higher) than most of the other hardwoods



13. Kappa number as a function of H-factor for RDH pulping of five hardwood species



14. Pulp rejects as a function of kappa number for RDH pulping of five hardwood species

KEYWORDS

Black liquors, effective alkali, hardwoods, kappa number, kraft pulping, pulping, rapid displacement heating, southern USA, sulfidity, temperature, white liquors, wood species.

studied over the entire *H*-factor range used. The high density of white oak (typical green-basis specific gravity = 0.55–0.64) may be a contributing factor to the pulping resistance demonstrated, as it was the most dense wood used in the pulping comparison. While oaks characteristically have large vessels running through the wood structure, those of white oak are commonly occluded with growths called tyloses that obstruct or completely block the vessel channels, thus inhibiting transport of pulping chemicals *(19, 20)*.

It is likely that the higher density of white oak and red maple was a factor in their slower delignification response. However, Fig. 14 shows that the pulping rejects obtained from the cooks of white oak and red maple were comparable (at a given kappa number) with the other species studied, suggesting that diffusional limitations were not entirely responsible for the lower extent of delignification at a given *H*-factor.

Figure 15 shows the pulp yield vs. kappa number for the five hardwood species. The sweetgum and white oak had the lowest pulp yields at a given kappa number. Red oak and yellow poplar maintained the highest pulp yields at a given kappa number. The difference between the highest and lowest yields is about 3%. Such differences would have a significant effect on the operation and profitability of a mill pulping hardwoods. The fact that the pulping responses were varied across the species tested emphasizes the diverse structural and chemical differences common among hardwoods.

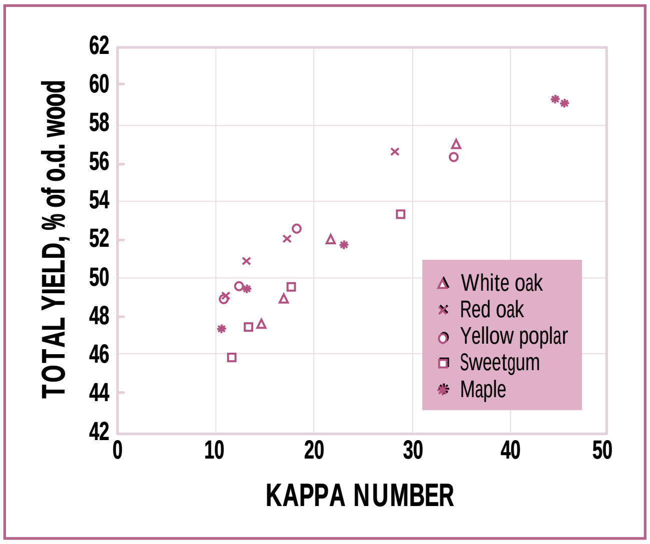
Finally, Fig. 16 shows the residual alkali concentration at the end of the pulping phase of the cook. While it appears that there are differences in the residual alkali concentrations—for example, red oak shows a higher residual alkali concentration than other species—these differences do not appear to be too dramatic. It would be of interest in future work to measure the alkali consumption throughout an entire RDH cook for these wood species.

CONCLUSIONS

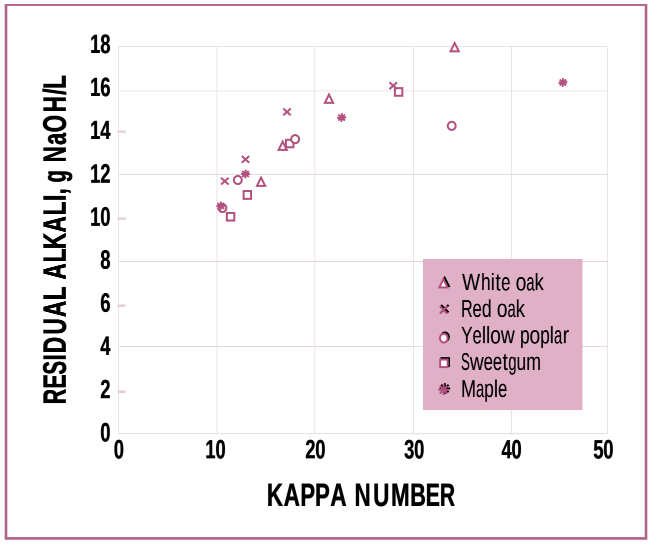
Southern hardwoods were pulped using a laboratory RDH process. Traditional hardwood kappa numbers were achieved at lower *H*-factors than required by conventional batch kraft pulping. Extended delignification to kappa no. 10–15 was demonstrated using a white-liquor charge of 14% EA and 165°C pulping temperature. Pulping yields at a given kappa number were lower for RDH pulping than for conventional batch cooking, but the RDH and conventional cooks produced the same amount of screen rejects at a given kappa number.

In varying the conditions of the RDH cooks, pulping temperatures of 160–170°C appeared to produce pulps of comparable kappa number and yield at a given *H*-factor. Increasing the white-liquor effective-alkali charge to the RDH cooks accelerated delignification, similar to the results seen in conventional batch kraft pulping, but with a slight decrease in pulp yield at a given kappa number.

Depletion of the residual alkali concentration in the black liquor



15. Total pulp yield as a function of kappa number for RDH pulping of five hardwood species



16. White-liquor residual alkali as a function of kappa number for RDH pulping of five hardwood species

diminished the rate of delignification, but it did not change the yield at a given kappa number. That is, alkali depletion did not change the pulping selectivity for lignin removal. Moreover, a minimum black-liquor alkali concentration was not found below which the rate of delignification slowed to that of conventional pulping. However, 7 g NaOH/L initial residual alkali appeared to be the minimum value for maintaining detectable levels of alkali in the liquor at the end of the black-liquor pretreatment phase.

Pulping results for five hardwood species showed that white oak had the slowest rate of delignification, with higher kappa numbers than the majority of the hardwoods over the *H*-factor range considered. Red maple exhibited a delayed response to pulping, requiring a minimum *H*-factor of approximately 900 to reach low kappa numbers. Red oak and yellow poplar demonstrated the greatest selectivity for lignin removal, while sweetgum and white oak had the poorest selectivity. TJ

Matheison, graduate student, and Gustafson, associate professor, are affiliated with the College of Forest Resources, University of Washington, Box 352100, Seattle, WA 98195-0001.

The support of Willamette Industries Inc. for this research is gratefully acknowledged.

Received for review Dec. 12, 1994.

Accepted Oct. 30, 1995.

LITERATURE CITED

1. Swift, L. and Norman, R., "RDH—The pulping system of the future: A progress report," *SPCI 87 New Available Techniques and Current Trends Conference Proceedings*, Stockholm, Sweden, 1987, p. 564.
2. Evans, J.C.W., *Pulp Paper* 63(7): 132(1989).
3. Young, J., *Pulp Paper* 63(10): 61(1989).
4. Tikka, P. O., *TAPPI Pacific Section Annual Seminar Proceedings*, TAPPI PRESS, Atlanta, Sept. 1990.
5. Kaiser, M. and Pierre, R., *TAPPI 1986 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, pp. 627–32.
6. Sainiemi, J., *TAPPI 1986 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 643.
7. Mera, F. E. and Chamberlin, J. L., *Tappi J.* 71(1): 132(1988).
8. Grant, R. S., *Tappi J.* 66(3): 121(1983).
9. Tikka, P. O., Virkola, N. E., Pursiainen, S. A., *et al.*, *Tappi J.* 71(2): 51(1988).
10. Matheison, B. A., Master's thesis, University of Washington, Seattle, 1991.
11. Vikstrom, B., Lindblad, M. S., Parming, A., *et al.*, *TAPPI 1988 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 669.
12. LeMon, S. and Teder, A., *Svensk Papperstid.* 76(111): 407(1973).
13. Sjoblom, K., Mjoberg, J., and Hartler, N., *Paperi Puu* 65(4): 227(1983).
14. Pu, Q., McKean, W. L., and Gustafson, R. R., *Appita* 44(6): 399(1991).
15. Andrews, E. K., *Tappi J.* 72(11): 55(1989).
16. Sjoblom, K., *Nordic Pulp Paper Res. J.* 3(1): 34(1988).
17. Technical Association of the Pulp and Paper Industry, *Pulp and Paper Manufacture*, Vol. 5, *Alkaline Pulping*, TAPPI PRESS, Atlanta, 1989, p. 117.
18. Vroom, K. E., *Pulp Paper Mag. Can.* 58(3): 228(1957).
19. Koch, P., *Utilization of Hardwoods Growing on Southern Pine Sites*, Agriculture Handbook No. 605, Vol. 1, USDA Forest Service, Washington, DC, 1985, pp. 295, 303.
20. Panshin, A. J. and deZeeuw, C., *Textbook of Wood Technology*, McGraw-Hill, New York, 1980, pp. 207, 568, 607.