Delignification by hot alkali extraction

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ABSTRACT: Previous studies have shown that brownstock lignin content can be reduced by slow leaching with water. Laboratory results obtained in this study show that delignification can be increased substantially by extraction in alkaline conditions at elevated temperature. The method shows promise as a means of delivering low-kappa-number brownstock to the bleach plant without suffering losses of bleached yield or pulp strength.

KEYWORDS: Bleaching, defibration, delignification, hot alkali extraction, kappa number, kraft pulps, leaching, lignin content, oxygen, pH, pretreatment, temperature, washing.

The release of lignin compounds from cooked and washed kraft pulp fibers can be enhanced under suitable conditions. However, the mechanisms of lignin transfer are complex. The rate and extent to which dissolved lignin can be released from within the fiber are governed by diffusion and sorption phenomena as well as by the molecular size, porosity, and structure of the cell-wall matrix.

Goring (*1*) has studied these mechanisms and concluded that transfer occurs in two distinctly different phases:

1. A rapid phase (seconds) during which dissolved matter is removed from the fiber surface and the lumen
2. A slow phase (hours) during which macromolecules, mainly lignin, diffuse from the fiber wall into the surrounding liquid.

Previous work has shown that the rate of diffusion is influenced by the cationic strength of the wash liquor (*2*) and by the temperature (*3, 4*). It is also known that the rate of diffusion is strongly dependent on pH. Lignin begins to precipitate at pH below 10 (*5*). The pH of liquid entrained within the fibers can drop so much in a countercurrent washing chain that dissolved lignin precipitates and becomes unavailable for further extraction. At high pH, however, lignin reacts with free alkali, especially at elevated temperature (*6*). The fiber swelling that occurs under alkaline conditions also can have a favorable impact on the transfer of lignin from fibers.

This study (*7*) examines the conditions under which lignin can be extracted from kraft pulp fibers and explores the limits of lignin extraction. The practical implications of the findings are also discussed.

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Testing

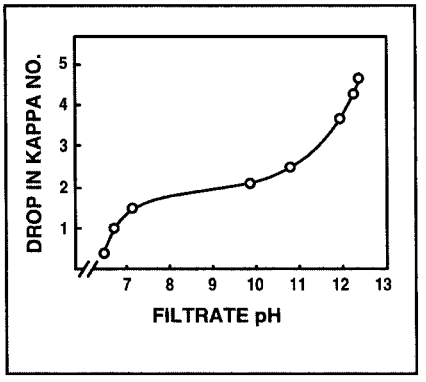
Kraft pulps were cooked from Scandinavian pine chips in laboratory digesters to kappa no. 25–32 and then fiberized. The fiberized pulps were washed to different degrees using varying amounts of pure 45°C tap water. All pulps were treated in medium consistency. Temperature during treatment was varied between 100°C and 170°C. Time of treatment also was varied, as was the alkalinity and ionic strength of the suspension liquid phase.

Extraction of lignin from well-washed pulp

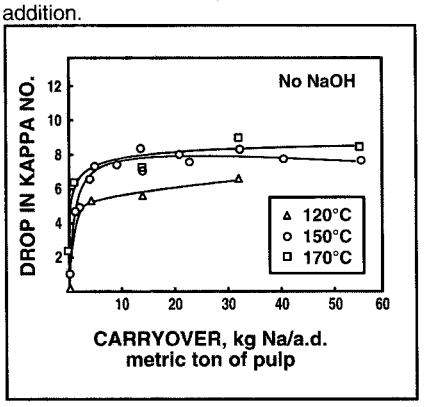
Figure 1 shows the results obtained upon treatment of a well-washed pulp (kappa no. 29.5) at 150°C for 30 min at 10% consistency. The initial result was a kappa number drop of less than one unit. This modest drop was independent of Na ionic strength. The pH of the liquid phase remained at 6.7–7.0. Apparently, the low pH of the well-washed pulp caused the dissolved but entrained lignin to precipitate within the fiber wall. Lignin extraction was improved by addition of alkali to the pulp. An alkali charge in excess of 3% NaOH added on pulp was required to obtain filtrate with pH greater than 12. The associated drop in kappa number was only 4.7 units at best.

A kappa number drop of 6.4 units was obtained by extending the extraction time to 240 min. Again, the Na ion concentration had no significant impact on performance. A kappa number drop of roughly ten units was obtained by raising the treatment temperature to 170°C (full cooking temperature) and adding 10% NaOH on pulp.

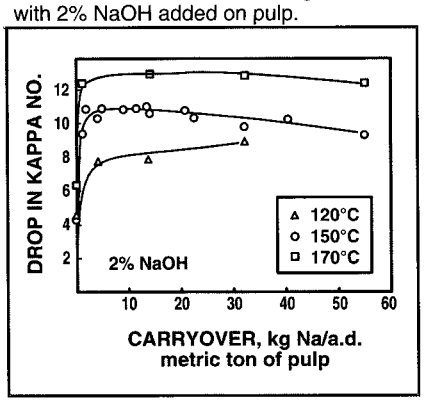
1. Delignification as a function of filtrate pH for a well-washed softwood kraft pulp (kappa no. 29.5). Extraction conditions: 10% consistency, 150°C, 30 min, alkali addition of 0–3% NaOH on pulp (pH 12 obtained at 3% NaOH).



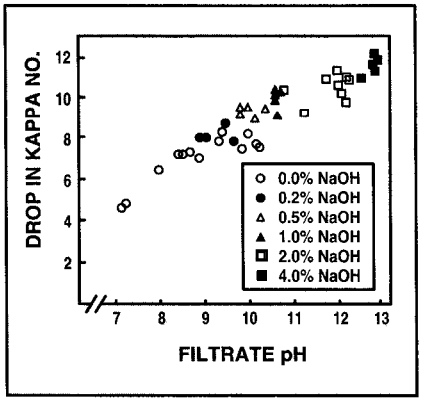
2. Delignification as a function of black-liquor carryover to the extraction phase for kraft pulp (kappa no. 31.4) at three treatment temperatures. Other extraction conditions: 10% consistency, 30 min, no alkali addition.



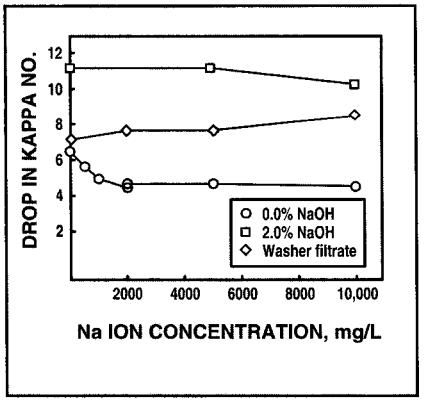
3. Delignification as a function of black-liquor carryover to the extraction phase for kraft pulp (kappa no. 31.4) at three treatment temperatures. Other extraction conditions: same as in Fig. 2 but with 2% NaOH added on pulp.



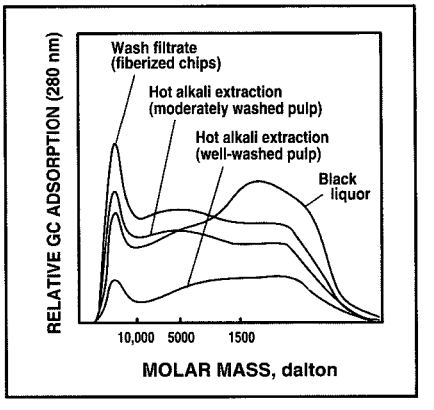
4. Delignification as a function of filtrate pH for kraft pulps (kappa no. 30.4–31.4) at various levels of alkali addition. Other extraction conditions: 10% consistency, 150°C, 30 min, black-liquor carryover of 1.5–55 kg Na/a.d. metric ton of pulp.



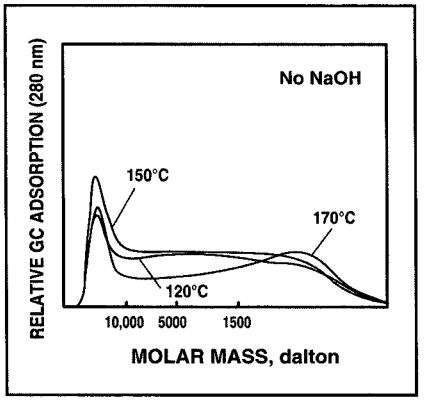
5. Delignification as a function of Na ion concentration in the filtrate for kraft pulp (kappa no. 30.4) at three levels of alkali addition. Other extraction conditions: 10% consistency, 150°C, 30 min, black-liquor carryover of 4.5–4.9 kg Na/a.d. metric ton of pulp.



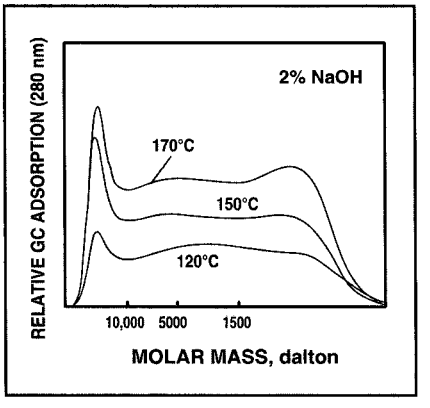
6. Distribution of molar mass in original black liquor, in wash filtrate from untreated chips, and in filtrates from hot alkali extraction (150°C, 30 min, 2% NaOH) of a well-washed pulp and a moderately washed pulp (carryover of 9.3 kg Na/a.d. metric ton). Pulp kappa no. 29.5–31.4.



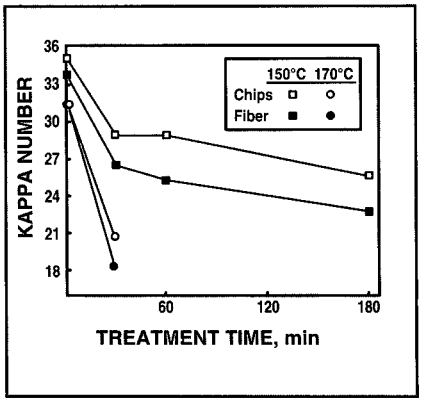
7. Effect of extraction temperature on distribution of molar mass in hot alkali filtrate for kraft pulp (kappa no. 30.4). Other extraction conditions: 10% consistency, 30 min, no alkali addition, black-liquor carryover of 4.5 kg Na/a.d. metric ton of pulp.



8. Effect of extraction temperature on distribution of molar mass in hot alkali filtrate for kraft pulp (kappa no. 30.4). Other extraction conditions: same as Fig. 7 but with 2% NaOH added on pulp.



9. Kappa number as a function of extraction time at temperatures of 150°C and 170°C for cooked chips and fibers. Other extraction conditions: 10% consistency, 2% NaOH added on pulp.



Impact of pretreatment washing

The results obtained with well-washed pulp suggested that more lignin could be extracted from the pulp if pretreatment washing were halted before the pH of the liquid within the fiber dropped below a level at which significant lignin precipitation could occur. To prove this point, a series of tests was carried out with pulp that had been incompletely washed prior to extraction.

A pulp cooked to kappa no. 31.4 was fiberized and washed with water so that the carryover in the pulp to be treated varied from 0 to 55 kg Na/a.d. metric ton of pulp. **Figure 2** shows a marked improvement in extractability, even with no alkali addition. The figure also shows that the beneficial effect of the residual black liquor in the pulp peaks at modest carryover levels. **Figure 3** shows that extractability improved further upon addition of 2% NaOH on pulp. Both Figs. 2 and 3 demonstrate a clear temperature effect, with extraction improving at elevated temperature. **Figure 4** illustrates that extractability is clearly dependent on pH. Kappa number reductions of 12–13 units have been achieved at high pH, corresponding to a 38% reduction in the original residual lignin.

The Na ion concentration again had no significant impact on delignification, as seen in **Fig. 5**, which shows the effect of washing with dilute black liquor containing Na ion at concentrations of 0–10,000 mg/L. The washing liquor in a countercurrent industrial washing chain always contains a certain amount of alkali. Figure 5 shows that the alkalinity of the black liquor helps somewhat, but not as much as direct addition of NaOH.

Effect of fiber swelling

Fiber swelling during extraction was studied by measuring the pulp's water-retention value (WRV). There was no clear relationship between WRV and extractability, indicating that the impact of alkali addition cannot be explained by the open pore structure caused by fiber swelling. Apparently, the alkali somehow reacts directly with lignin.

Molar mass distribution of extracted substances

The molar mass distribution in the filtrate changes when alkali reacts with lignin during extraction. Gelchromatographic (GC) measurement (Sephadex G-50 M) of filtrates containing extracted substances showed that the molar mass distribution of black liquor deviates considerably from that measured from washing or extraction filtrate. **Figure 6** compares the molar mass distributions of extracted substances in the original black liquor, in the wash filtrate collected from untreated fiberized chips, and in the filtrates after hot alkali extraction of a well-washed pulp and a pulp containing carryover of 9.3 kg Na/a.d. metric ton. As seen in Fig. 6, the black liquor contains significantly more small molecules than the filtrates. This suggests that (a) larger molecules are left behind in the fiber material during the early stages of washing or (b) substances already transported out of the chips during the cook are being broken down into smaller aggregates.

Figures 7 and 8 show that elevated treatment temperature and alkali addition reduce the average molar mass of the substance extracted, while the fraction of large molecules over 10,000 dalton remains unchanged. This suggests that some of the dissolved material in the fiber-wall matrix is being broken down into smaller molecules and hence transformed into extractable size. However, the results also may reflect lignin macromolecules splitting in the free-liquid phase. Because of the limitations of the analytical method used, the results are not conclusive.

Extraction from cooked chips

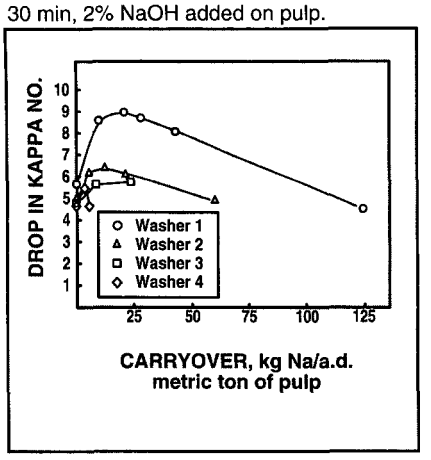
Many industrial processes involve washing of chips before fiberization. Examples are HiHeat washing in continuous digesters and liquor displacement in batch digester systems. It is hence interesting to compare the rate and extent of lignin extraction from chips and fibers under otherwise comparable conditions. The data in **Fig. 9** clearly show that extraction from pulp fibers is faster and more efficient, although a considerable proportion of lignin can be extracted from cooked chips.

Extraction from commercial pulps

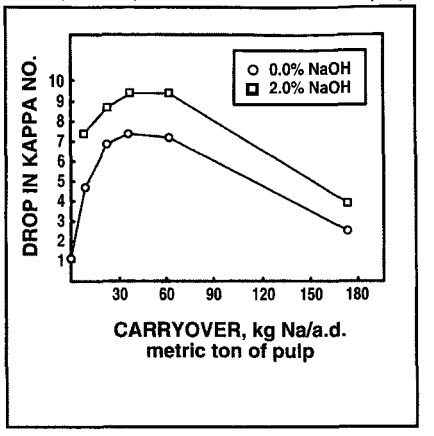
Industrial processes involve delay times at conditions that facilitate extraction, similar to what has been studied here with laboratory pulps. It is thus likely that lignin is extracted to some extent in all current mill processes. We carried out extraction experiments on pulps taken from various points of industrial processes in an effort to establish the potential for further delignification.

Figure 10 shows the kappa number drops achieved with pulps taken from drum washers 1–4 in a mill with conventional batch cooking. The results imply that a further kappa number reduction of 6–8 units could be achieved in that mill by applying a hot alkaline-extraction stage. Corresponding data from a plant using digester displacement are presented in **Fig. 11**. The maximum effect (9-unit drop in kappa number) is reached if extraction is carried out using 2% NaOH on a pulp that is washed down to a carryover corresponding to 30–60 kg Na/a.d. metric ton. Extraction of samples taken from the blow line of a continuous digester with HiHeat wash showed a kappa number drop of 5–6 units.

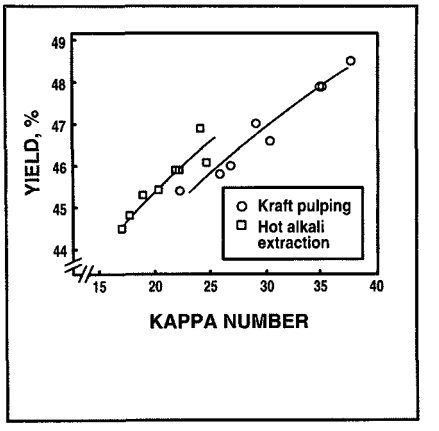
10. Delignification after hot alkali extraction of pulp samples (kappa no. 28–33) taken from drum washers in a batch kraft mill. Extraction conditions: 10% consistency, 150°C, 30 min, 2% NaOH added on pulp.



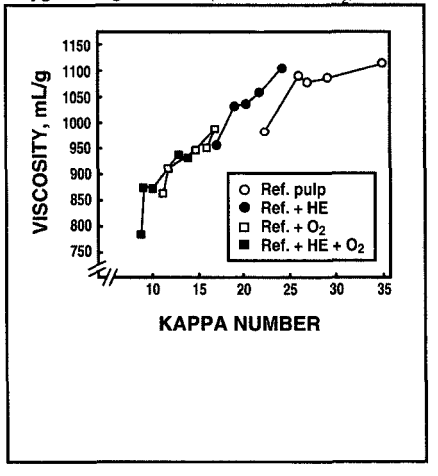
11. Delignification after hot extraction of pulp samples (kappa no. 24.6) taken from kraft batch cooking with digester displacement. Extraction conditions: 10% consistency, 150°C, 30 min, 0 or 2% NaOH added on pulp.



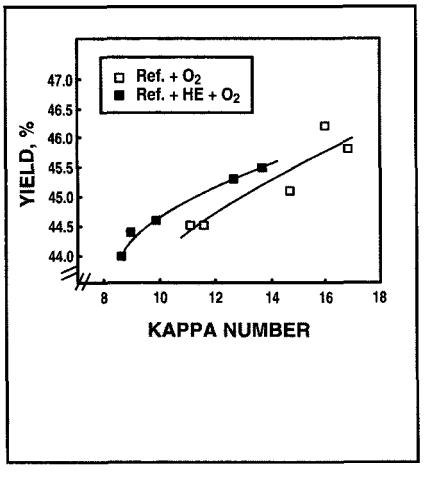
12. Yield as a function of kappa number for hot alkali extraction and for kraft pulping. Extraction conditions: 10% consistency, 150°C, 30 min, 2% NaOH added on pulp.



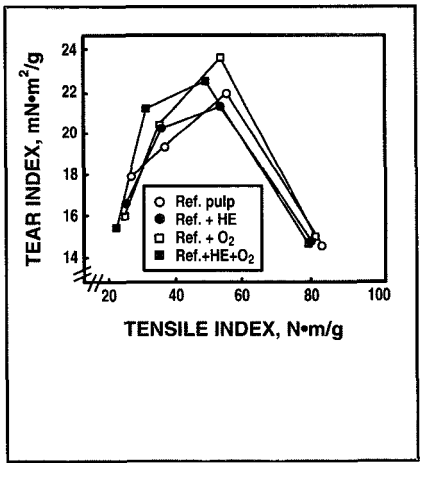
13. Viscosity as a function of kappa number for pulps delignified by standard kraft pulping (Ref.), kraft pulping plus hot extraction (Ref. + HE), kraft pulping plus oxygen delignification (Ref. + O_2), and kraft pulping plus hot extraction plus oxygen delignification (Ref. + HE + O_2)



14. Pulp yield as a function of kappa number for oxygen-delignified kraft pulps with or without extraction



15. Tear index vs. tensile index for (D+C)EDED-bleached kraft pulps delignified with or without extraction



Selectivity of extraction

The data presented so far have focused on lignin reduction as expressed by a drop in kappa number. What happens with the carbohydrates? Results from a separate study presented in **Fig. 12** show that the kappa number reduction achieved by hot alkali extraction is more selective than that achieved by direct cooking. This suggests that extraction dissolves carbohydrates relatively less than cooking. **Figure 13** shows that pulp viscosity is better retained in extraction and that this seems to prevail also after oxygen delignification. **Figure 14** shows that the total yield after oxygen delignification is higher for extracted pulps than for pulps that have only been cooked.

Bleaching

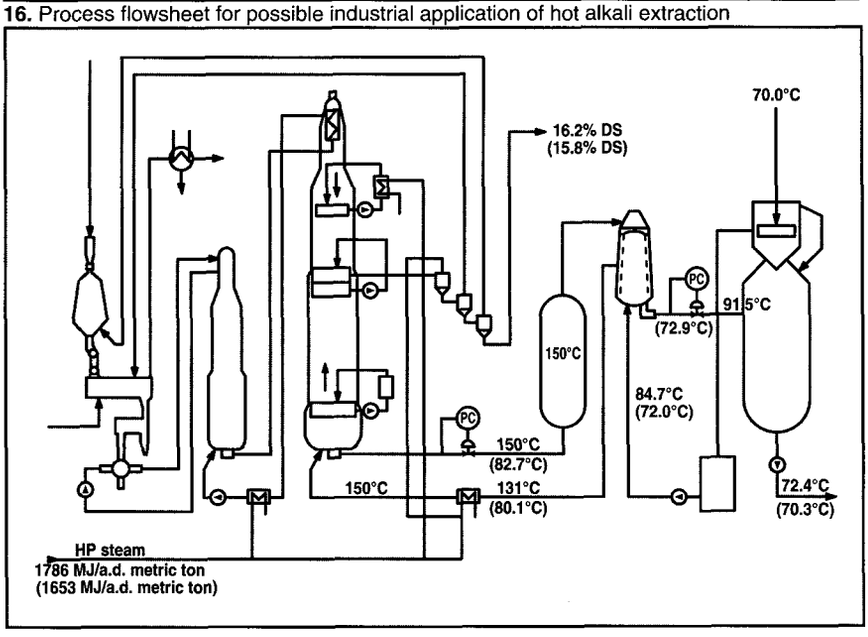
Results for pulps bleached with a (C+D)EDED sequence are presented in **Table I.** The data show an excellent response to bleaching for the extracted pulps. The total yield of the fully bleached, extracted, and oxygen-delignified pulp is only 0.3 unit lower than that of the reference pulp, which was bleached from kappa no. 25.9. The oxygen-delignified reference pulp had a 0.2-unit lower yield than the corresponding extracted/oxygen-delignified pulp. This suggests that the improved selectivity of extraction is maintained through bleaching. The fact that it is possible to delignify softwood pulp down to kappa no. 9 (Ref. + HE + O_2) without losing yield or strength holds some promise for future process applications.

I. Bleaching response for kraft pulps delignified with and without hot alkali extraction*

	Reference pulp	*Ref. + HE*	*Ref. + O_2*	*Ref. + HE + O_2*
		Unbleached pulp		
Kappa number	25.9	18.9	11.6	9.0
Viscosity, mL/g	1091	1033	910	873
Yield, %	45.8	45.3	44.5	44.4
Brightness, % ISO	24.2	29.2	36.7	40.4
		Bleached pulp		
Viscosity, mL/g	996	952	875	816
Yield, %	43.4	43.6	42.9	43.1
Brightness, % ISO	87.6	88.2	88.9	89.5
Active chlorine, %	9.18	7.74	4.82	4.30
Bleaching yield, %	94.8	96.3	96.4	97.0

*HE = hot alkali extraction; O_2 = oxygen delignification.

16. Process flowsheet for possible industrial application of hot alkali extraction



Pulp strength

In terms of strength, extracted and oxygen-delignified pulps compare well with the corresponding reference pulps, as demonstrated in **Fig. 15.**

Discussion and conclusions

Efficient hot alkali extraction is best carried out using fiberized chips, high temperature (150°C), and pretreatment washing to a carryover level of 20–40 kg Na/a.d. metric ton of pulp. For digesters blown at 90°C, where circulating liquor must be cooled before digester displacement, operation at this temperature increases heat consumption (as 14-bar steam) by an additional 2300 MJ/a.d. metric ton of pulp. However, the heat economy can be improved considerably if the pulp can be blown hot at a pressure that does not cause the steam to flash.

Figure 16 shows a possible application in which the additional heat demand is only 130 MJ/a.d. metric ton of pulp. A standard continuous cooking system with pressure diffuser is modified by adding a pressurized reactor (retention time 0.5 h, temperature 150°C, and pressure 5.0 bar) between the digester blow valve and the pressure diffuser. Filtrate from the pressure diffuser is heated with mainly flash steam to control blow temperature. Part of the additional heat demand is compensated by a reduced need for evaporation because of the higher dry-solids content of extracted liquor. Application of such a system would slightly increase the load to the recovery boiler and the demand for caustic.

Delignification by extraction is more selective than residual delignification by direct conventional cooking. Consequently, lignin content after cooking and washing can be reduced without excessive loss of yield. Moreover, delignification by extraction is additive with oxygen delignification. Some of the chemicals used in the oxygen-delignification stage are consumed by dissolved lignin entrained within the fiber wall. Extraction with hot alkali prior to oxygen delignification reduces the amount of such lignin, which means that more chemical can be applied to dissolution of lignin from the fiber. TJ

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