Production of bleachable pulp through catalytic oxygen–alkaline delignification of high-yield mechanical pulp

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ABSTRACT: Oxygen–alkaline (OA) delignification of ultra-high-yield pulp was carried out using a new catalyst. The catalyst accelerates OA delignification by a factor of 10 or more, so that the rate of catalytic delignification at 100°C is about equal to the rate of noncatalytic delignification at 150°C. The selectivity of delignification increases at the lower temperature, resulting in a 6–8% increase in pulp yield (based on oven-dry wood) and a 10–90% increase in viscosity compared with noncatalytic delignification at 150°C. Delignification at 100°C also opens the possibility of using conventional oxygen-bleaching equipment (mixers, towers) to delignify the mechanically separated fibers of high-yield and ultra-high-yield pulps.

KEYWORDS: Catalysts, delignification, high yield pulps, mechanical pulps, oxygen alkali pulps, oxygen pulping.

Oxygen–alkaline (OA) pulping of wood has several advantages: an absence of toxic and malodorous reagents and products, high pulp yield [55–58% of oven-dry (o.d.) wood], high pulp brightness (60–65% ISO), easy bleachability, and good strength properties. Efforts to develop commercially viable OA pulping processes have been ongoing since the 1970s. The chief impediments to development of a commercial process were oxygen's low solubility and high reactivity toward lignin. Together, these problems created a highly nonuniform distribution of oxygen across the thickness of the wood chip. Not until the mid-1980s did the first reports appear about the OA pulping of regular wood chips, which was made possible by the development of a unique pulsating digester by Russian specialists *(1)*. There also were concurrent efforts to develop an OA pulping process for the mechanically separated fibers of high-yield and ultra-high-yield pulps *(2, 3)*. These efforts were discontinued because the inevitable mechanical damage to fibers during separation and beating of high-yield pulps led to unacceptable decreases in the yield and strength of OA pulps *(3)*.

A new catalyst for the oxygen-delignification process was presented recently at the All-Russian Scientific Research Institute of the Pulp and Paper Industry (VNIIB) *(4)*. The catalyst—named KDK—opens a new approach to OA delignification of high-yield and ultra-high-yield pulps. Laboratory results in this report suggest that the catalyst accelerates OA delignification of high-yield pulps to such an extent that process temperatures can be reduced from 150°C to 100°C without increasing the pulping time.

The low pulping temperature results in the stabilization of polysugars in fibers, which would account for the observed mitigation of the yield and strength problems associated with OA delignification of high-yield pulps. The benefits of the catalyst are demonstrated by using the OA process to delignify samples of explosive autohydrolysis (EAH)

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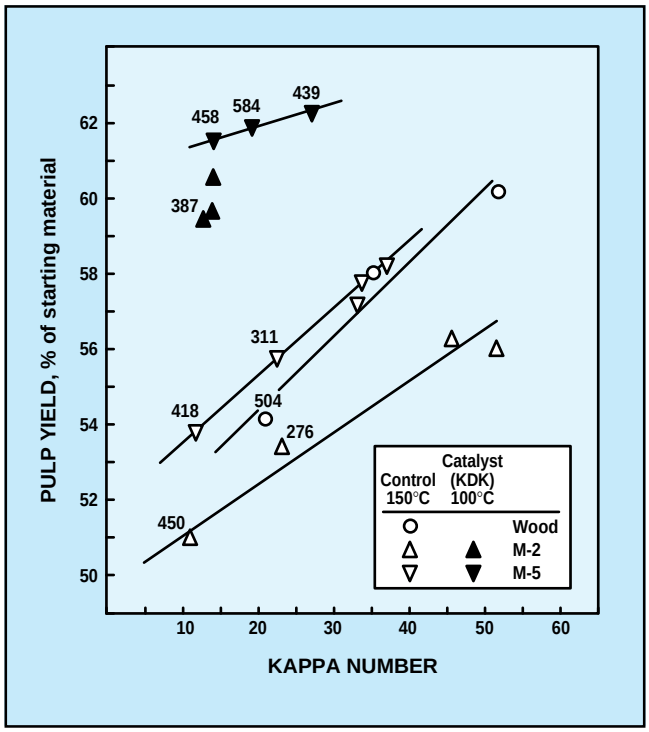
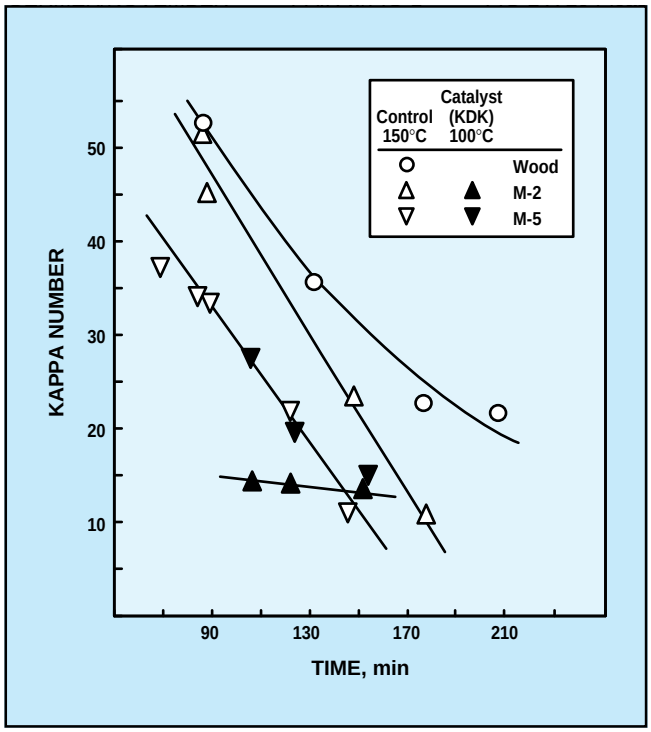
1. Pulp yield as a function of kappa number after OA delignification of birch wood (150°C) and EAH birch pulps (150°C or 100°C). OA delignification at 100°C was assisted catalytically. The numbers above the data points represent pulp viscosity (cm^3/g).



2. Kappa number as a function of pulping time after OA delignification of birch wood (150°C) and EAH birch pulps (150°C or 100°C). OA delignification at 100°C was assisted catalytically.



pulp—an ultra-high-yield semi-product—with and without the catalyst.

Experimental

Production of explosive autohydrolysis pulp

The two samples of EAH pulp used in the experiments were prepared by steaming birch chips at 220°C (428°F) in a reactor for 2 min (sample M-2) and 5 min (sample M-5) followed by explosive discharge into a blow vessel. Prior to steaming, the chips were soaked in a solution containing 3% sodium hydroxide and 2% hydrogen peroxide (based on o.d. wood). No special screening was performed with the EAH samples, except that the largest chunks of pulp, apparently different in the degree of fiber separation from the rest of the sample, were manually removed.

Oxygen–alkaline pulping

The OA cooks were performed with a 7.5-g/L NaOH solution in autoclaves of 130-mL capacity. The autoclaves were submerged in a glycerin bath and shaken reciprocally in the horizontal plane to improve agitation of the contents. Moreover, the liquor–wood ratio was increased to 30, and oxygen pressure was boosted to 2.94 MPa to facilitate mass transfer. Both the oxygen and the alkaline solution were introduced into the autoclaves before cooking. The portion of the autoclaves that was filled with the oxygen was 0.54. The total amount of catalyst added was about 0.5% (based on o.d. wood). This relatively large addition of catalyst served the research purpose of emphasizing changes, making them easier to observe. Further research showed that the amount of catalyst can be lowered without a significant loss of efficiency.

Viscosity was determined using solutions of the pulp samples in FeTNa (ferrous tartratesodium) according to ISO 5351/2-81.

Results and discussion

Noncatalytic OA delignification of EAH pulps

Two EAH pulp samples (M-2 and M-5, steamed at 220°C for 2 min and 5 min, respectively) were utilized in the experiments. The two EAH samples and a wood sample were noncatalytically OA-delignified to obtain controls for comparison with the catalytically delignified samples. The EAH samples were processed for the purpose of further biochemical treatment. Therefore, both the yield and the viscosity of the OA-delignified laboratory EAH pulps may be lower than would be expected for OA-delignified EAH pulps produced for papermaking *(5)*.

Figure 1 demonstrates that both EAH samples can be delignified at the usual OA-delignification temperature of 150°C. The yield for Sample M-2 was 0.8–4% lower than for the wood sample, while the yield for Sample M-5 was the same to 0.5%

higher than for the wood. The improvement in yield for Sample M-5 is probably a consequence of increased cellulose crystallinity resulting from deacetylation of hemicellulose, which is typically observed in EAH processing of wood *(6)*. For Sample M-2, the deacetylation apparently did not develop to an appreciable degree during the 2 min of autohydrolysis.

The activation of lignin, the weakening of the wood matrix, and the increased fiber penetrability—all of which are observed in high-yield and ultra-high-yield pulps *(7)*—facilitate OA delignification. Consequently, the EAH samples delignified more quickly than the wood sample, as seen in **Fig. 2**. OA delignification to the target kappa no. 20–40 for Sample M-2 was 1.15–1.3 times quicker than for wood. For Sample M-5, delignification was 1.6–1.8 times faster than for wood. Note that the *proportion* of lignin in Samples M-2 and M-5 was higher than that in the original wood because of partial hydrolysis and removal of hemicellulose during EAH processing of wood.

The higher rate of delignification for the EAH pulps consistently corresponds to higher pH values in the resulting waste liquors. For example, the waste liquor from the OA delignification of wood to kappa no. 22 had a pH of 8.7, while the waste liquor from the OA-delignified EAH pulps had a pH of 9.4–9.5 at kappa no. 22. This suggests that OA delignification could be carried out with a smaller alkali charge for EAH pulps than for wood.

The aforementioned advantages of OA delignification of EAH pulp at 150°C are not sufficient to attract the attention of pulp producers. There are two significant drawbacks. The first is the low viscosity of the OA-delignified cellulose obtained from the EAH pulp. At kappa no. 21–23, viscosity of the wood pulp is higher than that of the EAH pulps by a factor of 1.6–1.8, as seen in Fig. 1. The second drawback stems from problems with existing equipment. Conventional digesters cannot evenly and adequately distribute oxygen. Pulsating digesters easily accommodate OA cooking for chips of various size, but they are not designed for processing fibers.

Low-temperature (100°C) catalytic OA delignification of EAH pulps

The results of OA delignification of EAH pulp look quite different when the KDK catalyst is added to the process. The catalyst enables a decrease in the pulping temperature from 150°C to 100°C, which leads to a 6–8% increase in yield (o.d. weight) for EAH pulp, as seen in Fig. 1. Considering that the yield of the EAH pulp is above 90% of o.d. wood *(5)*, the resulting yield of the catalytically OA-delignified pulp may be 1.5–2% higher (based on o.d. wood) than the yield of OA-delignified pulp obtained directly from wood at 150°C.

In addition to the increased yield, the viscosity of the catalytically delignified product is also increased by 10–90%. Moreover, the viscosity of Sample M-5 at kappa no. 19.7 after catalytic delignification (100°C) was 16% higher than that of noncatalytically delignified wood pulp (150°C) at kappa no. 19.7.

It is quite likely that the conservation of cellulose, obtained through the catalytic OA delignification at 100°C, is even higher than is shown by the viscosity tests. The observed high yield is mainly due to a decrease in solubility and a consequent greater retention of hemicellulose in the pulp obtained at the lower temperature. The higher content of the hemicellulose, which has a relatively low molecular weight, should mask the results of viscosity tests by lowering them.

The kinetic results of the OA delignification at 100°C are significant as well, as seen in Fig. 2. For example, noncatalytic OA delignification (150°C) of the M-2 sample to kappa no. 22.7 took 1.4 times longer than catalytic OA delignification (100°C) of the M-2 sample to kappa no. 14.4. On the other hand, both the catalytically and noncatalytically OA-delignified M-5 samples required about the same duration of time to achieve a given kappa number. A comparison of the times required to achieve a given kappa number for the catalytically delignified EAH pulps (100°C) and the noncatalytically delignified wood samples (150°C) shows that the catalyst accelerates the process by a factor of 1.7–1.9. Using a temperature coefficient of 1.6, the lowest coefficient found in the literature for OA delignification of wood *(8)*, one can calculate that the catalyst increases the rate of OA delignification by a factor greater than 10.

There is no known catalyst that has the same activity and can produce the same effect. It is reported *(9, 10)* that at 100–120°C, the OA delignification of pulp and partially digested wood could be accelerated 3–5 times with an addition of salkomine [N,N-bis(saliciliden)-ethylenediamine cobalt (II)] in amounts of 0.1–1% of the o.d. raw material. During the course of this study, the addition of 0.9% salkomine was attempted with OA delignification, but no catalytic effect was observed for EAH pulp.

Practical and commercial considerations

Effective catalysts can open new opportunities for obtaining bleachable pulp from high-yield and ultra-high-yield semiproducts. Two facts—(a) that effective OA delignification could be achieved at about 100°C and (b) that the semiproduct is in the pulp state—make it conceptually feasible to cook in ordinary equipment, similar to the well-known mixers and towers used in the oxygen–alkaline stage of bleaching. This approach opens the possibility of producing bleachable pulp for white paper grades at the same pulp mill that produces high-yield and ultra-high-yield semiproduct for newsprint, corrugat-

ing medium, and other packaging papers. Such an approach adds a degree of flexibility and can improve market position.

It is quite probable that two or three stages of conventional bleaching equipment (mixers, towers) would be required to obtain the desired degree of delignification. Using several OA stages is not new for the pulp industry; 11% of worldwide installed capacity *(11)* already uses two-stage oxygen–alkaline bleaching. From the experimental data presented here, it is clear that hardwood pulp can be delignified to as low as kappa no. 10.

As mentioned before, the activation of lignin, the weakening of the wood matrix, and the increase in fiber penetrability observed in high-yield and ultra-high-yield pulps facilitate OA delignification. The high-yield and ultra-high-yield semiproduct could be subjected to screening or light refining if the fibers are separated unevenly *(5)*. This could facilitate more-uniform OA delignification, perhaps decreasing the number of bleaching stages and curtailing the demand of bleaching chemical. We believe that three stages of the ECF or TCF bleaching—typically recommended for OA hardwood pulp—would be sufficient to obtain a brightness of 87–90% ISO *(12)*.

There are about 16 varieties of high-yield and ultra-high-yield semiproducts produced commercially today *(13)*, all of which could qualify for the catalytic method of OA pulp production. Differences in chemical composition, physical properties, morphology, and other qualities among the various semiproducts would result in a variety of OA pulps, each with its own specific features.

There are no toxicology data for the KDK catalyst in the literature. It is known, however, that the components of KDK are not really toxic. Besides, the catalyst concentration in the waste liquor after the washing stage was calculated to be 0.2–2 ppm. This concentration is lower than the contaminant limit for many toxic substances.

The use of KDK is not without tradeoffs. A primary drawback is that the catalyst is expensive. However, there are several ways to decrease costs:

- Reuse the extract cooking liquor upon completion of the initial stage of OA delignification, i.e., after completion of the main reactions that produce oxidative fragmentation of the lignin in the solid phase *(14)*.
- Minimize the catalyst load through process optimization.
- Develop a catalyst-recovery method, an approach that appears quite feasible.

The described catalytic method is not an alternative to the pulsating method used with direct OA delignification of wood chips *(12)*. However, the proposed method demonstrates that the potential of OA delignification has not yet been fully tapped.

Conclusion

A recently developed catalyst that accelerates oxygen–alkaline (OA) delignification may make it possible to apply this process to high-yield and ultra-high-yield pulps. The catalyst, known as KDK, increases the delignification rate by a factor of 10 or more. OA delignification with this catalyst provides a range of benefits:

- Process temperature can be reduced to 100°C.
- Process duration at 100°C can be shortened by a factor of 1.4–1.9.
- Yield can be increased 6–8% based on o.d. wood or 1.5–2% based on raw wood.
- An easily bleachable product can be obtained at kappa no. 10–20.
- Cellulose degradation can be reduced, as evidenced by the higher viscosity of high-yield pulps after catalytic OA delignification. Viscosity was 10–90% greater than for high-yield pulps treated in the absence of catalyst and 15% greater than for wood after conventional OA delignification at 150°C.
- There is a possibility of using conventional equipment designed for the oxygen–alkaline delignification stage of pulp bleaching. ■

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The author is grateful to Professor P. P. Erinsh (Institute of Wood Chemistry of the Latvian Academy of Sciences) for providing the EAH and wood samples used in this study.

Received for review March 29, 1994.

Accepted April 28, 1995.