

Methanol-reinforced kraft pulping

Erik Norman, Leelo Olm, and Ants Teder

ABSTRACT: *The addition of methanol to a high-sulfidity kraft cook on Scandinavian softwood chips was studied under different process conditions. Delignification and the degradation of carbohydrates were accelerated, but the effect on delignification was greater. Thus, methanol addition improved selectivity. The positive effect of methanol could also be observed for modified kraft cooks having a leveled out alkali concentration and lower concentrations of sodium ions and dissolved lignin at the end of the cook. Methanol addition had no discernible effect on pulp strength or on pulp bleachability.*

KEYWORDS: *Betula, bibliographies, chips, degradation, delignification, kraft pulping, mechanical properties, methanol, Picea abies, Pinus sylvestris, processes, selectivity.*

One way to reduce the effluent load from the production of fully bleached pulp is to improve the cooking process. The aim is to achieve a more selective delignification so that more lignin can be removed during pulping without any negative effects on pulp quality. A prolonged delignification to low kappa numbers reduces the amount of bleaching chemicals needed. It is also an advantage if the pulp can be made easier to bleach, especially with nonchlorine chemicals.

In several of the new processes under development, the use of organic solvents has gained interest. One application, besides the "pure" organosolv processes, is to use the solvent as a reinforcement in an existing process as a way of increasing the delignification and improving the selectivity. In contrast to the "pure"

organosolv processes, however, the solvent-reinforced pulping processes do not have any advantages in chemical recovery. Indeed, the solvent-reinforced processes require both inorganic recovery and solvent recovery systems.

Alcohol-reinforced pulping processes have been proposed for high-yield bisulfite pulps (1-2). Bublitz showed that the addition of 30% alcohol to an acid sulfite or bisulfite process increases delignification. The effects of adding different alcohols to soda processes and to soda-AQ processes have been studied in many works (3-9). The Organocell process, a modified methanol-reinforced soda-anthraquinone process, has been in full-scale operation since late 1992 (10). Interesting results have also been reported from the group behind the ASAM process (11). Alkaline sulfite

pulping with the addition of anthraquinone and methanol gives low-kappa pulps with very high pulp viscosity and high brightness. ASAM pulps from softwood have strength properties and yields comparable to those of kraft pulps. The major advantage of the ASAM pulps, however, seems to be good bleachability.

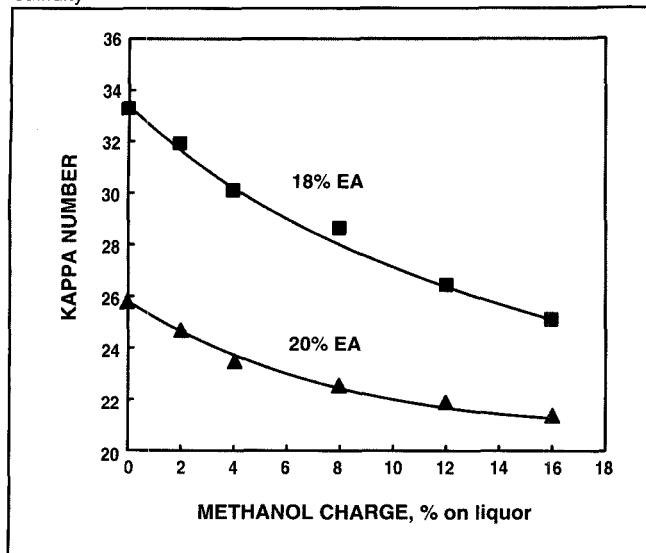
Reinforcement of kraft processes by alcohol addition has been studied to a minor extent. Kraft pulping of eucalyptus with the addition of ethanol has been reported to increase delignification and yield (12). However, a recent and more extensive study on methanol kraft pulping of eucalyptus showed that methanol does not improve the delignification or the selectivity of kraft pulping under normal conditions (13).

The kraft process is by far the dominant pulping process, and a great deal of research has been directed at improving its selectivity. In the early 1980s came the modified continuous cooking and extended batch pulping concepts (14), and in the late 1980s came the RDH (rapid displacement heating) (15) and Superbatch processes (16). A way of further improving the delignification in the kraft process could be to add a solvent. The most likely solvents for industrial use are the lower alcohols like methanol and ethanol.

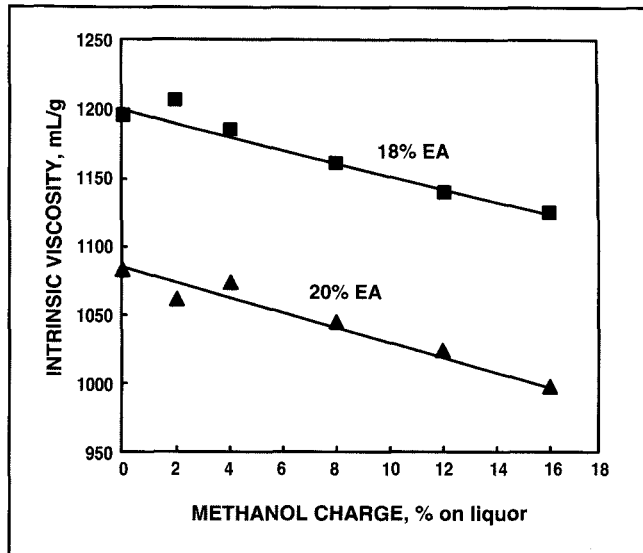
In an earlier introductory work (17), we studied the addition of methanol to a kraft process and found that methanol improved delignification. In the study reported here, the aim has been to examine more thoroughly the effect of methanol addition to a kraft cook on Scandinavian wood species.

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1. Kappa number as a function of methanol charge for a conventional kraft cook on softwood at 18% and at 20% effective alkali and 40% sulfidity



2. Intrinsic viscosity (scan cm 15:88) as a function of methanol charge for a conventional kraft cook on softwood at 40% sulfidity and at 18% and 20% effective alkali



Results and discussion

Delignification

In a kraft cook on Scandinavian softwood chips, a mixture of *Pinus silvestris* and *Picea abies*, the initial addition of methanol increased delignification compared to a conventional kraft cook. Figure 1 shows how the kappa number after a conventional one-stage kraft cook on softwood varied with the amount of methanol added, given as a percentage of the liquor. The two cooking series were carried out at two different levels of alkali charge (18% and 20% effective alkali as NaOH) at a liquor-to-wood ratio of 4:1 and sulfidity of 40%. Pulping times and temperatures were the same in both series. The methanol charge is defined as a weight percent, with the weight of methanol divided by the combined weight of methanol and water.

At a charge of only 2% charge, the methanol already has a clear effect on delignification. The lignin content in the pulp decreases further as the methanol charge increases, but the decrease levels off at higher methanol charges. A 16% methanol addition to a conventional softwood kraft cook at 40% sulfidity and 18% effective alkali reduces the kappa number by 7 units. Figure 1 also shows that the effect of

methanol is considerably less at a higher charge of effective alkali.

The upper limit for extra delignification by methanol addition has not been reached, however, in the range of methanol charges examined. This "extra" delignification is defined as the difference in lignin content, calculated on wood, between a conventional kraft pulp and a corresponding kraft methanol pulp, divided by the lignin content of the conventional pulp. A relatively low methanol charge is technically desirable, however, because it gives a limited pressure increase during pulping, which makes it possible for a mill to use its existing equipment without modifications.

Degradation of carbohydrates

Kraft pulping results in considerable carbohydrate degradation when delignification is extended, as a result of the peeling reaction and the alkaline hydrolysis of glycosidic bonds during the cook. The result is a lower pulp yield and lower pulp viscosity and thus the risk of a lower pulp strength.

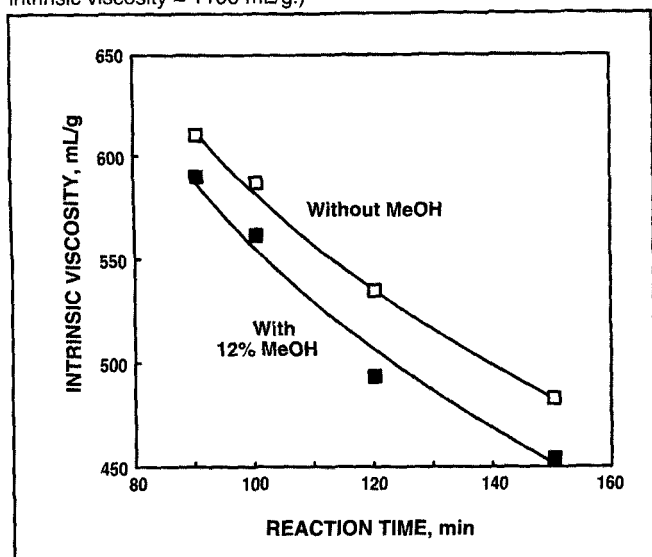
This is the case also for a methanol kraft cook. Not only is the delignification increased, but the carbohydrate degradation is also accelerated by the addition of methanol. In Fig. 2, the intrinsic viscosity of methanol kraft

pulp is shown as a function of methanol charge in the cook. At both effective alkali charges, 18% and 20% effective alkali as NaOH, the drop in intrinsic viscosity is about 50–100 units.

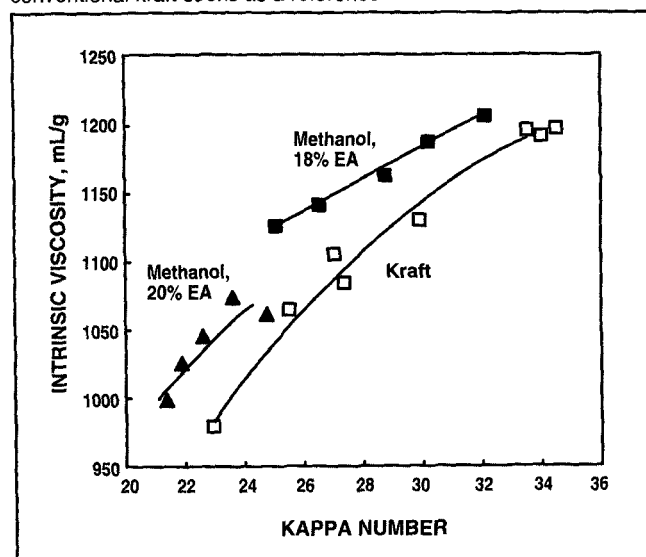
The decrease in pulp viscosity as a result of methanol addition could be either a direct effect of methanol on the attack of alkali on carbohydrates or an indirect morphological effect caused by increased delignification. Experiments were carried out to determine how the viscosity of cotton linters is affected in a cook at 170°C in the presence of hydroxide and hydrogen sulfide ions, with and without addition of 12% methanol. Presented in Fig. 3, the results showed that the presence of methanol increases the viscosity drop under alkaline conditions in the absence of lignin.

Methanol thus increases carbohydrate degradation even when no delignification is involved. The difference is not large, only 30 viscosity units, but the effect is clear. There is thus a direct effect of methanol on alkali degradation of carbohydrates. Other cooks carried out under the same conditions show that the viscosity of the cotton linters, after the alkaline treatment, is little affected at lower methanol charges.

3. Intrinsic viscosity as a function of reaction time at 170°C. (Borohydride-reduced cotton linters. $[\text{OH}^-] = 0.30M$. $[\text{HS}^-] = 0.20M$. Initial intrinsic viscosity = 1100 mL/g.)



4. Intrinsic viscosity as a function of kappa number for two series of methanol-reinforced conventional kraft cooks and for a series of conventional kraft cooks as a reference



Selectivity

Both the delignification and the carbohydrate degradation are thus accelerated by the addition of methanol to a kraft cook. However, the delignification is accelerated more than the carbohydrate degradation, so the addition of methanol to the cook results in a more selective process.

Figure 4 shows the intrinsic viscosity as a function of kappa number for conventional kraft cooks and for two series of methanol-reinforced kraft cooks at two different levels of alkali charge. In the conventional cook, the delignification was increased by increasing the effective alkali charge. In each series of the methanol-reinforced kraft cooks, the effective alkali charge was held constant (at 18% and at 20% respectively), and the increase in delignification was achieved by increasing the methanol content.

As the figure shows, the viscosity is about 100 units higher for the methanol-reinforced cook at the same kappa number at the lower level of effective alkali. The viscosity loss per kappa number was about 20 mL/g for the kraft cook and about 10 mL/g for the methanol-reinforced kraft cook—i.e., about half that of the conventional kraft cook. At the higher alkali charge of 20%, the viscosity drop for the metha-

nol-reinforced cook is greater, but the viscosity is still about 50 units higher than that of the conventional cook.

The total yield for the reinforced cook was about 1% higher than that of the conventional cook, after cooks to equivalent kappa numbers. The amount of rejects was affected little by the addition of methanol.

Influence of cooking conditions

Our results indicate that the positive effect of methanol addition on delignification during kraft cooking decreases when the cooking is extended to achieve low kappa numbers.

Figure 5 shows the extra delignification (previously defined) achieved by methanol addition plotted against the kappa number reached in the conventional pulp. No matter how the increased delignification is achieved, whether by an increase in the effective alkali charge, by an increase in sulfidity, or by prolonged reaction time, the relationship between extra delignification and the kappa number is almost the same for all the pulps. This outcome means either that the extra delignification achieved by the addition of methanol is directly related to lignin content during the cook or that the extra delignification happens, by chance, to depend on the conditions of

alkalinity, sulfidity, and reaction time, to the same extent as Fig. 5 describes.

To investigate this matter, we carried out three conventional kraft cooks, with different chemical charges. The reaction times were different and were chosen so that without methanol the pulps produced from the three cooks would have the same kappa number of 34.

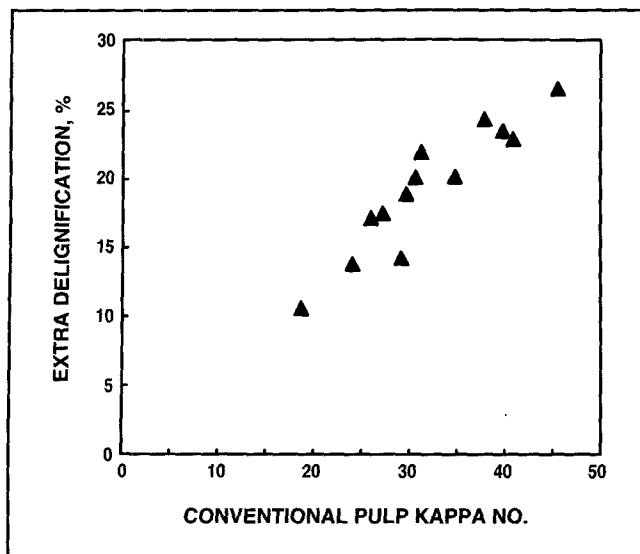
Presented in Table I, the results show that at the same kappa number an increase in chemical charge slightly decreases the extra delignification obtained by methanol addition. Thus, it is possible that the hydrogen sulfide and hydroxide ions compete with the methanol as the delignifying agent. However, the major effect of methanol addition on delignification remains the same, which means that the extent of extra delignification depends mainly on the degree of delignification.

Results from experiments in which methanol was added in different parts of a kraft cook (not shown here) also indicated that the methanol accelerates delignification in the early part of the cook but has little influence on the residual delignification at the end of the cook.

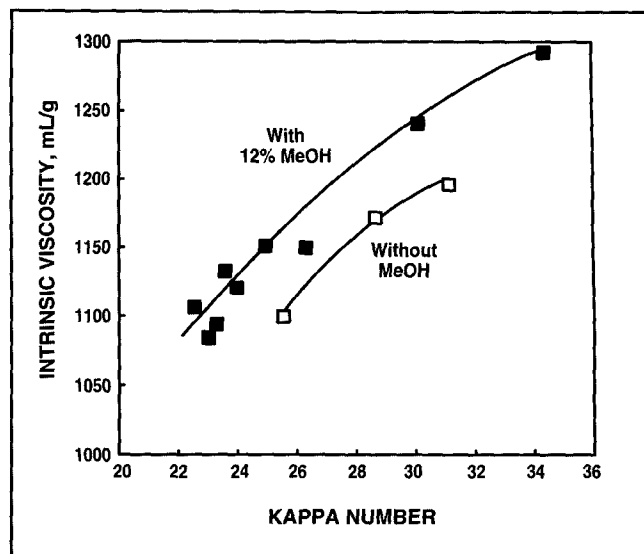
Modified cooking

The results on methanol-reinforced, conventional kraft cooks suggest that

5. Extra delignification achieved by methanol addition as a function of the kappa number reached in the conventional pulp



6. Intrinsic viscosity as a function of kappa number for methanol-reinforced modified cooks with and without methanol addition of 12% by weight



methanol addition may not be suitable for achieving low kappa numbers in *modified* kraft pulping. This is not true, however. The addition of methanol is also advantageous in the case of modified continuous kraft cooking—i.e., for kraft cooking with a leveled out alkali concentration and low concentrations of sodium ions and dissolved lignin at the end of the cook.

Figure 6 shows the kappa number plotted against intrinsic viscosity for a series of modified cooks with and without the initial addition of 12% methanol. The sulfidity was 40%, and the alkali charge was increased to increase the delignification. The viscosity of the methanol-reinforced, modified kraft pulp is about 50 units higher at the same kappa number than that of a modified reference pulp without methanol addition. Therefore, the addition of methanol to the modified cook increases the delignification and renders the process more selective in the same way as it does for the conventional cook.

The addition of methanol to only the countercurrent zone of a laboratory-modified kraft cook had no positive effect on delignification. The addition of methanol both initially and in the countercurrent zone had no additional effect on delignification, com-

7. Results of conventional kraft cooks carried out at different chemical charges with and without methanol

Effective alkali, %	Sulfidity, %	Time at 170° C, min	Kappa number		Decrease in kappa number
			Kraft	Kraft + methanol	
18	40	120	34	26	8
20	40	70	34	27	7
18	60	78	34	28	6

pared to that achieved solely with initial methanol addition. The methanol is thus active in the beginning of the cook, but its addition at the end of the cook has no effect on delignification.

The yield and rejects for the reinforced modified cook were the same as for the modified cook without methanol addition.

Kraft methanol pulping of birch

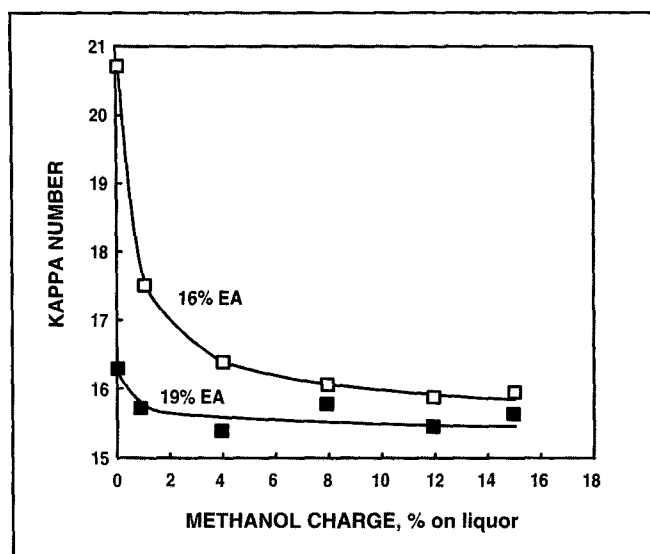
Softwoods are more difficult to delignify than hardwoods in organosolv pulping, even if it is possible in some catalyzed systems (18–19). In soda-alcohol processes, softwoods delignify quite well although the pulping of hardwoods by such processes is easier (6, 9). It might be expected therefore that the effect of the methanol addition to a kraft cook would

be even greater in the kraft pulping of hardwoods.

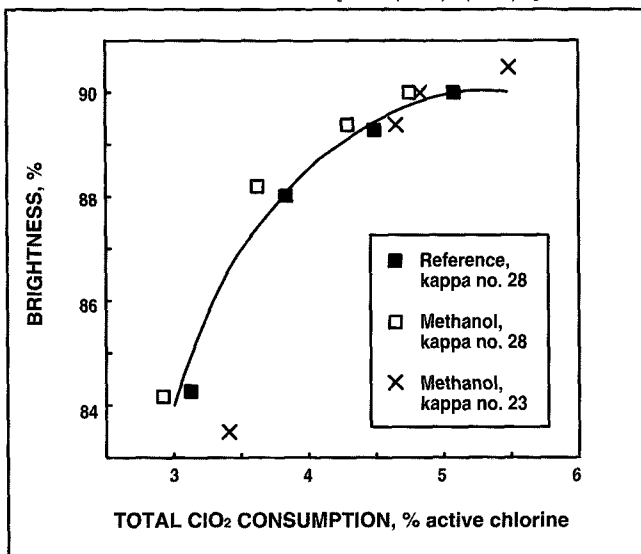
A kraft cook of birch chips, a mixture of *Betula pendular* and *Betula pubescens*, showed that the effect of methanol addition was fairly substantial even with small additions—about 20% extra delignification at a methanol charge of 4%, as shown in Fig. 7 (20). However, the delignification did not increase with further addition of methanol, and it was not possible to extend the delignification beyond the “kappa number wall” at kappa no. 15, which is characteristic of birch (21). At higher alkali charges, the effect of the methanol addition on delignification was less for hardwood, and it was not possible to delignify beyond the kappa number wall at these conditions either.

The selectivity in the methanol-reinforced kraft cook on birch was im-

7. Kappa number as a function of methanol charge for methanol-reinforced kraft pulping of birch



8. Brightness as a function of total consumption of chlorine dioxide, % active chlorine, for the bleaching of modified kraft pulps produced with and without methanol addition[D100(E+P)D(E+P)D]



proved—about 100 mL/g higher viscosity at a given kappa number than in the case of the conventional cook. The pulp yield and rejects were unchanged.

Bleachability

Two softwood pulps with kappa nos. 23 and 28 produced by modified methanol-reinforced kraft pulping were prebleached with oxygen and were bleached subsequently with different bleaching sequences. The bleachability was then compared with that of an oxygen-bleached modified kraft pulp at kappa no. 28 produced without the addition of methanol.

In earlier trials, the oxygen stage was carried out in the presence of methanol, and the results showed an improved selectivity in oxygen bleaching, measured as viscosity at a given kappa number (17). The positive effect of solvents has also been reported in other studies (11, 22–24). In an industrial application, it would be an advantage if the methanol could be used in both cooking and in the oxygen stage. In this study, however, the oxygen stage was carried out without methanol addition.

In the medium-consistency oxygen stage, all pulps were delignified to the same kappa no. 14–15. Because the vis-

cosity drop for the kraft methanol pulps was greater, all the pulps had almost the same viscosity after the oxygen stage. It is commonly known that a pulp with higher viscosity at a given kappa number will lose more viscosity in the oxygen stage at the same delignification level. However, practically all of the viscosity gain from the methanol addition in the cook was lost in the oxygen stage, which was unexpected.

The pulps were then subjected to a chlorine-gas-free bleaching sequence: D100(E+P)D(E+P)D, with 2 kg and 1 kg of peroxide per ton of pulp in the first and second alkali stages, respectively. Figure 8 shows the pulp brightness plotted against the total chlorine dioxide consumption. The kraft methanol pulp at kappa no. 28 has a somewhat lower consumption at a given brightness. However, the difference in bleachability between the pulps is slight, and the bleachability in this sequence can be said to be the same for the three pulps examined.

The bleachability was also tested in two chlorine-gas-free sequences, ZED and QPD, and in two totally chlorine-free sequences, ZEZ and QPZ. The letter “Q” stands for a pretreatment with EDTA (ethylene diamine tetraacidic acid) at 60°C and at a pH of

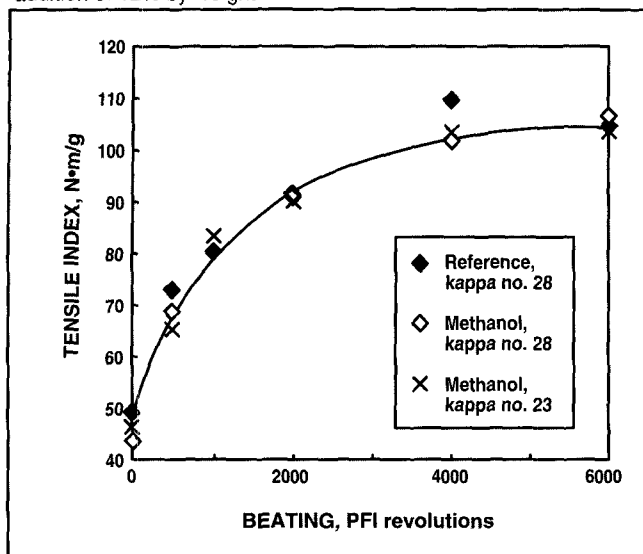
5.5–6.5 (25). In each of these sequences, bleachability was the same for all pulps.

Strength properties

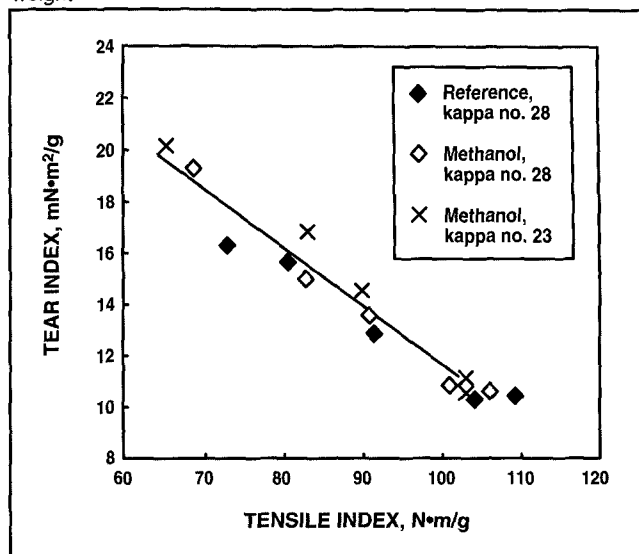
The mechanical properties of the three different pulps bleached by the D100(E+P)D(E+P)D sequence were evaluated after beating in a PFI mill. Figure 9, in which tensile index is plotted as a function of the number of PFI revolutions, shows that the beatability is the same for all three pulps. In Figure 10, the tear index shows the same relationship with tensile index for all three pulps.

Thus, the bleachability and the mechanical properties of the pulps are the same for the methanol-reinforced kraft pulps and the conventional kraft pulp. Consequently, the presence of methanol in the kraft cook does not seem to change the chemical structure of the residual lignin in the pulp and does not have any negative effects on the mechanical properties. The chemistry of delignification during the methanol-reinforced kraft cook seems to be the same as that of the conventional kraft cook. This observation is supported by a comparison between the structure of the residual lignin from a methanol-reinforced kraft cook and that of the residual lignin from a con-

9. Tensile index as a function of the number of PFI revolutions for bleached modified kraft pulps cooked with and without methanol addition of 12% by weight



10. Tear index as a function of tensile index for bleached modified kraft pulps cooked with and without methanol addition of 12% by weight



ventional cook (to be reported in a separate publication).

Conclusions

The addition of methanol, both to the conventional process and to the modified kraft process, results in a faster delignification and an increase in carbohydrate degradation. In spite of the increased carbohydrate degradation, the selectivity of the methanol-reinforced kraft process is better than that of the conventional kraft process. This means that delignification can be extended to somewhat lower kappa numbers without extensive loss of pulp viscosity and pulp yield. The addition of methanol to a kraft process does not, however, improve the bleachability or the strength properties of the pulps produced.

Reinforcement of the process by the addition of methanol should be fairly easy to apply in an existing kraft mill. The pressure in the digester will be somewhat higher, but that should be limited if the methanol charge is held within reasonable limits. The only investment required is the installation of an improved methanol recovery system.

The positive effects of adding methanol, whether to a conventional cook or to a modified kraft cook, are

limited in magnitude, however. This fact must be kept in mind in considerations about employing this process modification. □

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