# Modified kraft cooking with polysulfide: yield, viscosity, and physical properties

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## ABSTRACT

*This study on Scandinavian softwood focused on the effects of polysulfide in modified continuous cooking (MCC) and isothermal (ITC) kraft cooking. The polysulfide was assumed to be generated by partial white liquor oxidation. A polysulfide sulfur charge increased the carbohydrate yield. The selectivity regarding pulp viscosity was about the same for pulps produced with and without polysulfide, provided the polysulfide cook was carried out at a 10% higher white liquor sulfidity. The tear strength was lower for the polysulfide pulps at a given kappa number, as expected.*

***Application:***

*Polysulfide could be used in a modified kraft cook to low kappa numbers to produce pulp with a higher carbohydrate yield, compensating the yield loss in low kappa pulping.*


MODIFIED CONTINUOUS COOKing (MCC) is well established industrially, with at least 35 MCC digesters in eight countries *(1)*. The MCC process introduced in the 1980s is characterized by a low initial concentration of alkali and low concentrations of dissolved lignin and sodium ions towards the end of the cook *(2)*.

The further development of the MCC process is isothermal cooking, or the ITC process. In the "washing" stage of the ITC process, 1–2% of alkali is charged. The temperature is increased to the maximum cooking temperature, which is the same as the maximum temperature in the cocurrent and countercurrent cooking stages. The "washing" stage thus becomes a second countercurrent cooking stage. The maximum cooking temperature in the earlier parts of the cooking stage is also lower in the ITC process than in the MCC process, with the result that the *H*-factor is kept constant in spite of the longer cooking time.

Owing to these improvements, the ITC process is more selective than the MCC process, producing pulps with a higher pulp viscosity and carbohydrate yield at a given kappa number. The improvement in selectivity allows a further decrease in kappa number *(1)*. When selective delignification in modified kraft cooking processes is extended to low kappa numbers of 18–20, however, hemicellulose is lost along with the lignin in the final countercurrent part of the cook.

This loss of hemicellulose not only reduces the yield of the bleached pulp but also makes these pulps difficult to beat in the subsequent papermaking process. As conventional continuous kraft cooking has given way to modified continuous kraft cooking, beatability has decreased at equivalent carbohydrate yields *(3)*. (Beatability pertains to the number of beating revolutions necessary to reach a certain tensile index.) Thus, there is a need to improve the yield of hemicellulose in kraft pulps produced by modified kraft cooking processes.

Polysulfide can be used as an additive to improve the hemicellulose yield in a kraft cook. Our objective in this research was to study the effects of polysulfide addition on pulp yield, pulp viscosity, and physical pulp properties.

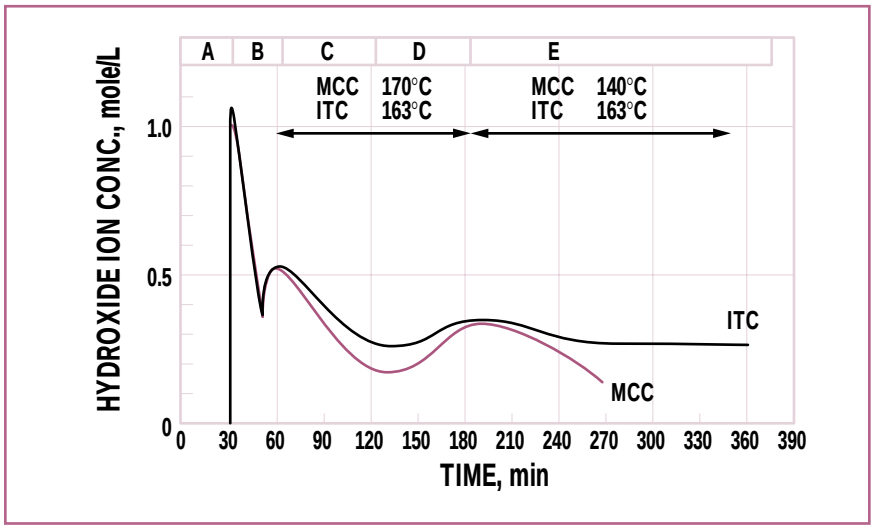
## BACKGROUND

### *Anthraquinone vs. polysulfide*

The main decrease in carbohydrate yield when cooking Scandinavian softwood is in the loss of hemicellulose, mainly glucomannan *(4)*. To a minor extent, the yield is also decreased by the loss of cellulose *(5)*. The mechanism responsible for the larger part of the loss of glucomannan is the primary peeling of the polysaccharide chain by alkali in the initial stage of the cook *(6)*. This peeling reaction can be limited by the oxidation of the reducing glucosidic end groups of the carbohydrate chains to carboxylic end groups *(7)*.

To improve the total pulp and hemicellulose yield in a kraft cook, two well-known additives can be used—anthraquinone and polysulfide. They protect the end groups of the carbohydrate chains by oxidizing the carbonyl groups to aldonic acids. Anthraquinone has a synergistic effect with polysulfide on the yield increase in both conventional and extended modified kraft cooking *(8–10)*. In turn, an increased carbohydrate yield reduces the load on the recovery boiler.

Anthraquinone still cannot be generated in a kraft mill, however, which means additional costs. Anthraquinone accelerates the delignification reactions in a kraft cook, especially when the sulfidity is low. When the sulfidity is high, as in Scandinavian mills at 35–40%, the effect of anthraquinone on delignification is very low and is probably of no economic interest *(11)*. On the other hand, polysulfide can be generated in a pulp mill. Thus, polysulfide could




*1. Hydroxide ion concentration profiles in MCC- and ITC-type cooks, both with and without polysulfide. (A–E: evacuation for MCC or steaming for ITC, impregnation, co-current cooking, countercurrent cooking, and high heat washing.)*

prove to be economically beneficial in modern kraft cooking.

### Polysulfide generation

In a pulp mill, polysulfide can be generated in three different ways. The first method is to charge external sulfur to the white liquor according to the following reaction:

$$n\ S(o) + HS^- + OH^- \rightarrow S_nS^{2-} + H_2O \quad (1)$$

Polysulfide is formed, and hydrogen sulfide ions in the white liquor are consumed to some extent. The polysulfide solution consists of an equilibrium mixture of different polysulfide ions, with $n$ between 1 and 5.

Polysulfides decompose thermally at higher temperatures to hydrogen sulfide and thiosulfate ions *(12)* according to Reaction 2:

$$S_nS^{2-} + (n-1)\ OH^- + (1 - n/4)\ H_2O \rightarrow (1 + n/2)\ HS^- + (n/4)S_2O_3^{2-} \quad (2)$$

In this case, the main part of the cook would be carried out at a higher hydrogen sulfide ion concentration than in the corresponding kraft cook *(13)*. The sulfidity in the process will increase to such a level that the extra added sulfur will be emitted as sulfur dioxide in the flue gas. This method is thus not feasible for industrial use, which has to meet environmental demands regarding air pollution.

The second method is internal sulfide oxidation. One alternative is to separate sulfur from the process *(14)*, using the separated sulfur to produce polysulfide according to Reaction 1. Another alternative is to produce polysulfide through a direct catalytic oxidation in which a part of the hydrogen sulfide in the white liquor is oxidized to polysulfides according to Reaction 3:

$$(n + 1)\ HS^- + n/2\ O_2 \rightarrow (n - 1)\ OH^- + S_nS^{2-} + H_2O \quad (3)$$

This reaction is the main reaction in white liquor oxidation by the MOXY process *(15)*, which is an industrially available method for partial oxidation of white liquor. As a side reaction, about one-third of the reacting hydrogen sulfide will react to thiosulfate according to Reaction 4:

$$2\ HS^- + 2\ O_2 \rightarrow S_2O_3^{2-} + H_2O \quad (4)$$

If this method were used, the result would be a substantial reduction in the content of hydrogen sulfide ions in the whole kraft cook. This low $HS^-$ concentration is not favorable for the selectivity of the cook. Consequently, this method is difficult to accept from a pulp quality standpoint, where the ambition is to cook to low kappa numbers while keeping pulp viscosity at a high level *(13)*.

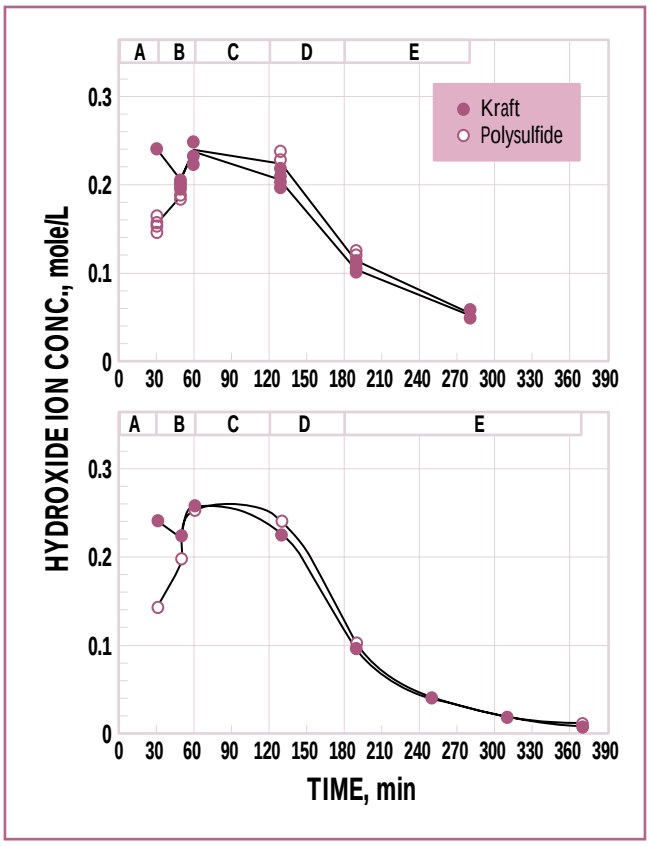
The third method is recommended here as a compromise. The procedure is to raise the white liquor sulfidity somewhat and then use white liquor oxidation *(15)*. This approach makes it possible to keep the hydrogen sulfide ion concentration at a high level in the cooking liquor, with no change in the total sulfur emission from the pulp mill *(16)*.

There also might be ways to increase the sulfidity in the cook, such as allowing hydrogen sulfide ions to absorb into the wood in the beginning of the cooking process. This modification will increase the concentration of hydrogen sulfide ions in the initial part of the cook *(17)*. An increase in the initial concentration of hydrogen sulfide ions is also possible in working with two white liquors with different sulfidities. High sulfidity liquor then should be used in the beginning of the cook, and low sulfidity should be used toward the end *(2)*.

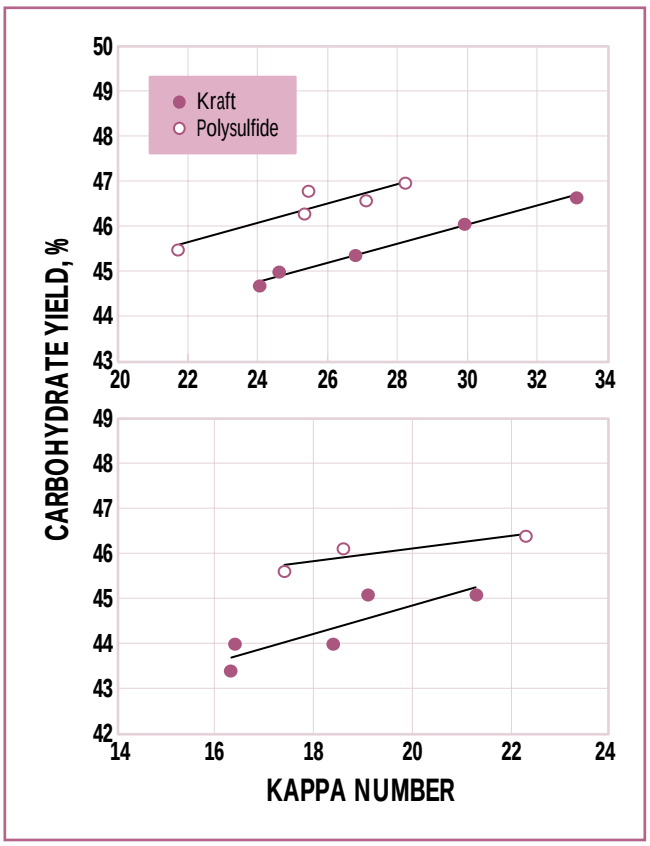
### Additional considerations

According to previous findings regarding conventional kraft cooking, the yield increase resulting from the polysulfide addition will have a negative influence on the tear strength, with a lower tear index at a given tensile index *(18)*. However, an increase in hemicellulose content will normally give a pulp with a better beatability—that is, a pulp that is easier to beat to a given tensile index.

Recent studies *(9, 19)* confirm the yield increase and the lower tear strength for MCC cooks with polysulfide, extended to a kappa number of about 20. In those investigations, however, the researchers did not




*2. Profiles for hydrogen sulfide ion concentration for the MCC- and ITC-type cooks*




*3. Effect of polysulfide on the unbleached carbohydrate yield in the MCC- and ITC-type cooks*

consider the sulfur balance in polysulfide preparation. Steps were not taken to raise the sulfidity, in the chemical recovery, enough to preserve the high sulfidity in kraft cooking without polysulfide.

Polysulfide pretreatment and cooking to very low kappa numbers, from 20 to 10, have recently been shown to give not only a yield increase but also a slightly faster delignification in the residual phase of the cook, together with an improved relationship between pulp viscosity and kappa number. The improvement was about 100 viscosity units in the kappa number range of 20 to 10 *(20)*.

As stated, our objective was to study the effect of polysulfide addition in modified cooking. The industrial MCC and ITC processes were simulated with a simple laboratory procedure of the modified kraft type, according to STFI standard cooking procedures. Polysulfide was applied to raise the carbohydrate yield in relation to a reference. The polysulfide was assumed to be produced by the MOXY process *(15)*. Our aim was to compensate for the loss of glucomannan in the final part of the cook by reducing the loss of glucomannan in the initial part of the cook.

## MATERIALS AND METHODS

### *Wood*

The wood used in the experiments was industrial Scandinavian softwood chips (*Picea abies* and *Pinus sylvestris*). The chips were screened in a slot screen, and the fraction of chips with thicknesses between 2 mm and 6 mm was used. Bark and knots were removed by hand sorting.

Chips for the MCC-type cooks had a dry content of 95% and were stored at room temperature. Chips for the ITC-type cooks had a dry content of 57% and were stored frozen.

### *Modified kraft MCC*

The first part of this study included a simulation of the modified continuous cooking (MCC) process with a modified kraft MCC-type laboratory cooking process *(17)*. The cooks were performed in a stainless steel digester with a charge of 1 kg of air-dry wood chips and a forced liquor circulation.

The laboratory cook was started with a 30-min evacuation of the charged chips. A first charge of the cooking liquor followed, with about 80% of the effective alkali charge. The wood chips were impregnated with cooking liquor for 30 min with nitrogen gas at a pressure of 5 bar. The pressure was released to come down to atmospheric pressure. The temperature was raised to 130°C, and a second impregnation was done at this temperature. A second charge of effective alkali was added after 20 min of the total impregnation time of 30 min. The liquor-to-

| | Temp., °C | Time, min | Pulp conc., % |
|---|---|---|---|
| O | 100 | 60 | 12 |
| $D_1$ | 60 | 30 | 8 |
| E+P | 60 | 60 | 10 |
| $D_2$ | 70 | 120 | 10 |
| E | 70 | 60 | 10 |
| $D_3$ | 70 | 240 | 10 |

***I. Bleaching conditions in the OD(E+P)DED sequence***

| | $D_1$* | P | $D_2$* | $D_3$* |
|---|---|---|---|---|
| Charge, kg/metric ton | | | | |
| Polysulfide | 16.6 | 4.0 | 18.7 | 9.4 |
| Reference | 15.8 | 4.0 | 17.8 | 8.9 |
| Consumption, kg/metric ton | | | | |
| Polysulfide | 16.6 | 2.9 | 18.6 | 7.7 |
| Reference | 15.8 | 3.0 | 17.8 | 7.7 |

*As active $ClO_2$

***II. Chemical charges and consumption, ITC-type cooks***

wood ratio was then 4:1, and it was kept at that level during the remaining stages of the cook.

The cooking procedure was split into four zones:

1. An impregnation at 130°C, where polysulfide was able to stabilize the polysaccharides. (Afterwards, the temperature was raised rapidly to 170°C.)
2. A 60-min co-current zone
3. A 60-min countercurrent zone
4. A washing zone of 90 min at 140°C *(17)*.

After the cooks, the chips were carefully washed. The chips were defibrated in a rod disintegrator, and the shives were collected on a 0.2-mm open thickness sieve. Tap water was used for the MCC part of the study.

### *Modified kraft ITC*

The ITC process was simulated in the same digester with a procedure similar to that used for the simulated MCC cooks. The impregnation procedure for the ITC cooks was somewhat different from the MCC cooks, partly because the chips were wet. Steaming instead of evacuation was used prior to the charge of cooking liquor.

In the cooking zone, the temperature was raised only to 163°C and was kept there throughout the co-current and the countercurrent zones. The third cooking zone simulates a countercurrent washing zone with alkali addition for 180 min at 163°C. Deionized water was used for the ITC part of the study.

### *Cooking liquor*

Polysulfide cooking liquor was prepared by dissolving sulfur in an aqueous solution of natrium sulfide ($Na_2S$) to form polysulfides ($Na_2S_nS$), according to Reaction 1. Thiosulfate ($Na_2S_2O_3$) and hydroxide (NaOH) were added to the cooking liquor. The amount of thiosulfate added corresponded to a 30% side reaction, according to Reaction 4. The polysulfide cooking liquor was thus a simulation of the type of cooking liquor that would be obtained by oxidation of white liquor in the MOXY process (Reaction 3). The degree of oxidation was assumed to be 60%.

In the MCC-type cooks, the charge of polysulfide was 1.6% polysulfide sulfur, on dry wood, in the initially charged cooking liquor. In the ITC-type cooks, the polysulfide charge was 1.7% polysulfide sulfur, on dry wood. To establish a comparison with the reference cook without polysulfide, the alkali charge was adjusted, as mentioned, in both the MCC-type and ITC-type kraft cooks to reach the same kappa number at the same time in the polysulfide cooks as in the reference cooks.

The effective alkali charge before sulfur dissolution was raised by about 10% in the cooks with polysulfide. We added this alkali to compensate for the alkali consumed when sulfur is dissolved in white liquor to yield polysulfides (Reaction 1), in contrast to the production of alkali in the oxidizing processes (Reaction 3). If the effective alkali had been determined by titration after polysulfide had formed, the same effective alkali charge would have been required for both the polysulfide cooks and the cooks without polysulfide *(21)*.

The initial effective alkali charge was 14.5%, as NaOH on dry wood. A further 3–5% was added after 20 min of the impregnation stage. **Figure 1** shows alkali concentration profiles for the MCC-type and ITC-type cooks, both with and without polysulfide. These profiles are based on the mean values of the hydroxide ion concentrations determined at room temperature on samples from different stages of the cooks. The alkali concentration profiles during the different parts of the MCC and ITC cooks were about the same, as the figure shows. This figure also shows the intervals for the evacuation or steaming stage (A) followed by the four cooking zones (B–E).

### *Bleaching*

The pulps of ITC kraft were bleached under ECF (elemental chlorine free) conditions to high brightness (89% ISO) with oxygen, chlorine dioxide, and peroxide. The bleach sequence was OD(E+P)DED.

Before oxygen delignification (O), magnesium was charged (0.8% $MgSO_4$, on dry pulp) to give a higher selectivity in the oxygen bleaching stage *(22)*. Alkaline extraction was reinforced with peroxide (E+P). In the final D stage, the chlorine dioxide charge was adjusted to reach the brightness of 89% ISO. Bleaching conditions are presented in **Tables I and II**.

### *Strength properties*

The strength properties were tested on only one reference ITC pulp and

one polysulfide ITC pulp. The pulps were bleached before physical testing to reduce the possible influence of residual lignin in the pulp.

Mechanical strength properties were determined according to routine test methods: PFI beating by SCAN-C18:65/C24:67, sheet formation by SCAN-C26:76, and sheet properties by SCAN-C28:76. The zero-span tensile strengths were tested according to a method by Cowan (Pulmac instrument zero-span tester) *(23)*. Before the zero-span tensile tests, sheets were rewetted by 45 min of soaking in deionized water.

Other properties were analyzed as follows: wood dry content by SCAN-CM 39:88, pulp dry content by SCAN-C3:78, kappa number by SCAN-C1:77R, and viscosity by SCAN-CM 15:88. Effective alkali was analyzed according to a modified version of the method by Wilson, which involved titration with 0.25*M* HCl until the first inflection point *(24)*. Hydrogen sulfide ions were analyzed according to SCAN-N31:94.

| | Reference | Polysulfide |
|---|---|---|
| After cook | | |
| Kappa number | 27.4 | 27.4 |
| Viscosity, mL/g | 1080 | 1110 |
| Total yield, % on wood | 47.1 | 48.5 |
| Carbohydrate yield, % on wood | 45.2 | 46.5 |
| After oxygen delignification | | |
| Kappa number | 14.3 | 13.1 |
| Viscosity, mL/g | 960 | 990 |
| Carbohydrate yield, % on wood | 44.3 | 45.5 |
| Carbohydrates, % on pulp | | |
| Cellulose | 78.6 | 77.4 |
| Glucomannan | 8.5 | 10.1 |
| Xylan | 8.9 | 8.2 |
| Carbohydrates, % on wood | | |
| Cellulose | 37.0 | 37.5 |
| Glucomannan | 4.0 | 4.9 |
| Xylan | 4.2 | 4.0 |

***III. Carbohydrate composition in kraft MCC-type pulps with polysulfide and without polysulfide (as a reference)***

## RESULTS AND DISCUSSION

### *Hydrogen sulfide ion concentration*

To be able to use a polysulfide pretreatment based on white liquor oxidation, it is essential to work with a high sulfidity in the chemical recovery system to ensure that enough hydrogen sulfide ions are available in the cook. The sulfidity in the white liquor (i.e., in chemical recovery) was therefore raised from 40% for the kraft cooks to 50% for the polysulfide cooks. This 10% sulfidity increase, combined with hydrogen sulfide ion oxidation to polysulfide, gave us the result we expected. After the impregnation zone, the hydrogen sulfide ion concentration for the polysulfide cook was the same as for the reference cooks (**Fig. 2**).

In the impregnation zone of the polysulfide cooks, the hydrogen sulfide ion concentration was lower than it was in the reference cooks. This decrease is a result of hydrogen sulfide ion consumption by the MOXY process. However, when the polysulfide is thermally decomposed during the rise to cooking temperature, the hydrogen sulfide ion concentration reaches the same level as in the reference cooks.

The concentration of hydrogen sulfide ions falls from the countercurrent cooking zone until the end of the cook. This decrease originates mainly from the exchange of cooking liquor and "washing" liquor, which has a very low concentration of hydrogen sulfide ions. The exchange of liquors simulates the countercurrent stages.

### *Yield increase*

Polysulfide pretreatment in the MCC-type cooks gave an increase in carbohydrate yield of 1.2% at kappa no. 24, in comparison with the reference, as shown in **Fig. 3**. Polysulfide pretreatment in the ITC-type cooks gave an increase in carbohydrate yield of 1.5% at kappa no. 19, as the figure also shows. Polysulfide pretreatment thus gave approximately the same percentage increase in carbohydrate yield as the polysulfide charge (1.6% polysulfide sulfur for the MCC cooks and 1.7% for the ITC cooks). Both the carbohydrate yield and the polysulfide charge were calculated on dry wood.

The yield increase from polysulfide pretreatment is somewhat lower in the modified kraft cook of MCC and ITC, however, than the yield increase in the conventional continuous kraft cook. In the conventional case, a polysulfide sulfur charge to the cooking liquor of 1.6–1.7% (calculated as sulfur on dry wood) results in an increase of about 3% in carbohydrate yield gain at kappa no. 46 *(25)*. The lower increase in carbohydrate yield for the modified cooks can perhaps be explained by the higher hydroxide ion concentration in the final part of the cook. Also contributing to the lower increase would be the withdrawal of cooking liquor from the digester during the countercurrent cooking zone and the "washing" zone. Dissolved polysaccharides are removed with the cooking liquor, and the re-precipitation of dissolved polysaccharides is therefore less.

The carbohydrate yield increase associated with polysulfide addition originates from increases in gluco-

**KEYWORDS**
*Bibliographies, mechanical properties, modified kraft process,* Picea abies, Pinus sylvestris, *polysulfide pulping, polysulfides, sulfidity, viscosity, yield.*

mannan and cellulose, as presented in **Table III**.

***Pulp viscosity***

The selectivity, or the viscosity at a given kappa number, was studied with and without polysulfide pretreatment, for both an MCC and for an ITC laboratory cooking process. The viscosity of the MCC-type pulp, at kappa no. 24, was slightly higher for the polysulfide pulp (**Fig. 4**, top). Conversely, the viscosity of the ITC-type pulps was slightly higher for the reference, without polysulfide at kappa no. 19 (**Fig. 4**, bottom).

The difference in pulp viscosity, at a given kappa number, was thus small for both the MCC and ITC laboratory processes. The sulfidity increase of 10% was slightly too high in the MCC cooks and too low in the ITC cooks to reach the same pulp viscosity in polysulfide and reference cooks. However, the reason for this small difference is not known.

Polysulfide pulps can give a faster consumption of bleaching chemicals and thus a smaller viscosity loss during bleaching *(27)*. The viscosity for the ITC-type pulps tested for strength properties was 1135 mL/g after the cook, 1000 mL/g after oxygen delignification, and 895 mL/g after the bleaching. Thus, there were no differences in viscosity after bleaching between polysulfide and reference pulps. (For both of these pulps, the kappa numbers were 19 after the cooking and 10 after oxygen delignification.)

***Strength properties***

Polysulfide will negatively affect pulp strength, especially at a high charge of polysulfide and when the cook is stopped at a high kappa number *(18)*. (The pulp's strength is its tear index at a constant tensile index.) Our study confirmed the lower tearing resistance for a polysulfide pulp, compared to that of the reference cook, when cooking was carried out to low kappa numbers at a low charge of polysulfide.

We evaluated strength properties only for the ITC-type process, at the same kappa number—i.e., at different carbohydrate yields. There was a 16% difference in tear index (at a tensile index of 90 (N•m)/g) between pulps produced with and without polysulfide pretreatment (**Fig. 5**). The pulps with polysulfide had a lower tearing resistance. The reason for the loss in tear strength is probably related to the higher yield. In other words, with higher yield, there were fewer load-bearing fibers in a specific weight sample of the pulp *(28)*. The loss in tear strength can also be considered to be related to the higher content of glucomannan and lower content of cellulose, as the contribution to the tear strength from glucomannan is not as great as the contribution from cellulose.

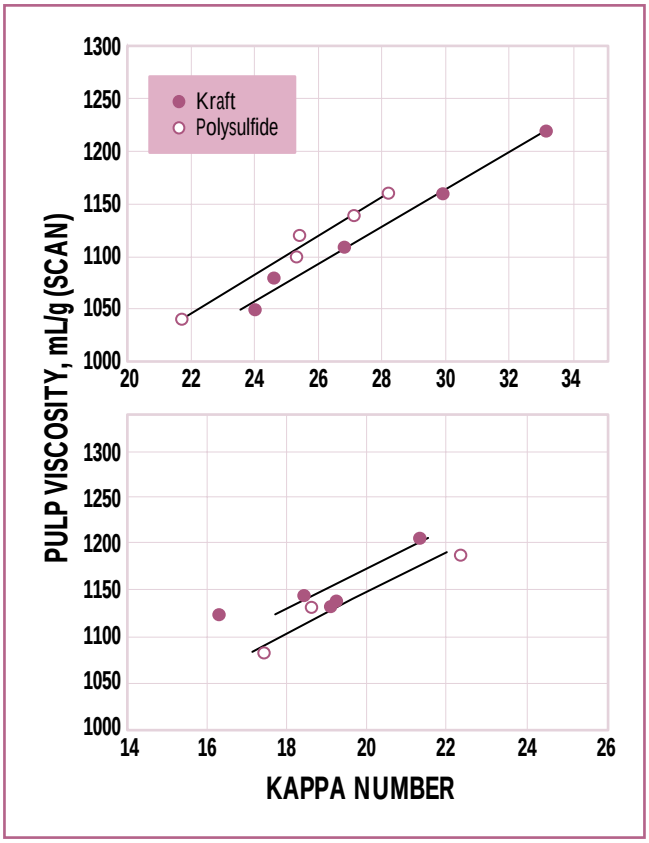
Fiber strength properties were also evaluated for these ITC-type pulps. The polysulfide pulps had a somewhat lower zero-span tensile index at 160 (N•m)/g, in relation to the reference of 162 (N•m)/g (+2 units for the tested beating effects). Thus there was no significant difference in fiber strength between the polysulfide and the reference ITC-type pulps.

No comparison was made in this investigation with a bleached modified kraft pulp at a higher unbleached kappa number and a higher carbohydrate yield. An ITC pulp of unbleached kappa no. 19 has a 15% higher strength than an ITC pulp and a conventional kraft pulp of kappa no. 27 *(1)*. This decrease in carbohydrate yield from kappa no. 27 to kappa no. 19 when the delignification is extended can be estimated as 1.6%, compared with the 1.5% increase in yield obtained as a result of polysulfide pretreatment in this study. The kraft pulps from modified cooks without polysulfide pretreatment are stronger than the reference pulp of the conventional kraft cook. Therefore, the polysulfide pretreatment combined with modified kraft cooking gives the same type of pulp as the conventional kraft pulp cooked to a higher kappa number. Also, the decrease in kappa number, in relation to pulp yield, made possible by polysulfide is of the same magnitude as the decrease made possible by modified cooking, in relation to pulp viscosity.

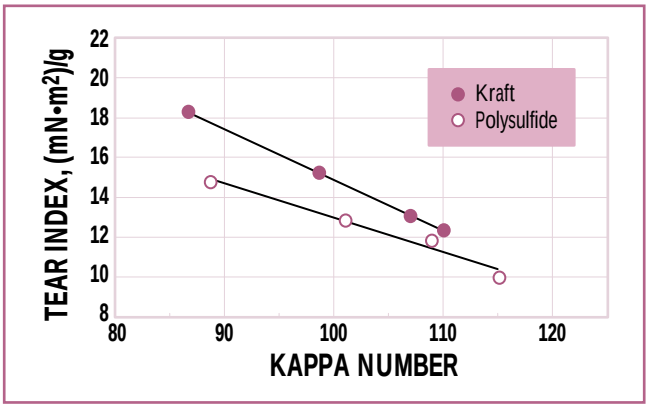
In a similar study of MCC-type cooks with and without polysulfide pretreatment, tear index at constant tensile index was 5–10% lower for the polysulfide MCC cook than for the reference MCC cook *(26)*. The decline in tearing resistance, because of polysulfide addition, also has been confirmed elsewhere recently *(9, 19)*.

The beatability for the ITC-type pulps was evaluated as the development of the tensile index after a given number of revolutions in a PFI mill (**Fig. 6**). The beatability was slightly higher for the ITC-type pulp with polysulfide pretreatment than for the ITC-type reference pulp. The tensile index at maximum beating (8000 revolutions) was 115 (N•m)/g for the polysulfide ITC pulp, compared to 110 (N•m)/g for the reference without polysulfide.

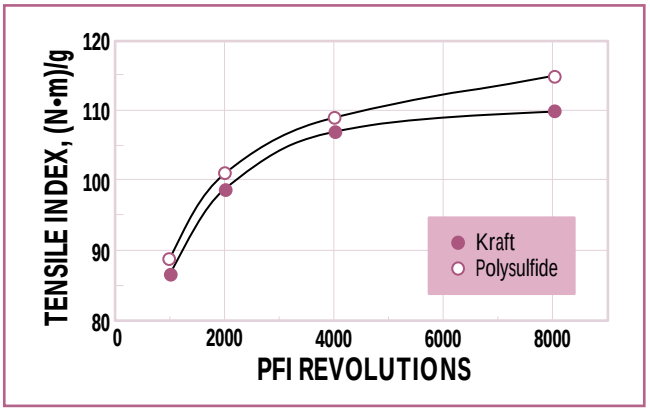
In the case of MCC-type cooks with and without polysulfide pretreatment, the maximum tensile index was 115 (N•m)/g, with no difference between polysulfide and reference pulps *(26)*. Others have concluded, however, that 15–20% less refining energy is required if polysulfide is applied to an extended modified cook on Southern pine *(19)*.




*4. Effect of polysulfide on unbleached pulp viscosity in the MCC- and ITC-type cooks*




*5. Effect of polysulfide in ITC-type cooks on bleached pulp tear index at a given tensile index. [Brownstock kappa no. 19 and pulp viscosity of 1135 mL/g (SCAN).]*




*6. Effect of polysulfide in ITC-type cooks on bleached pulp tensile index at different numbers of beating revolutions in a PFI mill*

### *Pulp performance in ECF bleaching*

The bleachability for the ITC-type cooks with and without polysulfide pretreatment was evaluated as consumed OXE [oxidation equivalents *(29)*] per ton of pulp and kappa number after the oxygen stage at a brightness of 89% ISO. The bleachability in the OD(E+P)DED bleaching sequence showed no significant difference between a polysulfide ITC-type pulp and a reference ITC-type pulp. The polysulfide pulp required 133 OXE per metric ton of pulp and kappa number to reach a pulp brightness of 89% ISO, whereas the reference pulp required 135 OXE per metric ton of pulp and kappa number. (The OXE calculations were based on the consumption of bleaching chemicals. Though not presented here, further details are available if needed.)

The bleachability of the MCC-type cooks with and without polysulfide pretreatment was evaluated as final ISO% brightness obtained at a constant chlorine dioxide charge in another study *(26)*. The unbleached kappa number was about 27 in this case. The results obtained in an ECF bleaching sequence, OD(E+P)D, were final ISO brightnesses of 88.0% for the reference pulp and 86.3% for the polysulfide pulp.

## CONCLUSIONS

The advantage of adding polysulfide (1.6–1.7% on dry wood) in a modified MCC or ITC cook to low kappa numbers would be a pulp produced to a higher yield (1.2–1.5% on dry wood). This higher yield would be achieved at the same selectivity, but the tear strength would be somewhat lower. This improvement can be obtained provided the sulfidity is raised by 10%. This 10% increase compensates for the loss in hydrogen sulfide ion concentration when polysulfide is produced in an oxidation process.

The tear strength at a given pulp yield (i.e., at 8 units higher kappa number for the reference) can be estimated to be the same for the polysulfide cook. The positive effect on beatability (tensile index after maximum beating) for the polysulfide pulps in relation to the reference was too low to be of significance. With an elemental chlorine-free bleaching sequence, the bleachability is about the same for both the reference and the samples pretreated with polysulfide, both for MCC- and ITC-type pulps.

Extended delignification in a polysulfide cook with a somewhat higher white liquor sulfidity thus seems to be an interesting alternative for further improvement of the modified kraft cooking of the MCC and ITC types. **TJ**

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