Improved modified kraft cooking

Part 3: Modified vapor-phase polysulfide cooking

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ABSTRACT: An improved modified kraft cooking process (1) consists of an initial vapor-phase stage followed by a liquor-phase stage. All sulfide is charged at the beginning of the vapor-phase stage, while alkali is divided between the two stages. Using this cooking technique, the effect of added polysulfide was studied. The increase in yield at a given kappa number was found to be univocally determined by the concentration of polysulfide in the initial phase of the cook. Consequently, at the same polysulfide concentration, the yield increase for a conventional polysulfide cook is nearly the same as that for a modified vapor-phase polysulfide cook. The increase in viscosity at a given kappa number was clearly related to the sulfide concentration in the initial phase of the cook. Consequently, at the same sulfur charge, a modified vapor-phase polysulfide pulp has somewhat lower viscosity than a modified vapor-phase kraft pulp, due to the lower sulfide concentration that resulted from the decomposition of polysulfide into the nonreactive thiosulfate in the polysulfide cook.

KEYWORDS: Heating, kappa number, polysulfides, selectivity, sulfides, sulfur compounds, vapor phases, viscosity, yield.

Polysulfide cooking was studied in the 1940s, and a great deal of research was conducted on the subject in the 1960s. A polysulfide cook was found to give a higher pulp yield than a conventional kraft cook *(2–5)*. During a polysulfide cook, carbonyl end groups in polysaccharides are oxidized to gluconic acid end groups by polysulfide, thus stabilizing the polysaccharides against alkaline degradation and increasing the pulp yield. In polysulfide pulping of softwood, the increase in pulp yield is mainly a result of an increase in glucomannan yield, and in the case of hardwood, the pulp yield increase is due to an increase in xylan yield.

In a pulp mill, polysulfide cooking liquor is normally generated by partial oxidation of sodium sulfide in the white liquor, which results in a lower sulfidity in the cooking liquor and thus a lower cooking selectivity. In our previous study *(1)*, a new modified kraft cooking process is described. The process has an initial vapor-phase stage followed by a liquor-phase stage with a high liquor-to-wood ratio (6:1). All the sulfide is charged at the beginning of the cook, while alkali is distributed between the two stages. This implies that the chemicals must be separated in the white liquor into a sulfide-rich and a sulfide-free cooking liquor, the former being charged at the beginning of the cook and the latter in the later part of the cook. Compared to a conventional kraft cook, this process shows an improved profile of sulfide and dissolved lignin concentrations, resulting in a significant improvement in cooking selectivity with respect to pulp viscosity.

Jian has studied the effect of polysulfide on pulp yield and strength properties in extended modified kraft cooking *(6)*. He found that with 2-3% polysulfide, a softwood pulp could be produced with a yield comparable to a conventional kraft pulp. In order to further improve the pulp yield, a modified vapor-phase polysulfide cook was studied in this work. As a result of the initial vapor-phase, the added

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I. Chemical charges for the different cooks

Cook type[a]	Na_2S[b], mole/100 g	Polysulfide excess sulfur[c], %	Total sulfur[b], mole/100 g	NaOH[b], mole/100 g	Total e.a.[c], % as NaOH
C K ref.	0.09	-	0.09	0.42	20.0
M V K	0.12	-	0.12	0.38	20.0
M V K	0.15	-	0.15	0.35	20.0
M V Ps	0.09	1	0.12	0.40	19.6
M V Ps	0.09	2	0.15	0.39	19.2

[a]C K ref. indicates conventional kraft reference with a liquor-to-wood ratio of 4:1.
M V K indicates modified vapor-phase kraft cook with an initial vapor-phase stage followed by a liquor-phase stage with a high liquor-to-wood ratio (6:1).
M V Ps indicates modified vapor-phase polysulfide cook, which involves the same cooking procedure as M V K, but with the addition of polysulfide in the initial vapor-phase stage.
[b]Moles/100 g wood
[c]% on wood

polysulfide reacted at a high concentration, which promotes its effectiveness. Note that this work was carried out in laboratory trials. More work on the chemical and water balances for a mill-scale implementation of the modified vapor-phase kraft process is in progress.

Experimental

Polysulfide solutions were prepared in a flask by dissolving elemental sulfur in sodium sulfide solution at 80–90°C. The air in the flask was dispelled by bubbling nitrogen gas through the sulfide solution. NaOH solution was added to the polysulfide solution before the cook to obtain the desired effective alkali charge.

The wood chips used were a mixture of industrial spruce and pine. After evacuation and charge of cooking liquor, the wood chips were impregnated and cooked as previously described *(1)*. The cooking temperature was increased from 70°C to 170°C at a rate of 1°C/min and then maintained at 170°C. The vapor-phase stage was terminated at H-factor 300. The cooked pulps were washed, and the black liquors and pulps were analyzed as previously described *(1)*. The chemical charges for the different cooks are shown in **Table I.**

In the modified vapor-phase polysulfide cooks, the total charge of initial effective alkali was slightly lower than in the conventional kraft reference and in the modified vapor-phase kraft cook, since one part of alkali in the white liquor was consumed when elemental sulfur was dissolved in the white liquor according to the equation:

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

The calculation of the alkali consumptions is based on certain assumptions given in the appendix.

Results

Effect on pulp yield

Figure 1 shows the influence of polysulfide charge on pulp yield and compares the pulp yield at a given kappa number for the modified vapor-phase polysulfide cooks and the conventional kraft reference. The polysulfide cooks, as expected, have a considerably higher pulp yield than the conventional reference; the higher polysulfide charge also results in a higher pulp yield.

Figure 2 shows the relationship between the yield increase with respect to a conventional kraft reference and the polysulfide excess sulfur concentration for the modified vapor-phase and the conventional polysulfide cook; the data in the latter case were taken from the literature *(2)*.

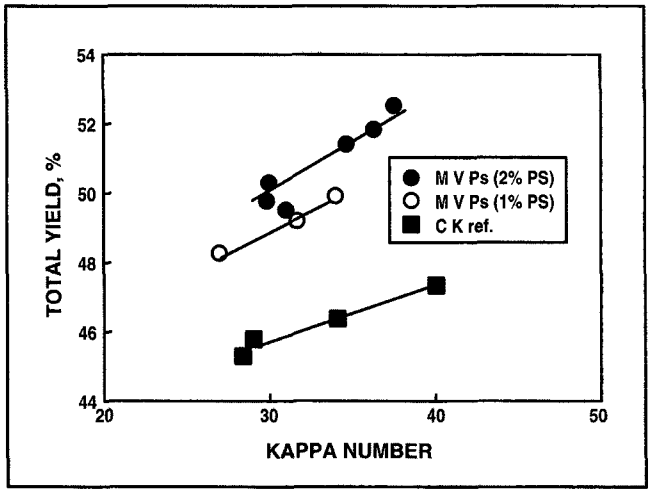
The polysulfide excess sulfur concentration was calculated based on the sulfur charge and the liquor-to-wood ratio as well as on the assumption that the charged elemental sulfur was totally transformed into polysulfide excess sulfur. The figure shows that the two types of polysulfide cooks have nearly the same relationship between yield increase and polysulfide excess sulfur concentration. This indicates that the higher pulp yield, in the case of the modified vapor-phase polysulfide cook (**Table II**), is probably due to the higher concentration of polysulfide excess sulfur resulting from the low liquor-to-wood ratio in the vapor-phase stage.

Effect on pulp viscosity

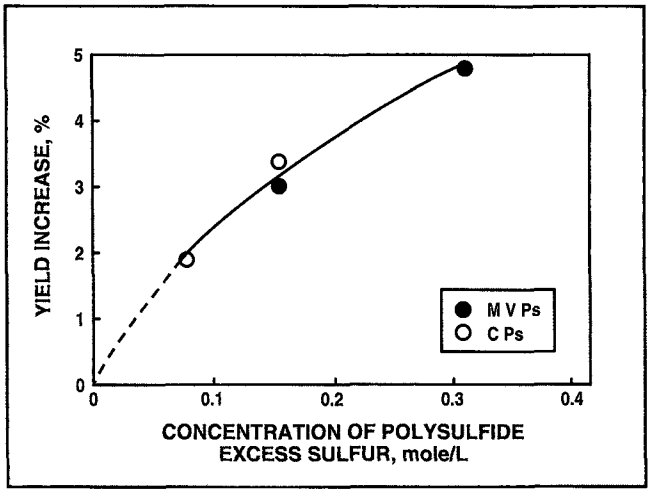
Figure 3 shows the effect of polysulfide charge on pulp viscosity. The modified vapor-phase polysulfide cooks give a significantly higher viscosity at a given kappa number than the conventional kraft reference. An increase in polysulfide charge leads to an increase in pulp viscosity.

The improvement in pulp viscosity demonstrated in Fig. 3 may be

1. Influence of the polysulfide (PS) charge on pulp yield. Variables in legend are defined in Table I.



2. Relationship between the yield increase (with conventional kraft at kappa no. 30 as reference) and polysulfide excess sulfur concentration for the modified vapor-phase and conventional polysulfide cooks. Variables in legend are defined in Table II.



II. Yield increase at kappa no. 30 with a conventional kraft cook as reference

Cook type*	*Yield increase for a charge of 1% polysulfide excess sulfur,* %-units
M V Ps	3.2
C Ps	2.0

*M V Ps indicates modified vapor-phase polysulfide cook.
CPs indicates conventional polysulfide cook.

due to the concentration increase of sulfide ions in the polysulfide cooks. Polysulfide ions decompose into hydrogen sulfide and thiosulfate ions at elevated temperatures *(7)* according to the equation:

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

An increase in sulfide concentration improves the cooking selectivity *(8)*. To study whether the improvement in pulp viscosity results solely from the increase in sulfide concentration in the polysulfide cooks or from the combined effect of sulfide and polysulfide, modified vapor-phase kraft cooks with different sulfide charges were carried out (chemical charges are shown in Table I). The modified vapor-phase polysulfide and the modified vapor-phase kraft cooks were then compared with respect to pulp viscosity. As shown in **Fig. 4,** the viscosity improvement at the same charge of extra sulfur is slightly higher in the case of the sulfide than in that of the polysulfide.

The polysulfide starts to decompose when the temperature is increased above 100°C. Of the decomposition products, the thiosulfate ions are nonreactive in the cooking liquor. Consequently, the sulfide concentration is lower in the polysulfide case than in the cook with extra sulfide added at a given percentage charge of extra sulfur. Based on this, **Fig. 5** shows the relationship between the viscosity improvement and the sulfide concentration (after the decomposition of the polysulfide); the sulfide concentration for the polysulfide cook is calculated based on certain assumptions (see the appendix). As shown in the figure, the modified vapor-phase polysulfide pulp gives a slightly higher pulp viscosity than the modified vapor-phase kraft pulp at a given sulfide concentration. The reason the polysulfide cook shows the better cooking selectivity with respect to pulp viscosity could be related to favorable reactions between polysulfide and lignin and to more sulfide being formed in the polysulfide cook than was assumed.

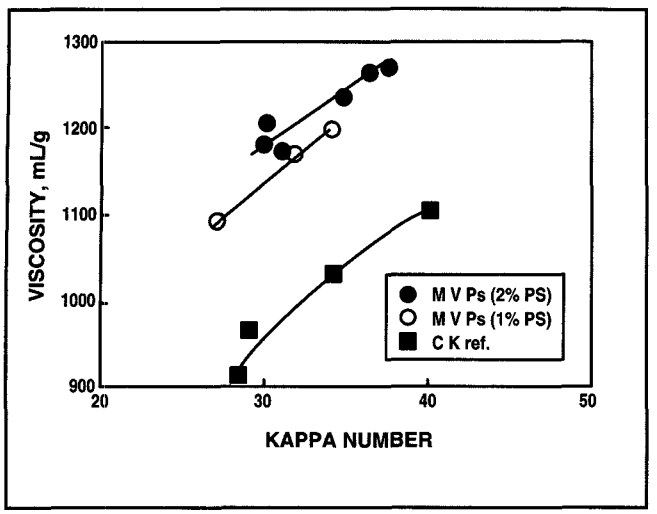
Polysulfide produced through catalytic oxidation of white liquor

In this laboratory study, the polysulfide was made by dissolving sulfur in white liquor. In a mill operation, the polysulfide is manufactured by partial oxidation of white liquor *(9)*. During these reactions, some sulfide is consumed in the formation of polysulfide as well as in a side reaction forming thiosulfate. In addition, some hydroxide ions are formed.

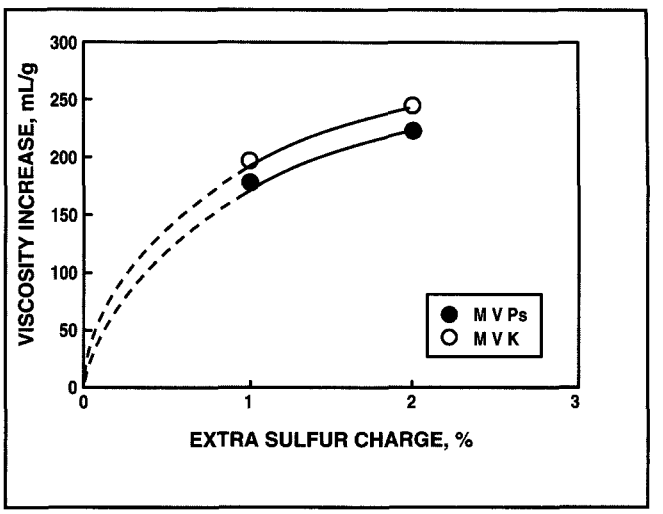
Knowing the original concentrations of sulfide in the processes (in the case of conventional kraft cook with an initial sulfide concentration of 0.22 mole/L) discussed in this paper and the stoichiometric relationships in the various reactions (see the appendix), it is possible to calculate the sulfide and polysulfide excess sulfur concentrations. Corresponding yield increases can be found in the figures, and the data are presented in **Table III.**

Compared to the other polysulfide alternatives, the modified vapor-phase polysulfide cook results in the highest yield increase as a result of the high polysulfide and hydroxide ion concentrations, which increase

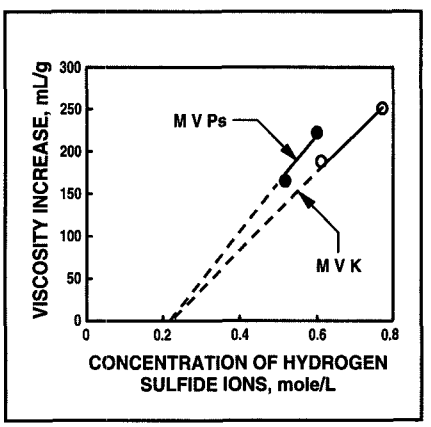
3. Influences of the polysulfide charge on pulp viscosity. Variables in legend are defined in Table I



4. Viscosity improvement (with conventional kraft at kappa no. 30 as reference) for the modified vapor-phase polysulfide cook and the modified vapor-phase kraft cook. Variables in legend are defined in Table I.



5. Relationship between the viscosity improvement (with conventional kraft at kappa no. 30 as reference) and sulfide concentration (after the decomposition of polysulfide) for the modified vapor-phase polysulfide cook and the modified vapor-phase kraft cook. Variables in legend are defined in Table I.



III. Yield increase over the conventional kraft reference at kappa no. 30 calculated for polysulfide cooking using catalytic oxidation of white liquor

*Cook type**	*Conc. of sulfide, mole/L*	*Conc. of polysulfide excess sulfur, mole/L*	*Yield increase, %-units*
C Ps	0.14	0.09	2.1
M Ps	0.10	0.06	1.6
M V Ps	0.27	0.18	3.3

*M Ps indicates modified polysulfide cook, which was based on adding polysulfide in a two-stage modified kraft cook with a liquor-to-wood ratio of 4:1 in both stages.

the stabilization of carbohydrates *(10)*.

Conclusions

A significant improvement in pulp yield can be obtained if polysulfide is added to the improved modified kraft cook. The yield increase in different polysulfide cooks is unambiguously related to the concentration of polysulfide excess sulfur at the beginning of the cook.

The selectivity with respect to viscosity is mainly related to the concentration of hydrogen sulfide ions in the cooking liquor in the first part of the cook after the decomposition of the polysulfide. The selectivity is, to a lesser extent, probably also influenced by the polysulfide. TJ

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Appendix

Calculation of the sulfide concentration (after the decomposition of the polysulfide) in the modified vapor-phase polysulfide cook

The calculations are based on the following assumptions:

- The charged elemental sulfur is totally transformed into polysulfide according to Eq. 1.
- The increase in sulfide concentration in the polysulfide cook at elevated temperatures is only the result of the polysulfide decomposition according to Eq. 2. The sulfide produced by reactions between polysulfide and carbohydrates is negligible, and that produced by reactions with other organic substances is also assumed to be negligible.

Equations 1 and 2 can be combined to give:

$$S^{\circ} + HO^{-} \rightarrow 0.5\ HS^{-} + 0.25\ S_2O_3^{2-} + 0.25\ H \qquad (3)$$

According to this equation, 1 mole S° decomposes into 0.5 mole HS^{-}.

At a charge of 1% elemental sulfur, 0.5 x (1/32) = 0.016 mole HS^{-} (based on 100 g wood chips) is produced. Since the sulfide in the white liquor is 0.09 mole HS^{-}, the total amount of sulfide in the cooking liquor after the decomposition of the polysulfide is 0.09 + 0.016 = 0.106 mole HS^{-}.

Consequently, the concentration of hydrogen sulfide ions is 0.106/0.2 = 0.53 mole/L, based on a liquor-to-wood ratio of 2:1 in the vapor-phase stage. In the same way, a sulfide concentration of 0.61 mole/L is obtained in the case of a 2% sulfur charge.

Calculation of alkali consumption in the manufacture of polysulfide

Based on the assumption that n in Eq. 1 equals 3, a 1% sulfur charge results in a consumption of (1/3) x (1/32) = 0.01 mole OH^{-} = 0.4% e.a. (as NaOH). Therefore, the net effective alkali charge becomes 20 – 0.4 = 19.6%. In the same way, a 2% sulfur charge results in an NaOH consump- tion of 0.8% e.a. and a net effective alkali charge of 19.2%.

Calculation of the polysulfide and sulfide concentrations (after the decomposition of the polysulfide) when assuming white liquor oxidation

In a mill operation system, sulfide in the white liquor is catalytically oxidized according to the equations:

$$(n+1)\ HS^{-} + (n/2)\ O_2 \rightarrow (n-1)\ OH^{-} + S_nS^{2-} + H_2O \qquad (4)$$

$$2\ HS^{-} + 2\ O_2 \rightarrow S_2O_3^{2-} + H_2O \qquad (5)$$

The calculations are based on the following assumptions:

- The degree of oxidation of hydrogen sulfide ions is 60%, and the polysulfide yield of the hydrogen sulfide ion oxidation is 65%.
- The liquor-to-wood ratio is 4:1 for both the conventional and the modified polysulfide cooks. The total chemical charge is 0.5 mole OH^{-} and 0.09 mole HS^{-} (based on 100 g wood chips). Seventy percent of the total chemicals are charged in the first part of the modified polysulfide cook.

Polysulfide concentration

Conventional polysulfide cook. According to the initial amount of hy- drogen sulfide ions, the degree of oxidation of hydrogen sulfide ions, and the polysulfide yield of the hydrogen sulfide ion oxidation,the amount of polysulfide excess sulfur in the conventional polysulfide cook is as follows:

$$S^{\circ} = 0.09 \times 60\% \times 65\% = 0.035 \text{ mole} \qquad (6)$$

Accordingly, the concentration of the polysulfide excess sulfur, based on a liquor-to-wood ratio of 4:1, is:

$$[S^{\circ}] = 0.035/0.4 = 0.09 \text{ mole/L} \qquad (7)$$

Modified polysulfide cook. Since 70% of the total chemicals are charged in the first part of the cook, the concentration of polysulfide is only 70% of that in the conventional polysulfide cook:

$$[S^{\circ}] = 0.09 \times 70\% = 0.06 \text{ mole/L} \qquad (8)$$

Modified vapor-phase polysulfide cook. With the same amount of polysulfide excess sulfur as in the conventional polysulfide cook, the concentration of polysulfide in the modified polysulfide cook is doubled due to the halved liquor-to-wood ratio (2:1) in the initial vapor-phase stage:

$$[S^{\circ}] = 0.035/0.2 = 0.18 \text{ mole/L} \qquad (9)$$

Sulfide concentration (after decomposition of the polysulfide)

Conventional polysulfide cook. As in the case of the sulfide concentration when elemental sulfur is added to the white liquor, the total amount of sulfide in the conventional polysulfide cook is the sum of the nonoxidized sulfide in the white liquor and the sulfide produced after decomposition of the polysulfide:

$$HS^{-} = (0.09 \times 40\%) + (0.035 \times 0.5) = 0.054 \text{ mole} \qquad (10)$$

$$[HS^{-}] = 0.054/0.4 = 0.14 \text{ mole/L} \qquad (11)$$

Modified polysulfide cook

$$[HS^{-}] = 0.14 \times 70\% = 0.10 \text{ mole/L} \qquad (12)$$

Modified vapor-phase polysulfide cook

$$[HS^{-}] = 0.054/0.2 = 0.27 \text{ mole/L} \qquad (13)$$