

Extended modified cooking of Southern pine with polysulfide: effects on pulp yield and physical properties

Jian Er Jiang

ABSTRACT: *The effects of polysulfide (PS) addition to extended modified cooking on pulp yield and physical properties were investigated in the laboratory. At about 17 kappa number, addition of 2% and 3% polysulfide was found to increase pulp yield by about 2% and 3%, respectively. Pulp tear, burst, and tensile properties were not affected to any noticeable degree by the polysulfide addition. Pulp refining energy requirement decreased by approximately 10% and 20%, respectively, with a 2% and 3% polysulfide charge.*

Extended modified cooking and PS pulping were shown to be two compatible technologies. This study demonstrates the potential of achieving both better physical properties and a higher yield with PS addition to extended modified cooking.

KEYWORDS: *Kraft pulping, modified kraft process, physical properties, pinus, polysulfides, pulp properties, yield.*

Extended modified cooking enables one to produce a softwood kraft pulp at a kappa number below 20 with physical properties comparable to a conventional kraft (CK) pulp at about 30 kappa number (1). This advance in extended delignification substantially decreases bleaching chemical charges as well as bleach effluent loads. Severe yield losses, however, ultimately occur when pulping to a lower kappa number. Therefore, finding ways to improve pulp yield in extended delignification becomes more impor-

tant than ever to make modified cooking economically more attractive.

Polysulfide (PS) is an effective pulping additive for increasing kraft pulp yields (2-10). Under alkaline conditions, PS oxidizes the aldehyde (reducing end) groups in polysaccharides to carboxylic groups, rendering the polysaccharides, in particular glucomannans, stable against the alkali-assisted end-wise degradation (peeling reactions). The yield increase for every 1% PS addition was found to decrease with cooking to a lower kappa

number, from 2% at 60 kappa number to 1.2% at about 28 kappa number (3, 7-9). In addition, PS pulps were shown to give a lower tear strength than a CK pulp at comparable kappa number. The lower tear strength was believed to be caused mainly by an increased interfiber bonding due to a higher retention of hemicelluloses and a smaller number of load-sharing fibers per unit pulp weight at a higher yield.

Two interesting questions arise: How does cooking to a much lower kappa number affect the yield improvement by PS addition? If PS is still effective at lower kappa numbers, how does a higher pulp yield affect the physical properties of extended modified pulps? Therefore, the objective of this study was to investigate the effects of PS addition to extended modified cooking on pulp yield and physical properties.

Experimental

Southern pine chips were screened to remove fractions thinner than 3 mm, thicker than 8 mm, and longer than 45 mm. A 20-liter digester equipped with circulation and indirect heating was employed.

PS liquor was prepared by dissolving 250 g elemental sulfur in 2 L sodium sulfide solution at about 60°C. The initial concentration of sodium sulfide, or nominal sulfidity, in the PS cooks was controlled to be the same as

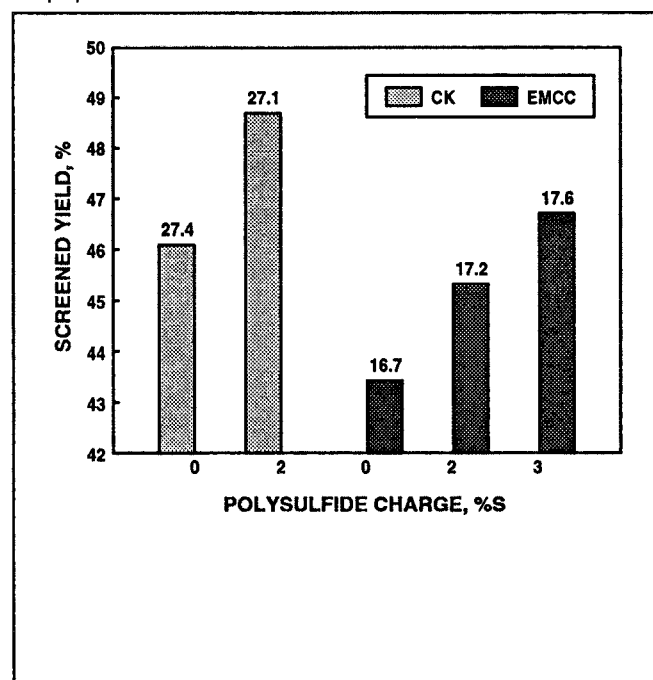
Jiang is manager-R&D laboratory at Kamy, Inc., Ridge Center, Glens Falls, NY 12801.

I. Summary of pulping results and conditions

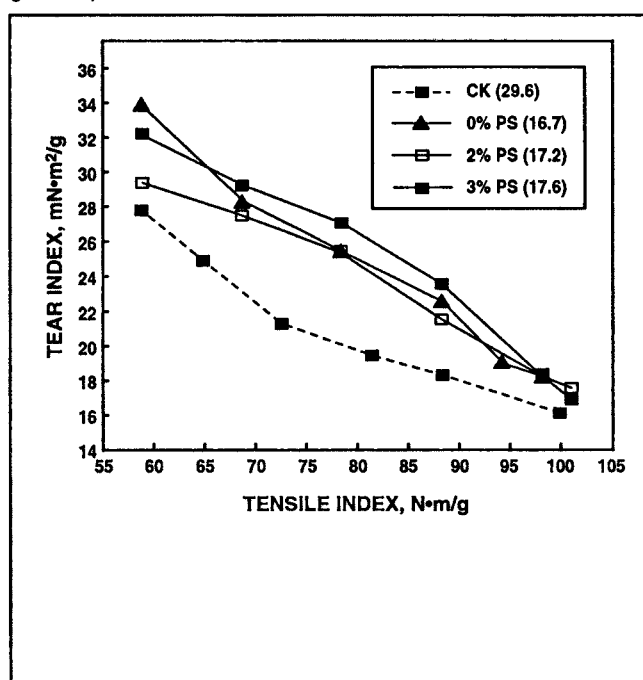
	Conventional kraft cooks			Extended modified cooks		
Cook number	A3011	A2893	A2896	A3070	A3071	A3072
Polysulfide, % S on wood	0	0	2	0	2	3
Nominal sulfidity, % AA	30	30	30	31	30	30
Impregnation stage:						
Total time, min	45	45	45	45	45	45
Time at temperature, min	30	30	30	30	30	30
Temperature, °C	110	110	110	110	110	110
EA charge, % Na ₂ O on wood	15.3	16.0	17.0	10.9	10.9	13.0
L/W ratio, L/kg	4.0	4.5	4.5	3.2	3.2	3.2
First cooking stage:						
Total time, min	124	130	130	60	60	60
Time at temperature, min	94	100	100	45	45	45
Temperature, °C	170	170	170	165.0	165.2	165.3
EA charge, % Na ₂ O on wood	...	...	...	3.9	3.9	3.9
L/W ratio, L/kg	...	...	...	4.0	4.0	4.0
Countercurrent stage:						
Time, min	...	...	...	240	240	240
Temperature, °C	...	...	...	165	165.2	165.3
H-factor	1560	1720	1690	2960	3020	3050
Screened yield, % on wood	46.2	46.1	48.7	43.4	45.3	46.7
Rejects, % on wood	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Kappa number	29.6	27.4	27.1	16.7	17.2	17.6
Viscosity, mPa-s	39.7	35.8	43.2	31.6	36.0	39.4

Other conditions common to all cooks: presteaming at 110 °C for 5 min.

1. Effect of PS addition on pulp yield. CK = conventional kraft cooking; EMCC® = extended modified continuous cooking. Kappa numbers of the pulps are shown above the columns.



2. Comparison of tear vs. tensile strength of the CK reference and three modified pulps at various PS charges. Pulp kappa numbers are given in parentheses.



II. Summary of pulp physical properties

	CSF, mL	PFI rev.	Bulk, cm ³ /g	Burst index, kPa·m ² /g	Tensile index, N·m/g	Tear index, mN·m ² /g
A3011						
CK reference	723	500	1.73	3.8	58.9	27.8
0% PS	600	4500	1.49	6.8	87.3	18.4
29.6 kappa no.	500	6600	1.46	7.1	92.2	17.5
39.7 mPa·s	400	8400	1.44	7.3	97.1	16.8
	300	10100	1.43	7.4	100.1	16.1
A3070						
EMCC control	771	0	2.06	2.8	48.1	33.8
0% PS	600	4600	1.62	6.8	95.2	20.2
16.7 kappa no.	500	6400	1.60	7.3	97.1	18.8
31.6 mPa·s	400	8300	1.59	7.7	100.1	17.8
	300	10200	1.57	8.1	103.0	17.0
A3071						
EMCC	762	0	2.11	3.1	45.1	31.4
2% PS	600	4000	1.60	7.6	92.2	19.7
17.2 kappa no.	500	5600	1.59	7.8	96.1	18.7
36.0 mPa·s	400	7400	1.58	8.1	99.1	18.1
	300	9400	1.57	8.2	101.0	17.5
A3072						
EMCC	760	0	2.11	3.0	50.0	33.5
3% PS	600	3800	1.64	7.2	95.2	20.8
17.6 kappa no.	500	5300	1.60	7.7	98.1	18.5
39.4 mPa·s	400	6700	1.58	8.2	100.1	17.1
	300	8300	1.54	8.5	102.0	16.9
A2893						
Bleached CK	765	0	2.08	1.5	19.6	23.0
88.6% ISO	600	3200	1.64	6.6	83.4	15.9
0% PS	500	4800	1.62	7.1	91.2	14.4
	400	6300	1.60	7.6	95.2	13.8
	300	8100	1.57	7.7	98.1	13.3
A2896						
Bleached CK	766	0	1.99	1.8	24.5	24.6
88.8% ISO	600	2500	1.67	6.6	84.4	14.5
2% PS	500	3900	1.61	7.3	92.2	12.6
	400	5200	1.57	7.7	97.1	11.9
	300	7000	1.56	7.8	99.1	11.5

that in the other cooks, by mixing the PS liquor with appropriate amounts of white liquor, NaOH solution, and water.

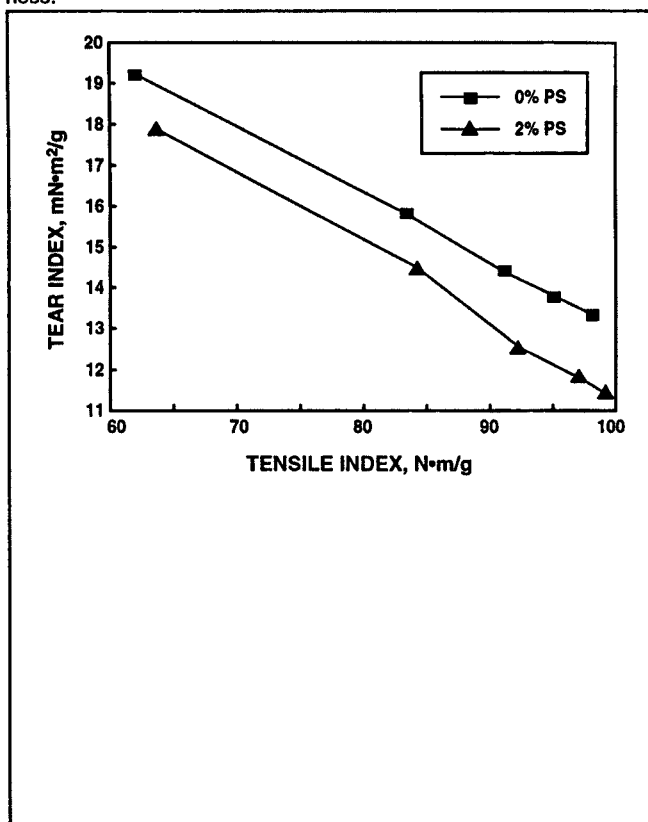
Major pulping conditions are given in Table I. Detailed laboratory pulping procedures can be found elsewhere (1). TAPPI methods were followed for all analytical tests, while CPPA methods were employed for tests of physical properties.

Effect on pulp yields

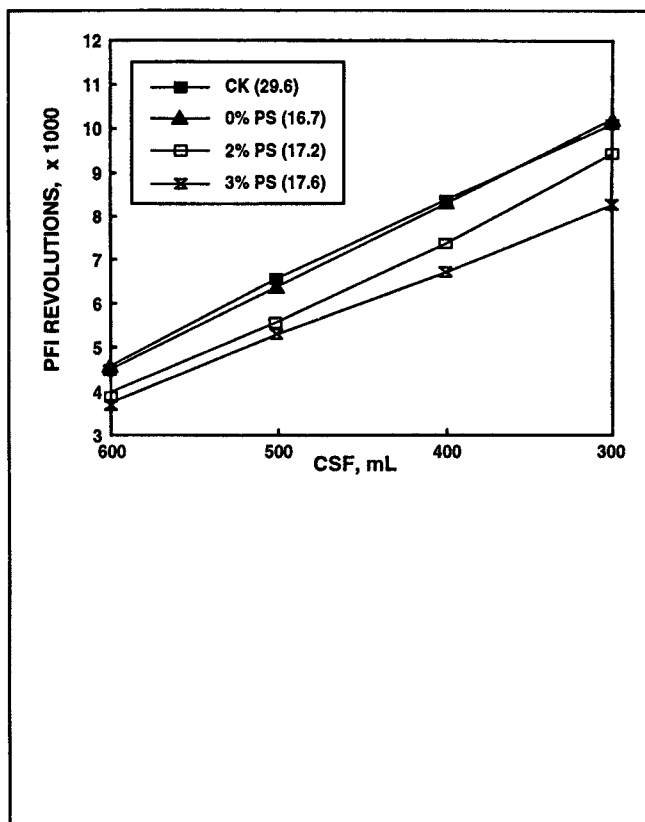
Addition of 2% and 3% PS to extended modified cooking was found to increase the pulp yield by about 2% and 3% (on wood), respectively, at a kappa number around 17 (Fig. 1 and Table I). These results demonstrate the potential of producing kraft pulps at a kappa number below 20 with yields close to that of a CK pulp at 30 kappa number, achieving substantial savings in bleaching chemicals and dramatic decreases in effluent loads.

We also found that charging 2% PS increased the pulp yield by about 2.5% when cooking to about 27 kappa number (Table I), suggesting that the yield increase from PS addition is larger at a higher kappa number. This is in good agreement with results from the previous studies (3, 7-9). In those studies, pulp yield was found to increase by 1.2-2% for every 1% of PS added, and to increase with a higher kappa number. Since both conventional and modified cooks were found to follow essentially the same yield-kappa rela-

3. Effect of 2% PS addition on tear vs. tensile strength of two bleached CK pulps. The pulps with unbleached kappa number of about 27 were bleached with a DEDD sequence to approximately 89% ISO brightness.



4. Effect of PS addition on refining of extended modified pulps. The CK reference pulp is included for comparison. Pulp kappa numbers are shown in parentheses.



tionship (1), a trend appears to exist that yield improvements from PS addition decrease with an increasing extent of delignification.

Two factors might be responsible for the decreasing effect on the yield improvement. One is the increased carbohydrate degradation when cooking below 30 kappa number, which is probably inherent with kraft processes. The other relates to a higher retention of hemicelluloses with PS pulps (3, 7-9). Because of their lower degrees of polymerization and amorphous structures, hemicelluloses are less stable than cellulose under alkaline pulping conditions, and more severe removal of hemicelluloses is expected to occur when cooking to a lower kappa number.

Effects on physical properties

The results from testing on physical properties of four unbleached pulps and two bleached pulps are given in

Table II. The CK pulp at about 30 kappa number served as the reference, while the modified pulp with 0% PS addition was used as the control.

Tear strength

Addition of PS to extended modified cooking did not appear to affect the pulp tear strength. Figure 2 shows that pulps with 2% and 3% PS charges gave tear at constant tensile comparable to the control pulp. All three modified pulps were found to be stronger than the reference CK pulp, suggesting that the improvement in tear strength from extended modified cooking can be maintained with PS charges up to 3%.

This finding is in apparent disagreement with the previous results (3, 7-9) that PS pulps showed a lower tear strength. The disagreement might result from differences in cooking methods, i.e., CK vs. modified or in kappa

numbers of the pulps, or both. Extended modified cooking is carried out under milder conditions, favoring cooking uniformity, decreasing cellulose degradation, and better preservation of fiber strength (1). The stronger extended modified pulps might be affected to a lesser degree by PS addition, probably because of a higher degree of polymerization for the cellulose, or a slightly higher cellulose yield (11). In addition, cooking to a lower kappa number lowers the content of hemicelluloses, hence decreasing the adverse effect on tear strength.

The result from comparison of tear vs. tensile strength for two bleached CK pulps (unbleached kappa number of about 27) is consistent with this explanation. As can be seen in Fig. 3, the PS pulp did show a considerably lower tear strength below 600-mL freeness (Table II) or above 60 tensile index.

Polysulfide Pulping

Burst and tensile strength

The PS pulps showed a burst and tensile comparable to the control pulp, and higher than the reference CK pulp at a given freeness (Table II). This means extended modified cooking to a lower kappa number improves the burst and tensile properties, probably by making the fibers more flexible without losses in fiber strength. In addition, a higher hemicellulose retention by PS addition (3, 7-9) showed no noticeable effect on burst and tensile properties.

Refining requirement

Compared to the control pulp, addition of 2% and 3% PS resulted in about 10% and 20% decreases, respectively, in refining to a given freeness (Fig. 4). This is in agreement with the literature and is attributable to a higher retention of hemicelluloses by the PS pulps. Both the CK reference pulp and

the control pulp showed comparable freeness development in Fig. 4, despite their large difference in kappa number.

Conclusion

Addition of 2% and 3% PS to extended modified cooking increases pulp yield by about 2% and 3%, respectively. This corresponds to producing a softwood pulp at a kappa number of about 20 and 15 with a yield comparable to a CK pulp at 30 kappa number.

Addition of PS does not appear to affect pulp tear, burst, or tensile properties to any noticeable degree at a kappa number around 17. Pulp refining energy requirement can be decreased by approximately 10% and 20%, respectively, with 2% and 3% PS addition.

Extended modified cooking and PS pulping are two compatible processes

that offer complementary advantages for extended delignification. This study demonstrates the potential of achieving both better physical properties and a higher yield by addition of PS to extended modified cooking. ■

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