DELIGNIFICATION OF HIGH KAPPA NUMBER SODA–ODiMAQ PULPS WITH A POLYOXOMETALATE

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ABSTRACT

The objectives of this study were (a) to investigate the possibilities for increasing the yield of chemical pulp by using two stages of delignification and (b) to evaluate the possibility of replacing the kraft process with a more environmentally benign pulping system. High Kappa number kraft, soda–anthraquinone (AQ) and soda–octahydrodimethylanthraquinone (ODiMAQ) pulps were produced and then delignified to Kappa number 30 with aqueous solutions of the polyoxometalate $Na_{4.9+2}$ $[SiV_{0.9}MoW_{10.1}O_{40}]$. Pulp yields and strengths were determined. The properties of these pulps were compared with those of Kappa 30 pulps produced by single-stage kraft, soda–AQ, and soda–ODiMAQ pulping. The high Kappa pulps delignified with a polyoxometalate (POM) were significantly higher in yield than were the single-stage pulps. The highest yield two-stage pulp was the POM-delignified kraft pulp. However, all the resulting pulps were somewhat weaker than the single-stage kraft pulp. As the Kappa number of the initial soda–ODiMAQ pulps was increased from 65 to 83 and finally 96, the POM delignification of these pulps to Kappa number 30 resulted in a constant level of pulp yield and significantly decreased pulp strength. Strong pulps were nevertheless produced in all cases. Soda–ODiMAQ delignification to approximately Kappa number 65 followed by POM delignification could be a replacement for kraft pulping.

INTRODUCTION

Significant increases in pulp yield can be achieved by stopping kraft or soda–anthraquinone (AQ) cooks at high Kappa numbers and delignifying the pulps to bleachable levels with aqueous solutions of a polyoxometalate. Polyoxometalate (POM) delignified kraft pulp was shown to give higher yield and stronger pulp than did POM-delignified soda–AQ pulp [1]. It was thought that a higher level of AQ than that used (0.20%) might yield results equivalent to those of kraft pulp, though a higher level might be too expensive.

Recently, Dimmel and co-workers showed that octahydrodimethylanthraquinone (ODiMAQ) is a much more effective delignification catalyst than is AQ [2]. In their opinion, ODiMAQ can be produced for about the same cost, per unit weight, as can AQ. This being the case, soda–ODiMAQ cooking followed by POM delignification might give better results than soda–AQ or even kraft followed by POM delignification, and yet be economically viable.

In the present study, lodgepole pine chips were cooked to high Kappa numbers with soda–ODiMAQ and then delignified further to Kappa number 30 with aqueous solutions of POM $Na_{4.9+2}$ $[SiV_{0.9}MoW_{10.1}O_{40}]$. The yield and strength results from these pulps were then compared with previous results from kraft and soda–AQ cooking of the same wood followed by delignification to Kappa number 30 with the same POM. Comparisons were also made with pulps produced from the same chips and delignified to Kappa number 30 by single-stage kraft, soda–AQ, and soda–ODiMAQ methods.

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Table I. Pulping conditions and results for single-stage cooks

	Pulp type[a]				
Conditions and results	Kraft	Soda–AQ	Soda–AQ	Soda–ODi	ła–ODi
Active alkali, %	20	20	20	20	20
Sulfidity, %	25	—	—	—	—
AQ, %	—	0.20	0.20	—	—
ODiMAQ, %	—	—	—	0.20	0.20
Temperature, °C	170	170	170	170	170
Heat-up time, min	60	60	60	60	60
Cooking time, min	110	160	110	110	90
Results					
Yield, %	48	46	47	46	48
Kappa no.	31	27	33	31	35
Viscosity, mPa·s	35	19	25	24	27

[a]AQ is anthraquinone; ODi is octahydrodimethylanthraquinone (ODiMAQ).

RESULTS AND DISCUSSION

Pulp Yield and Viscosity

Single-stage cooks. One kraft, two soda–AQ, and two soda–ODiMAQ pulps were produced in attempts to achieve Kappa number 30. The cooking conditions and results are shown in Table I. A level of 0.20% on oven-dry wood was used for both AQ and ODiMAQ. For a cooking time of 110 min, both kraft and soda–ODiMAQ produced pulps with Kappa number 31. For the same cooking time, soda–AQ gave a pulp with Kappa number 33. Soda–AQ pulping was thus only slightly slower than was kraft and soda–ODiMAQ. At Kappa number 31, the soda–AQ and soda–ODiMAQ pulp yields were about two points lower than that of the kraft pulp (46% versus 48%). The viscosity values were also significantly lower—about 24 mPa·s for both soda–AQ and soda–ODiMAQ and 35 mPa·s for kraft. Both catalyzed soda cooks were thus somewhat inferior to kraft cooking.

Two-stage cooks. The conditions used in producing the POM-delignified high Kappa number pulps, together with the results, are shown in Table II. Initially, pulps with a Kappa number of near 70 were produced and then POM-delignified to a Kappa number close to 30. Note that in the production of the high Kappa number pulps, the cooking time for the ODiMAQ-catalyzed soda cook was much shorter than that for the AQ-catalyzed cook (33 versus 48 min). The yield of the ODiMAQ-catalyzed cook (54%) was somewhat higher than the others (53%) considering the somewhat lower Kappa number (65 versus 68 and 71).

Conditions used in the POM delignifications were identical save for reaction times. The soda–AQ pulp took 5 min longer and the soda–ODiMAQ pulp 10 min longer than the kraft pulp to attain a final Kappa number of close to 30. The POM-delignified kraft pulp was significantly superior to the POM-delignified soda pulps. The POM-delignified kraft pulp had the highest overall yield (51%), the highest viscosity (40 mPa·s), and the lowest Kappa number (29). The second best pulp was the POM-delignified soda–ODiMAQ pulp, with an intermediate yield (50%) at a slightly higher Kappa number (30). However, the viscosity of this pulp was somewhat lower than that of the POM-delignified soda–AQ pulp (30 versus 36 mPa·s).

Delignification of higher kappa number soda–ODiMAQ pulps. We assumed that POM delignification of higher Kappa number pulps would lead to higher overall pulp yields. To check this assumption, two soda–ODiMAQ pulps with Kappa numbers of 83 and 96 were produced. These pulps were POM delignified to Kappa numbers close to 30. The conditions used in producing these pulps and the results are given in Table II. As Table II shows, while the overall yields of these pulps remained constant, viscosity decreased

Table II. Pulping conditions and results for two-stage cooks

	Pulp type					
Conditions and results	Kraft	Kraft	Soda–AQ	Soda–ODi	Soda–ODi	Soda–ODi
Conditions						
Active alkali, %	20	20	20	20	20	20
Sulfidity, %	25	25	—	—	—	—
AQ, %	—	—	0.20	—	—	—
ODiMAQ, %	—	—	—	0.20	0.20	0.20
Temperature, °C	170	170	170	170	170	170
Heatup time, min	60	60	60	60	60	60
Cooking time, min	110	55	48	33	30	28
Results						
Yield, %	48	53	53	54	59	61
Kappa no.	31	71	68	65	83	96
Viscosity, mPa·s	35	—	—	—	—	—
POM delignified with $Na_{4.9+2}[SiV_{0.9}MoW_{10.1}O_{40}]$						
POM, M		0.50	0.50	0.50	0.57	0.57
Consistency, %		3.0	3.0	3.0	3.0	2.0
End pH		6.6	6.9	6.6	7.3	7.4
Temperature, °C		140	140	140	150	170
Time, min.		50	55	60	420	480
Results						
Yield, %		51[a]	49[a]	50[a]	50[a]	50[a]
Kappa no.		29	33	30	32	34
Viscosity, mPa·s		40	36	30	24	16

[a]Overall yield.

greatly as the Kappa numbers of the single-stage pulps increased. This was probably due to the much longer reaction times in the POM stage. On the bases of yield and viscosity, an initial Kappa number of about 65 may be near optimum.

Comparison of single- and two-stage pulps. Excluding consideration of the POM-delignified soda–ODiMAQ pulps with initial Kappa numbers of 83 and 96, the three remaining two-stage pulps had both higher yield and higher viscosity (with the exception of the single-stage kraft cook) than did the single-stage pulps. The POM-delignified kraft pulp was clearly the best pulp, having the highest yield and highest viscosity with the lowest Kappa number. Considering all results, the two-stage method gives significantly higher pulp yields than does single-stage cooking.

Pulp Strength

All pulps were beaten in a PFI mill to a Canadian Standard Freeness (CSF) of near 350 and then tested for strength properties. Single-stage kraft cooking gave somewhat stronger pulp than that obtained by the other methods (Table III). Both single-stage kraft and soda–ODiMAQ pulps were slightly stronger than the two-stage pulps. This may have been due to the increased yield of the two-stage pulps, which resulted in somewhat fewer fibers in the standard handsheets. This can be illustrated by comparing kraft pulp with POM-delignified kraft pulp. Here the yield difference was 3 points (48% to 51%) or 6.3%; thus, there were 6.3% fewer fibers in the 60-g/m^2 handsheet. The tensile index was decreased by 8.2% (113.0 to 103.7), the burst index by 4.2% (9.10 to 8.72), and the tear index by 16% (13.0 to 10.9). The major factor in these differences (but not the only factor) was probably the decreased number of fibers in the handsheet.

Table III. Strength of lodgepole pine pulps

Pulp type	Initial Kappa no.	Yield[a] (%)	Kappa no.	Bright-ness (%)	PFI revs ($\times 10^3$)	CSF	Tensile index	Burst index	Tear index	Viscosity (mPa·s)
Kraft	31	48	31	20.8	9.6	355	113.0	9.10	13.0	35
Soda–AQ	27	46	27	21.6	5.0	366	94.9	7.29	13.2	19
Soda–AQ	33	47	33	19.9	11.25	366	91.5	7.14	13.6	25
Soda–ODi	31	46	31	20.8	9.0	364	104.6	8.49	12.6	24
Soda–ODi	35	48	35	20.2	10.0	351	113.7	8.50	13.2	27
Kraft/POM	71	51	29	14.9	9.0	352	103.7	8.72	10.9	40
Soda–AQ/POM	68	49	33	12.3	14.5	360	100.1	8.74	14.0	36
Soda–ODi/POM	65	50	29	12.6	11.5	350	101.9	8.53	11.6	—
Soda–ODi/POM	65	50	32	12.7	12.0	351	100.2	8.65	12.3	30
Soda–ODi/POM	83	50	32	10.6	8.0	355	76.2	6.53	9.5	—
Soda–ODi/POM	83	50	33	10.8	9.0	326	84.5	6.83	9.3	24
Soda–ODi/POM	96	50	34	10.1	7.5	359	88.6	6.63	7.8	16

[a]Overall yield.

Despite the lower yields, the single-stage soda–AQ pulps were somewhat weaker than the two-stage POM-delignified soda–AQ pulp. Apparently, soda–AQ cooking causes somewhat greater damage to the pulp carbohydrate polymers than does kraft or soda–ODiMAQ cooking. However, this is not apparent from the viscosity data, which are essentially equivalent. More damage may have been done to the hemicellulose polymers. These findings should be verified with future work.

Except for the two POM-delignified soda–ODiMAQ pulps with the high initial Kappa numbers (83 and 96), all single- and two-stage pulps were strong and could be used in place of kraft pulp. With proper application of wet-end chemistry, the strength deficits of these pulps could be compensated for. The decreased strengths and viscosities of the initial high Kappa number pulps may have been due, at least in part, to the higher reaction temperatures and longer times required to POM delignify these pulps to Kappa number 30.

Implications of Results

What might be some possible implications of our findings? Consider the situation where it is desired to increase the output of a kraft pulp mill that is limited in capacity by the size of its recovery furnace. In this case, instead of installing a larger recovery furnace, it would probably be more economic to install a POM-delignification system, which would permit the mill to pulp to a Kappa number of about 70 and to carry out the final delignification with the POM system. The lignin and carbohydrates removed by the POM delignification stage would be mineralized in the POM reoxidation reactor, thus relieving the recovery furnace of this load and permitting the mill to increase its capacity. As with POM bleaching [3], this system would be self-contained, comprising a delignification reactor, a reoxidation and mineralization reactor, and associated equipment.

Although a considerable amount of work has been done on suppressing the odor emitted from the kraft process, the problem still persists. At some future date, the public might demand and the Environmental Protection Agency might rule that the kraft process be abandoned. If this were to take place, soda–ODiMAQ pulping followed by the POM delignification system might be a feasible replacement. The pulp yield is significantly higher than that of the kraft process and the pulp strength, although somewhat less than that of kraft pulp, is more than adequate. Soda–AQ followed by POM delignification might also be feasible, although since AQ and ODiMAQ are equivalent in cost, based on overall yield the present data suggest that ODiMAQ would be preferred. This should be confirmed with future work.

CONCLUSIONS

Delignification of high Kappa number kraft, soda–AQ, and soda–ODiMAQ pulps to Kappa number 30 with polyoxometalate resulted in higher pulp yields than that of single-stage kraft, soda–AQ, or soda–ODiMAQ cooked to the same Kappa number. The highest-yield two-stage pulp was the POM-delignified kraft pulp. However, all the resulting pulps were somewhat weaker than the single-stage kraft pulp. As the Kappa number of the initial soda–ODiMAQ pulps was increased from 65 to 83 to 96, POM delignification of these pulps to Kappa number 30 resulted in a constant level of pulp yield and significantly decreased pulp strength.

EXPERIMENTAL

The chips were produced at the USDA Forest Service, Forest Products Laboratory (FPL) from submerchantable lodgepole pine (*Pinus contorta* Dougl. ex Loud.) logs from the tops of the trees. The logs were shipped to FPL from the Colville National Forest in eastern Washington. Logs were hand peeled and chipped to 19-mm-long chips in a four-knife commercial-size chipper. All chips were screened to remove particles greater than 38 mm and less than 6 mm long. Screened chips were thoroughly mixed in a large V-mixer, sealed in polyethylene bags, and stored at 4°C until pulped.

Kraft, soda–AQ, and soda–ODiMAQ cooks were performed in a 22-L stainless steel digester with a heat exchanger and liquor circulation system. Conditions are given in Tables I and II. All cooks employed a 5:1 liquor-to-wood ratio. After defibration of the cooked chips with a Bauer 305-mm-diameter disc refiner, the pulps were thoroughly washed, dewatered, and shredded; the pulps with a Kappa number above 65 were subsequently delignified to a Kappa number of about 30 with 0.50 M solutions of POM. The kraft, soda–AQ, and soda–ODiMAQ pulps with a Kappa number of about 30 and the POM-delignified pulps were subjected to physical testing.

ODiMAQ was synthesized employing the method described by Dimmel et al. [2]. POM $Na_{4.9+2}[SiV_{0.9}MoW_{10.1}O_{40}]$ was synthesized by mixing 1,000 g water with the following compounds in a 2.0-L Parr reactor: Na_2SiO_3 (105.9 g), $NaVO_3$ (100.9 g), MoO_3 (115.2 g), $Na_2WO_4\ 2H_2O$ (527.8 g), and WO_3 (1,505 g). The reactor was flushed and pressurized with oxygen to 1.48 MPa, heated to 210°C, and held at that temperature for 3.0 h. A homogeneous solution with no sediment was obtained. A portion of this solution was diluted with water to obtain a 0.50 M solution of POM.

All POM delignifications were performed in a 2-L Parr reactor. To obtain enough pulp for testing, two runs were made for each reaction condition. The consistencies shown are pulp weight divided by solution volume. The pulp and POM solutions were mixed throughout the reaction, using a spiral stirrer at 60 rpm. After the reactor had been closed and the mixing started, nitrogen was passed through the solution in the reactor for 15 min prior to heat up. The reactor was then sealed and heated. Reaction time was counted from the time the reactor contents reached reaction temperature until the reactor was placed in cold water. After cooling, the reactor contents were filtered using a crucible with a fritted glass bottom (coarse) and the pulp thoroughly washed (in the crucible) with reverse osmosis water. The pulp was then dewatered (in the crucible) and shredded prior to physical testing.

Kappa numbers were determined per TAPPI Method T236 and pulp viscosity per TAPPI Method T230. The pulps were beaten in a PFI mill to about 350 CSF in accordance with TAPPI Method T248; CSF was measured according to TAPPI Method T227. Handsheets weighing 60 g/m^2 were made per TAPPI Method T205. Tensile, burst, and tearing strengths were measured according to TAPPI Methods T494, T403, and T414. Brightness was determined in accordance with TAPPI Method T525.

ACKNOWLEDGMENTS

The authors acknowledge support by the USDA Forest Service, the U.S. Department of Energy, and the member companies of the Polyoxometalate Bleaching Consortium. We also thank Sara Fishwild for PFI beating, handsheet making, and pulp testing and Elisa Cree for Kappa number and viscosity determinations.

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