POTENTIAL SULFUR-FREE PULPING METHODS

Edward L. Springer, Rajai H. Atalla , Richard S. Reiner
USDA Forest Service, Forest Products Laboratory
Madison, Wisconsin

ABSTRACT

Lodgepole pine chips were pulped to Kappa numbers of about 70 using soda–AQ, soda–ODiMAQ, and kraft methods. At a catalyst level of 0.20% (oven-dry wood basis), cooking times for the soda cooks were significantly shorter than that for the kraft cook. The ODiMAQ catalyzed cooking time was much shorter than that of the AQ cook. It might be possible to replace the kraft process with a soda–ODiMAQ process for production of linerboard grade pulps. Delignification of the high Kappa soda–ODiMAQ pulp with oxygen and also with a polyoxometalate (POM) to Kappa numbers of about 30 resulted in higher yields of slightly weaker pulps than did pulping to Kappa 30 with the kraft process. Soda–ODiMAQ followed by oxygen sequence gave pulps much lower in viscosity than did soda–ODiMAQ followed by POM. If bleaching of oxygen-delignified pulp yields strong pulp, soda–ODiMAQ followed by oxygen delignification might be used to replace kraft pulping for the production of bleachable grade pulps. If the pulp is weak, soda–ODiMAQ followed by POM delignification might be used to replace kraft pulping.

INTRODUCTION

The current kraft pulping process has several significant advantages and a number of disadvantages. It can pulp essentially all wood species while producing strong pulps. Over the years, the kraft method has reached a very high state of development. Its major disadvantages are that it produces low yields of hard-to-bleach pulps and it generates odoriferous compounds, such as methyl mercaptan, which are very difficult to suppress or contain. Many alternative sulfur-free pulping methods have been proposed and some of them have been thoroughly investigated. However, none of these methods, to date, has been found to produce a kraft quality pulp at a cost comparable to that of kraft pulp.

Anthraquinone catalyzed soda pulping has been proposed as a replacement for kraft pulping. Under practical conditions, this method requires a longer cooking time than does kraft pulping and produces a lower yield of a somewhat weaker pulp [1]. Recently, some Swedish workers developed a new sulfur-free pulping process called “NovaFiber” [2], which consists of two stages: (a) a soda–anthraquinone pre-cook to about Kappa number 60 and (b) carbonate buffered oxygen delignification to Kappa number 30. These researchers claim greatly increased pulp yield and strength near that of kraft pulp. Based on some of our research findings, we expect that both stages of this process can be significantly improved.

Recently, Dimmel and co-workers showed that octahydrodimethylanthraquinone (ODiMAQ) is a much more effective delignification catalyst than is anthraquinone (AQ) [3]. In their opinion, ODiMAQ can be produced for about the same cost, per unit weight, as can AQ. We propose that ODiMAQ be used in place of AQ in the first stage of the process. The data presented in this paper will demonstrate the superiority of ODiMAQ to AQ.

In studying the delignification of high Kappa number pulps with polyoxometalates [1], we have found that polyoxometalates are significantly more selective in delignifying such pulps than is oxygen delignification. Consequently, we propose that the second stage of the process be replaced with a polyoxometalate (POM) delignification stage. Some data will be presented that demonstrate the superior selectivity of a POM delignification stage.

We thus propose replacing the kraft pulping process for production of bleachable grade pulps with a two stage process that consists of (a) a soda–ODiMAQ pre-cook to about 65 Kappa number, followed by (b) a POM delignification stage to about 30 Kappa number.

EXPERIMENTAL

The chips used in this study were produced at the USDA Forest Service, Forest Products Laboratory (FPL) from submerchantable lodgepole pine (*Pinus contorta* Dougl. ex Loud.) and were 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, small, commercial-sized 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 and were then 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 heat exchanger and liquor circulation system. The conditions used are given in Table I. 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 soda–ODiMAQ pulp with Kappa number 65 was subsequently delignified to Kappa numbers of about 30 with 0.50 M solutions of the POM and with oxygen. The conditions used are given in Table II. The pulps with Kappa numbers of about 30 were subjected to physical testing.

Octahydrodimethylanthraquinone (ODiMAQ) was synthesized using the method described by Dimmel et al. [3]. Polyoxometalate $Na_{4.9+2}[SiV_{0.9}MoW_{10.1}O_{40}]$ 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), $Na_2WO_4{\cdot}2H_2O$ (527.8 g), and WO_3 (1,505 g). The reactor was flushed and pressurized with oxygen to 1.48 MPa (200 lb/in^2 gauge) and then 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 then diluted with water to obtain a 0.50 M solution of POM.

The POM delignification was performed in a 2-L vertical Parr reactor. To obtain enough pulp for testing, two runs were required 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.

Oxygen delignification was performed in a 2-L horizontal Parr reactor equipped with anchor stirrers with Teflon tips, which scraped the walls and tumbled the pulp in the reactor. The stirrers turned at a rate of 30 rotations per minute. 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 treated as described for POM delignification.

Kappa numbers were determined per TAPPI Method T236 and pulp viscosities per TAPPI Method T230. The pulps were beaten in a PFI mill to about 350 CSF in accordance with TAPPI Method T248. The 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.

RESULTS AND DISCUSSION

Bleachable Grade Pulps

Lodgepole pine chips were cooked to Kappa numbers near 65 using both the soda–AQ and soda–ODiMAQ methods. Both catalysts were used at a level of 0.20% on ovendry wood. This is thought to be a realistic level since the cost of AQ has been decreasing in recent years. The pulping conditions and results are given in Table I**.** The soda–ODiMAQ cook was 15 min shorter than the soda–AQ cook, and it gave a 3 point lower Kappa number and 1 point higher yield. It thus appears to be superior to the soda–AQ cook.

In a subsequent set of experiments, the soda–ODiMAQ pulp was delignified with oxygen and polyoxometalate $Na_{4.9+2}(SiV_{0.9}MoW_{10.1}O_{40})$. Two experiments were performed in each case. The reaction conditions and results are given in Table II. Although the data show a slight increase in yield for POM delignification compared with oxygen

delignification, POM delignification resulted in a large increase in viscosity. The POM delignification was thus significantly more selective than the oxygen delignification.

Results of strength tests on 60-g/m^2 handsheets made from POM-delignified and oxygen-delignified soda–ODiMAQ pulps are shown in Table III, along with results for single-stage kraft pulp [1]. As the results indicate, the soda–ODiMAQ pulps were slightly weaker than the kraft pulp. Part of this strength difference may have been due to the higher yields of the pulps since fewer fibers would have been present in the standard handsheets.

Although viscosity values of oxygen-delignified pulps were considerably lower than those of POM-delignified pulps, oxygen-delignified pulps had slightly higher strength values. The oxygen pulps were also somewhat easier to beat (significantly fewer PFI revolutions). Replacing the kraft process with soda–ODiMAQ followed by oxygen delignification might be a reasonable possibility. If the pulp were subjected to bleaching, however, low viscosity, and the reduction in viscosity during bleaching, might give rise to a substantially weaker bleached pulp. This could probably be avoided by using the POM delignification stage instead of the oxygen stage. Bleaching trials should be performed.

Linerboard Pulps

Previous work on the pulping of lodgepole pine chips to Kappa numbers near 30 with the soda–ODiMAQ method showed that the resultant pulps were somewhat lower in yield, lower in viscosity, and weaker than kraft pulp [1]. Given these results, it seems unlikely that the soda–ODiMAQ method will be used to produce bleachable grade pulps. Some previously reported data on kraft, soda–AQ, and soda–ODiMAQ pulping of lodgepole pine chips to Kappa numbers around 70 seem to indicate that use of the soda–ODiMAQ method for production of linerboard grade pulps might be a possibility [1]. As the data in Table I indicate, cooking times to Kappa numbers near 70 were considerably shorter for the soda cooks, especially the soda–ODiMAQ cook. In addition, the yield of the soda–ODiMAQ cook was a little higher and the Kappa number significantly lower than that of the kraft cook. The strength of handsheets made from soda–ODiMAQ pulp is currently being evaluated. If it is essentially equivalent to the strength of handsheets from kraft pulp, the soda–ODiMAQ method could replace kraft pulping in the production of linerboard-type pulps. The advantages would be shorter cooking time and essentially odor-free pulping.

Table I—Kraft, soda-AQ, and soda-ODiMAQ pulping of Lodgepole pine

Pulping conditions and results	Kraft	Kraft	Soda–AQ	Soda-ODiMAQ
Pulping conditions				
Active alkali, %	20	20	20	20
Sulfidity, %	25	25	—	—
AQ, %	—	—	0.2	—
ODiMAQ, %	—	—	—	0.2
Temperature, °C	170	170	170	170
Heatup time, min	60	60	60	60
Cooking time, min	110	55	48	33
Total time, min	170	115	108	93
Results				
Yield, %	48	53	53	54
Kappa number	31	71	68	65

Table II—POM and oxygen delignification of Lodgepole pine soda–ODiMAQ pulps (Kappa no. 65)

Conditions and results	POM	POM	O_2	O_2
Conditions				
POM, M	0.50	0.50	—	—
NaOH, % on pulp	—	—	6.5	6.0
Mg, % on pulp	—	—	0.20	0.20
Consistency, %	3.0	3.0	10	10
Reaction temperature, °C	140	140	100	100
Pressure, kPa	515	515	720	720
Reaction time, min.	65	55	60	64
Final pH	6.6	6.6	10.4	10.6
Results				
Residue Yield, %	49[a]	50[a]	49[a]	49[a]
Kappa Number	30	32	27	32
Viscosity, mPa.s	29	30	19	20

[a]Overall yield.

Table III—Results of strength tests

Pulp type	Overall yield, %	Kappa number	CSF	PFI rev	Tensile index	Burst index	Tear index	Visc. mPa·s
Soda–ODi and POM	49	30	350	11,500	101.9	8.53	11.6	29
Soda–ODi and POM	50	32	351	12,000	100.2	8.65	12.3	30
Soda–ODi and O_2	49	27	319	8,000	105.1	8.71	13.1	19
Soda–ODi and O_2	49	32	337	9,500	105.3	8.34	12.8	20
Kraft	48	31	355	9,600	113.0	9.10	13.0	35

CONCLUSIONS

The pulping of lodgepole pine chips with the soda–AQ and soda–ODiMAQ methods to a Kappa number of about 70, while using a catalyst level of 0.20% on an oven-dry wood basis, required significantly less cooking time than that for kraft pulping. The time required for the soda–ODiMAQ cook was considerably shorter than that for the soda–AQ cook. Given these findings, and the expectation that ODiMAQ can be produced for the same cost as AQ, it may be possible to replace the kraft process for production of linerboard grade pulps with a soda–ODiMAQ process. An additional advantage would be the mitigation of the odor that accompanies kraft pulping.

Oxygen and POM delignification of lodgepole pine Kappa number 65 soda–ODiMAQ pulps resulted in higher yields of slightly weaker pulps. Viscosity of the oxygen-delignified pulp was much lower than that of the POM-delignified pulp. Bleaching the oxygen-delignified pulp might result in a much weaker pulp. This remains to be evaluated. If the bleached pulp remains strong, a soda–ODiMAQ process followed by oxygen delignification might be used to replace kraft pulping for production of bleachable grade pulps. If the bleached pulp is much weaker, soda–ODiMAQ followed by POM delignification might be used to replace kraft pulping.

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