Delignification of aspen wood using hydrogen peroxide and peroxymonosulfate

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ABSTRACT *Treatment of finely divided aspen wood with peroxymonosulfate at low pH, followed by alkaline extraction, resulted in nearly complete lignin removal. Treatment of the wood with hydrogen peroxide at optimum pH (pH 11), followed by alkaline extraction, removed at most 36% of the original lignin. Peroxymonosulfate can be easily produced by mixing hydrogen peroxide with concentrated sulfuric acid.*

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Wood and other lignocelluloses can be readily delignified using organic peroxides such as peracetic and performic acids (*1*). With the exception of studies using alkaline hydrogen peroxide, little research has been done on delignification with inorganic peroxides. The purpose of this work was to determine whether acidic hydrogen peroxide could delignify aspen wood and, if not, whether peroxymonosulfuric acid made by reacting hydrogen peroxide and sulfuric acid could delignify the wood. Aspen wood (*Populus tremuloides* Michx.) was chosen for study because it is easily delignified.

A few studies have been performed on delignification of lignocellulosic materials with alkaline hydrogen peroxide. Gould (*2*) found that approximately half the lignin present in agricultural residues, such as wheat straw, could be solubilized when the residue was treated at 25°C with an alkaline solution of hydrogen peroxide. The delignification was most effective at pH 11.5. McDonough *et al.* (*3*) studied the delignification of southern pine kraft pulp with alkaline hydrogen peroxide. They also found that approximately half the lignin present in the pulp could be removed. In both cases, the most efficient delignification occurred under reaction conditions where no stabilizers (to inhibit peroxide decomposition) were present and the rate of peroxide decomposition was at a maximum. For comparison, we initially studied the delignification of aspen wood with alkaline hydrogen peroxide.

Acidic hydrogen peroxide is a much stronger oxidizing agent than alkaline hydrogen peroxide. Under acidic conditions, the lignin macromolecule is extensively degraded and dissolved by hydrogen peroxide (*4, 5*). It seemed likely, therefore, that acidic solutions of hydrogen peroxide should more readily delignify wood than alkaline solutions.

Delignification using hydrogen peroxide

One-gram samples of mature aspen wood, ground to pass through a No. 40 mesh screen, were treated at room temperature (22°C) with a 5.0% solution of hydrogen peroxide adjusted to either pH 2.0 with sulfuric acid or to pH 11.0 or 11.5 with sodium hydroxide. A liquor-to-wood ratio of 10:1 was used, and the treatment time was 3 days except for the pH 11.5 condition, where treatment time was 12 days. Samples were also treated at the natural pH (pH 5.5) of the 5.0% solution of hydrogen peroxide. The samples were stirred initially but not agitated during treatment. After peroxide treatment, each sample was extracted with 1.0% NaOH at 50°C for 3 h. The results from these treatments are shown in **Table I.**

The most selective delignification occurred at pH 11.0, where 32% of the original lignin and 17% of the original carbohydrate were removed. Dividing the total weight of carbohydrate

removed by the weight of lignin removed (*C/L* ratio) gives an index of the selectivity of lignin removal (Table I). Increasing the pH to 11.5 and the treatment time to 12 days resulted in a small increase in lignin removal (to 36% of the original); however, the selectivity was slightly reduced (from *C/L* ratio 2.2 to 2.4). Lowering the pH to 2.0 increased the lignin removal only slightly from what it was at pH 5.5. Much more lignin was removed under alkaline conditions. Residual peroxide levels were not determined.

To determine the effect of treatment temperature on lignin removal, runs were made at 80°C. The results from these runs are also shown in Table I. The most effective delignification again occurred at pH 11.0; however, the selectivity of lignin removal was somewhat reduced from that at room temperature. None of the conditions studied resulted in low lignin contents in the final residue. Since acidic hydrogen peroxide was ineffective in delignification of aspen wood, we decided to attempt to delignify the wood with peroxymonosulfuric acid produced by adding sulfuric acid to hydrogen peroxide.

I. Delignification of 40-mesh aspen wood with 5% hydrogen peroxide at a liquor to wood ratio of 10:1

Run	Initial pH	Treatment Temp., °C	Treatment Time, days	Yield of residue, %	Lignin[a] in residue, %	C/L[b]
1	2.0	22	3	86	19.7	3.8
2	5.5	22	3	86	20.2	4.5
3	11.0	22	3	80	16.9	2.2
4	11.5	22	12	76	16.9	2.4
5	2.0	80	0.125[c]	81	18.8	3.1
6	5.5	80	0.125	82	19.3	3.4
7	11.0	80	0.125	74	17.2	2.6

[a] 19.9% lignin in original wood.
[b] Weight of carbohydrates removed divided by the weight of lignin removed.
[c] 3.0 h.

II. Production of peroxymonosulfuric acid by mixing hydrogen peroxide and concentrated sulfuric acid at ice bath temperature

Procedure	Concentration of H_2O_2 solution, %	Weight of 2°C H_2O_2 solution added, g	Weight of 22°C concentrated H_2SO_4 added, g	H_2SO_4:H_2O_2 (mole:mole)	H_2SO_5 yield (H_2O_2 basis), %
1	32	14.2	12.7	1:1	8
2	50	17.9	55.1	1.5:1	60
3	70	6.9	27.5	1.9:1	78

Generation of peroxymonosulfate

Adding concentrated sulfuric acid to solutions of hydrogen peroxide results in the production of peroxymonosulfuric acid (*6*). This acid is a much stronger oxidizing agent than hydrogen peroxide. It can also be produced by adding peroxydisulfuric acid salts to concentrated sulfuric acid. Zakis and Neiberte (*7*) found that they could delignify spruce sawdust to low lignin levels using peroxymonosulfuric acid in 50% H_2SO_4 at 20°C. They produced the peroxymonosulfuric acid by adding the ammonium salt of peroxydisulfuric acid to concentrated sulfuric acid. A high concentration of sulfuric acid seemed to be necessary for effective lignin removal. Based on these findings, hydrogen peroxide and sulfuric acid mixtures with a large excess of acid present should delignify finely divided aspen wood. Our previous data indicate that simply adjusting a 5.0% solution of H_2O_2 to pH 2.0 with concentrated sulfuric acid did not result in a solution that effectively delignified aspen wood.

Several experiments were performed to determine the conditions needed to produce significant quantities of peroxymonosulfuric acid. Cold hydrogen peroxide (2°C) was placed in a vial in an ice bath; concentrated sulfuric acid at room temperature was added, and the two were thoroughly mixed. An aliquot of this mixture was titrated using the method of Greenspan and MacKellar (*8*) to determine the yield of peroxymonosulfuric acid produced. Results of these procedures are shown in **Table II**. Using 32% H_2O_2 and a mole-to-mole ratio of acid to peroxide of 1:1, the yield of peroxymonosulfate was only 8%. This indicates that the yield was probably negligible when a few drops of concentrated sulfuric acid were added to 5.0% H_2O_2 to adjust the pH to 2.0. Using more concentrated hydrogen peroxide and a higher mole-to-mole ratio of acid to peroxide greatly increased the yield of peroxymonosulfate.

Delignification using peroxymonosulfate

Small quantities of the solutions containing peroxymonosulfate were carefully diluted with distilled water and used to treat 1-g samples of the No. 40 mesh aspen wood at room temperature (22°C). The weight of the peroxide-acid mixture used for a given total weight of solution (used to treat 1.00 g of wood) is shown in the third column of **Table III**. The concentration of the peroxymonosulfate anion in the initial solution is given in Column 4, and the equivalent total percentage of hydrogen peroxide in the initial solution is given in Column 8. The treated residues were extracted as described previously with 1.0% NaOH.

Initial runs were made using peroxymonosulfate prepared by Procedure 1. This resulted in very dilute solutions of peroxymonosulfate containing large amounts of acid and peroxide. In the first run (Table III), the initial concentration of peroxymo-

III. Delignification of 40-mesh aspen wood (1.00 g) using peroxymonosulfate at 22°C

Run	Source of HSO_5^-	Weight of mixture in total weight of solution,[a] g in g	HSO_5^- in initial solution, %	HSO_5^- consumed, %	H_2O_2 in initial solution, %	H_2O_2 consumed, %	Equivalent H_2O_2 in initial solution, %	Liquor-to-wood ratio	Initial pH	Treatment time, days	Residue yield, %	Lignin in residue,[b] %	TAPPI viscosity, mPa•s	C/L[c]
1	Proc. 1	1.35 in 10.0	0.45	[d]	2.1	[d]	2.3	10:1	0.4 (0.63*m*)[e]	3	71	11.8	[d]	1.5
2	Proc. 1	2.7 in 10.0	0.93	92	4.2	11	4.5	10:1	0.1 (1.26*m*)	3	66	5.3	[d]	1.1
3	Proc. 1	2.7 in 10.0	0.93	93	4.2	15	4.5	10:1	0.1 (1.26*m*)	6	63	3.4	12	1.1
4	Proc. 1	2.7 in 25.0	0.35	[d]	1.7	[d]	1.8	25:1	0.5 (0.51*m*)	3	73	11.5	[d]	1.3
5	Proc. 1	5.4 in 25.0	0.78	[d]	3.4	[d]	3.6	25:1	0.1 (1.01*m*)	12	58	0.9	11	1.2
6	Proc. 3	3.3 in 25.0	4.9	42	0.38	31	1.8	25:1	0.2 (1.05*m*)	1	60	0.4	11	1.0
7	Oxone[f]	...	4.9	38	0	0	1.5	25:1	1.6	1	63	2.8	27	1.1
8	Oxone	...	1.2	[d]	0	0	0.37	10:1	1.8	3	74	12.8	[d]	1.5

[a] Produced as in Table II.
[b] 19.9% lignin in original wood; values given are percent of residue.
[c] Weight of carbohydrates removed divided by the weight of lignin removed.
[d] d. = determined.
[e] Molality of the acids (H_2SO_4 and H_2SO_5) in solution.
[f] $KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$

nosulfate was only 0.45%, and the equivalent total concentration of hydrogen peroxide was 2.3%. Even under these conditions, a relatively large amount of lignin was removed. The lignin in the residue (11.8%) was much lower than that for the best of the hydrogen peroxide runs (16.9%), and the *C/L* ratio (1.5) was also much lower than that for the best of the peroxide runs (2.2). As illustrated by Runs 2 and 3, increasing the concentration of peroxymonosulfate and extending the reaction time gave even better results. Increasing the liquor-to-wood ratio from 10:1 to 25:1 gave a slight increase in selectivity from a *C/L* ratio 1.5 to 1.3 (compare Runs 1 and 4); however, this increase in selectivity came at the expense of a much larger quantity of peroxymonosulfate per gram of wood (2.7 g of mixture compared to 1.35 g). At this higher liquor-to-wood ratio, increasing the peroxymonosulfate concentration and treatment time also greatly increased lignin removal (compare Runs 4 and 5).

All the results mentioned were obtained using peroxymonosulfate produced using Procedure 1. Run 6 shows the result of drastically increasing the peroxymonosulfate concentration by using Procedure 3. Comparing Runs 6 and 4, the same equivalent concentration of hydrogen peroxide is present; however, the initial concentration of peroxymonosulfate was greatly increased in Run 6. The treatment time for Run 6 was reduced to one day. Despite this reduced treatment time, Run 6 shows a large increase in lignin removal compared with Run 4. This is undoubtedly an effect of the much higher initial concentration of peroxymonosulfate.

Another source of the peroxymonosulfate anion is Oxone®, a commercial product sold by DuPont (E. I. DuPont De Nemours and Company, Inc., Wilmington, Del., 1988). Oxone is a triple salt containing potassium peroxymonosulfate ($2\ KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$). Delignification of aspen wood with Oxone was compared with delignification using peroxymonosulfate from the peroxide-acid mixtures. In Run 7, an equivalent quantity of Oxone was substituted for the Procedure 3 mixture in Run 6. All other conditions were identical except that some hydrogen peroxide was present in Run 6 and the pH was much lower.

The results were quite similar. For Run 7, the yield of residue was a bit higher, and its lignin content was also somewhat higher. These significant differences were probably the result of the much lower pH in Run 6. This is reflected in the large difference in residue viscosities in Runs 6 and 7. The much higher hydrogen ion concentration in Run 6 undoubtedly increased the rate of carbohydrate degradation and also increased the rate of lignin removal. If this lower pH were taken into account, it appears that, with regard to delignification, the source of the peroxymonosulfate anion is of no importance.

Conclusions and recommendations

Low pH solutions of the peroxymonosulfate anion are much more effective in delignifying aspen wood than are alkaline solutions of hydrogen peroxide. This is probably because, under these conditions, peroxymonosulfate is a much stronger oxidizing agent than is hydrogen peroxide. The very low pH of the peroxymonosulfate solutions, produced by mixing hydrogen peroxide with sulfuric acid, results in marked attack on the carbohydrate constituents of the wood, resulting in low residue yields and low viscosities. A comparison of Runs 6 and 7 in Table III suggests that adjusting the pH of the solutions upward with a base such as sodium hydroxide might diminish the severity of the attack on the carbohydrates without greatly reducing the lignin-removing ability of the solutions.

For several of the peroxymonosulfate runs, the quantity of oxidants consumed was determined. For Run 6, 1.0 g of lignin was removed from the wood for each gram of oxidant consumed (calculated as hydrogen peroxide); for Run 2, the figure was 1.9 g of lignin removed for each equivalent gram of hydrogen peroxide consumed. Because only relatively small amounts of oxidants were consumed in delignifying the wood, it might be possible to use solutions of peroxymonosulfate generated by mixing hydrogen peroxide and sulfuric acid to improve the strength of high-yield mechanical or chemimechanical pulps or even to produce chemical pulps. Such solutions of peroxymonosulfate might also be used to restore or enhance the strength of unbleached softwood kraft wastepaper. Peroxymonosulfate might, in addition, be used to replace chlorine and chlorine dioxide in pulp bleaching. It also might be used to delignify agricultural residues, such as straw and corn stover, to enhance their enzymatic digestibility.□

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