Delignification of aspen wood with pernitric acid

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ABSTRACT: This study evaluated the feasibility of delignifying aspen wood with pernitric acid. Treating finely divided aspen wood with dilute aqueous pernitric acid and extracting it with dilute alkali readily delignifies the wood. Pernitric acid consumption is excessive due to its rapid self–decomposition. Mixing concentrated hydrogen peroxide with concentrated nitric acid easily produces pernitric acid. Such mixtures present a serious explosion hazard requiring extreme care in their preparation and use.

KEYWORDS: Delignification, hydrogen peroxide, nitric acid, peroxymonosulfuric acid, pernitric acid, populus tremuloides, viscosity.

Organic peroxides such as peracetic and performic acids will effectively delignify wood and other lignocellulosics. The use of performic acid as a pulping agent is under active investigation *(1, 2)*. We recently found that the inorganic peroxide, peroxymonosulfuric acid, will readily delignify these materials. Hydrogen peroxide is quite ineffective, however *(3, 4)*. On the basis of these findings, it seemed highly likely that other inorganic peroxyacids might also be effective in delignification. Consequently, we initiated an exploratory study on delignification of wood with other inorganic peroxyacids.

Treating hardwood fiber and alkaline pretreated chips at a low temperature with an aqueous solution of peroxymonosulfuric acid and then extracting the degraded lignin fragments with dilute aqueous alkali will easily delignify the fiber and the chips *(5, 6)*. The resulting pulps are strong and easily bleachable. The alkali used in the extraction can be ammonium hydroxide. One proposal suggests combining the treating and extraction liquors for use as a fertilizer *(7)*. This proposed waste liquor disposal method would be much more attractive if the treating liquor also had some fertilizer value.

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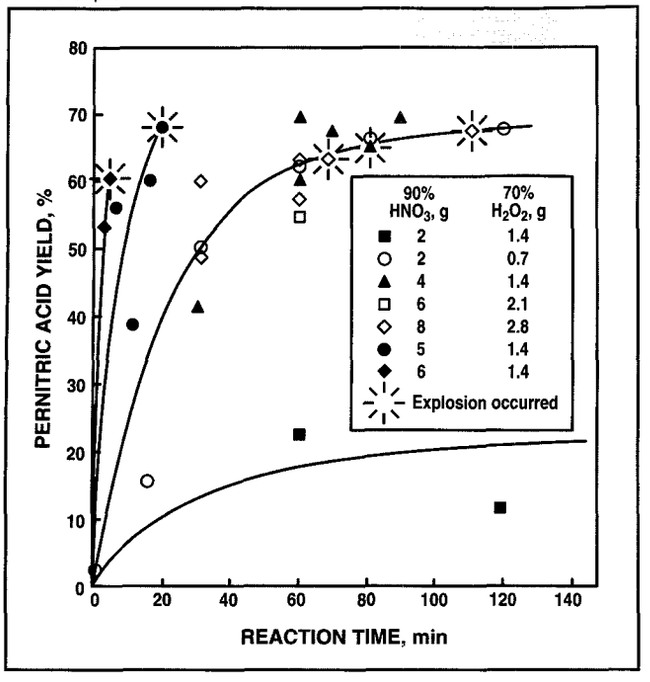
On the basis of this consideration, we decided to study the possibility of delignifying wood with pernitric acid. We chose finely divided aspen wood as the substrate for study because it delignifies easily. Success with aspen delignification would suggest further pulping studies.

Generation of pernitric acid

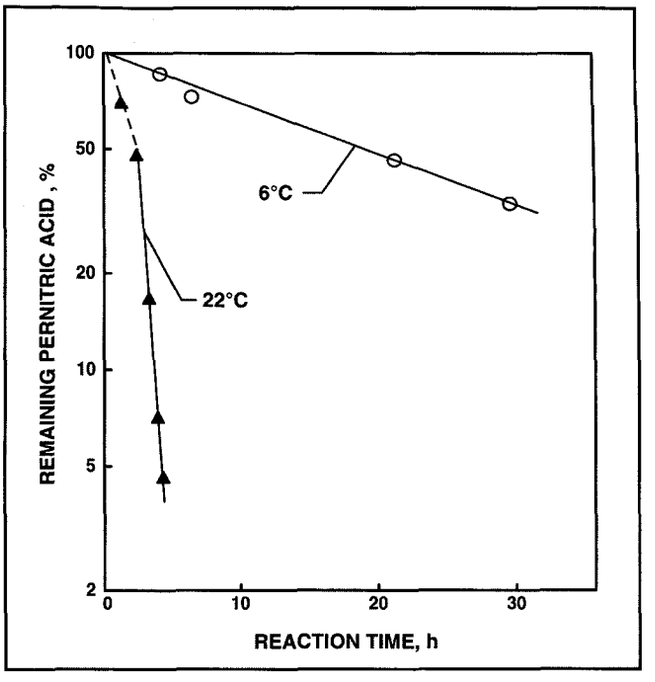
There are several methods for preparing pernitric acid *(8, 9)*. We initially chose the method described by Kenley, Trevor, and Lan that uses only concentrated hydrogen peroxide and concentrated nitric acid *(9)*. Several attempts at generating pernitric acid by this method were unsuccessful. After adding a drop of peroxide to the chilled nitric acid in an ice bath, a puff of yellowish–brown vapor would occur after a fraction of a second. Apparently, when the drop of peroxide mixed with the acid, some pernitric acid formed and then immediately decomposed to nitric acid and oxygen.

Because this method was unsuccessful, we employed an alternative method similar to that used in generating small batches of peroxymonosulfuric acid *(3)*. We placed a small quantity of 90% nitric acid in a vial in an ice bath and instantly added an appropriate, smaller quantity of chilled (from a refrigerator) 70% hydrogen peroxide. A PTFE coated bar stirred the mixture for an appropriate period ranging from less than 1 min to 2 h depending on the

1. Yield of pernitric acid as a function of reaction time and conditions where explosions occurred



2. Decomposition of pernitric acid



ratio of reactants. We then rapidly diluted with distilled reverse osmosis (RO) water. To obtain high yields of pernitric acid based on input peroxide, there was a substantial excess of nitric acid, i.e., an amount more than that dictated by the stoichiometry.

We studied the effects of the ratio of nitric acid to peroxide and the reaction time on the yield of pernitric acid based on peroxide. For a given ratio of acid to peroxide and a given total quantity of reactants, excessive reaction time would inevitably result in an explosion. Accordingly, no more than 3 g of 70% hydrogen peroxide was used, and the reaction was always performed under an exhaust hood and behind a clear plastic shield. A 1-L polyethylene beaker usually covered the vial containing the reactants. Any explosion would propel this beaker upward to strike the top of the exhaust hood. Neither the vial nor the beaker would break. The contents of the vial were expelled, however. **Figure 1** shows the conditions and yields when generating pernitric acid. The method of Greenspan and MacKellar *(10)* determined the remaining unreacted hydrogen peroxide and pernitric acid formed. Samples containing pernitric acid were analyzed immediately to reduce any errors resulting from its decomposition.

Figure 1 denotes conditions under which explosions occurred by the star burst–type symbols. The data varied considerably. The reaction times shown for the explosions were the minimum times at which explosions occurred. It was occasionally possible to increase the time without explosion. The data points at reaction times longer than those of the explosions show this. The reaction times at which explosions occurred depended upon both the ratio of acid to peroxide and the total quantity of reactants present. The larger the amount of reactants present, the shorter the times at which explosions occurred. Because yields were not measurable when an explosion occurred, the star bursts have a position on the curves drawn through the data points at the shortest time at which an explosion occurred. As shown, the data points for the various reaction conditions scattered irregularly. The reasons for this are unknown. Reaction conditions were carefully controlled. Minute traces of heavy metals present in the reactants and the water may have been responsible for the scattering of the data.

Yields of pernitric acid greater than 60% could occur under proper conditions. Explosions invariably happened, however, before achieving 70% conversion of the peroxide. Reaction times to obtain a given yield were a function of the acid to peroxide ratio—the higher the ratio, the shorter the time. At high ratios, only a few minutes were necessary.

On the basis of the large variability of the data and the ease of obtaining explosive mixtures, it appeared that pernitric acid was quite unstable and would readily decompose, especially at higher concentrations. If decomposition of pernitric acid in dilute aqueous solution was too rapid, it might possess little ability to function as an oxidizing agent. It would therefore lose the ability to degrade

I. Delignification of 40–mesh aspen wood (1.00 g) using pernitric acid and a mixture of nitric acid and hydrogen peroxide

	Pernitric acid, run 1	*Nitric acid plus hydrogen peroxide*
Reagent solutions:		
90% HNO_3, g	4.00[a]	4.00[b]
70% H_2O_2, g	1.35	1.40
Distilled RO water, g	24.60	24.60
Yield of HNO_4, %	69	Trace
Weight of solution added to 1.00 g wood[c]	25.0	25.0
Initial HNO_4, %	5.7	Trace
HNO_4 consumed, %	100	-
Initial H_2O_2, %	1.1	3.2
H_2O_2 consumed, %	77	50
Treatment temperature, °C	22	22
Treatment time, min	305	305
Final pH	0.2	0.2
Residue yield, %	63	84
Lignin in residue[d], %	5.0	18.6
TAPPI viscosity, mPa·s	7.3[e]	-

[a]Mixed at 0°C for 60 min, then water added
[b]Added to the water immediately
[c]1.00 g o.d. basis; wood moisture 6.0%
[d]19.9% lignin in original wood; values are percentage of residue
[e]Chlorited

the lignin in wood. Because of this consideration, we performed some experiments on the decomposition of pernitric acid in dilute aqueous solutions.

Decomposition of pernitric acid

We generated pernitric acid by adding 1.35 g of chilled (from a refrigerator) 70% hydrogen peroxide to 4.0 g 90% nitric acid in a vial in an ice bath. After 60 min, the mixture was diluted with 24.6 g of distilled RO water. The solution was then analyzed and was 0.68 *m* (5.4%) in pernitric acid. The total acidity of the solution was 1.93 *m* based on the input of nitric acid. Half the solution remained at room temperature (22°C) and the remaining half at refrigerator temperature (6°C) with periodic analysis of each of the two samples.

Figure 2 shows the results from these decomposition experiments. Percentage of pernitric acid remaining was plotted on a logarithmic scale vs. time on an arithmetic scale. At 22°C, there was an induction period where the rate increased slowly until attaining a constant rate. No induction period occurred for the 6°C data. The resulting straight lines indicate that the decomposition follows a first–order rate equation.

Temperature affected decomposition rate. Dilute pernitric acid decomposed rapidly at 22°C. About half the original peroxide was gone in 2 h. At 6°C, half the peroxide was gone in about 18 h. This rapid decomposition made it problematical whether pernitric acid could be effectively employed in the delignification of wood. We decided nevertheless to attempt the delignification of finely divided aspen wood.

Delignification of aspen wood

The generation procedure used in the decomposition work produced a 5.7% solution of pernitric acid. Then 25 g of this solution was added to 1.00 g (o.d. basis) of finely divided aspen wood (passing a 40–mesh screen, 6.0% moisture). The mixture was held at 22°C for 305 min. The liquor was drained from the solid residue. The residue was washed thoroughly with RO water. The solid residue was then extracted with a 1.0% solution of sodium hydroxide at 50°C for 2 h, thoroughly washed again with RO water, and air-dried. The residue was dried in a vacuum oven overnight at 60°C, and its yield was determined. It was then analyzed for lignin content, and its 0.5% cupriethylenediamine (CED) viscosity was determined. Because the residue was not completely soluble in the CED solution, it was delignified using the chlorite procedure given in the Experimental section. **Table I** shows the results.

Nitric acid and hydrogen peroxide both possess some ability to delignify wood. Therefore, we also performed a control experiment where the same quantities of nitric acid and hydrogen peroxide used in generating the pernitric acid were immediately added to water. Then 25 g of this mixture was added to a 1.00-g sample of aspen wood. The identical procedures used with the pernitric acid delignification were then followed. The pernitric acid solution was effective in delignification

of the wood. It reduced the lignin content to 5.0%. The mixture of nitric acid and hydrogen peroxide was quite ineffective under the conditions employed. The pernitric acid delignification took just over 5 h at 22°C indicating the highly reactive nature of pernitric acid. Although pernitric acid decomposes rapidly at 22°C, at least some fraction of it reacts with and fragments the lignin and some carbohydrates of the wood.

Although the wood rapidly delignified using pernitric acid, the viscosity of the delignified residue was quite low. Research on delignification of aspen wood with peroxymonosulfuric acid found that decreasing the treatment temperature reduces the damage to the wood carbohydrates *(11)*. In an attempt to reduce carbohydrate damage (increase viscosity) and simultaneously reduce pernitric acid decomposition, the finely divided aspen wood was treated with pernitric acid at 6°C. Two treatments were carried out for 48 h at 6°C. A 3.6% solution of pernitric acid was prepared and added to two samples of aspen wood at liquor to wood ratios of 10:1 and 25:1. The post–treatment procedures were identical to those used previously. **Table II** gives the results of these experiments.

The wood was effectively delignified in 48 h at 6°C. The viscosities of the delignified residues were still very low, however. Decreasing the reaction temperature did not result in a significant reduction in carbohydrate damage. Reducing the liquor to wood ratio from 25:1 to 10:1 resulted in less effective delignification. This was probably due to the presence of insufficient peroxide at the 10:1 liquor to wood ratio.

On the basis of previous experience with peroxymonosulfate delignification, we expected that less carbohydrate damage would occur if a high concentration of peroxide were present and there was a short reaction time *(11)*. We also found that a pretreatment of the initial wood with dilute mineral acid to remove traces of heavy metals before peroxide treatment resulted in significant increases in residue viscosities. We performed experiments to determine the effectiveness of these measures in reducing carbohydrate damage when delignifying with pernitric acid. To determine the effect of removing heavy metals from the wood, a sample of the 40–mesh aspen wood was pretreated by holding the wood for 30 min at 22°C in a 0.40 *m* solution of sulfuric acid in distilled RO water at 20:1 liquor to wood ratio. After pretreatment, the wood sample was thoroughly washed with distilled RO water and air dried before pernitric acid treatment. **Table III** gives the results of these experiments.

With a concentration of 11.0% pernitric acid in the treatment solution and a reaction time of only 2.0 h, nearly complete delignification took place for both the acid pretreated and the untreated aspen wood. The viscosities of the delignified residues were again very low, however. High concentration of oxidant and short reaction time apparently did not significantly reduce carbohydrate damage. Removal of trace metals by acid pretreatment may have had a slightly positive effect. The effect was insignificant compared with that found with peroxymonosulfuric acid, however *(11)*.

From the results obtained to date, it is possible to delignify finely divided aspen wood with pernitric acid. A high consumption of pernitric acid occurs, however, and the carbohydrates of the delignified residue undergo extensive damage. These two observations may relate. The rapid self–decomposition of pernitric acid may be a major factor in the degra-

II. Delignification of 40–mesh aspen wood (1.00 g) using pernitric acid at 6°C

	Run 2	*Run 3*
Weight of solution[a] added to 1.00 g wood[b], g	25.0	10.1
Initial HNO_4, %	3.6	3.6
HNO_4 consumed, %	100	100
Initial H_2O_2, %	1.8	1.8
H_2O_2 consumed, %	42	43
Treatment temperature, °C	6	6
Treatment time, h	48	48
Final pH	0.2	0.3
Residue yield, %	61	68
Lignin in residue[c], %	3.5	8.7
TAPPI viscosity, mPa·s	7.5	9.4[d]

[a]Reagent solution:
90% HNO_3, 6.00 g; mixed at 0°C for 60 min, then water added
70% H_2O_2, 2.10 g
Distilled RO water, 36.90 g
Yield of HNO_4, 54%
[b]1.00 g o.d. basis; wood moisture 6.0%
[c]19.9% lignin in original wood; values are percentage of residue
[d]Chlorited

III. Effects of acid pretreatment and high concentration of pernitric acid on delignification of 40–mesh aspen wood (1.00 g)

	Run 4, not pretreated	*Run 5, H_2SO_4 pretreated*
Weight of solution[a] added to 1.00 g wood[b], g	25.0	25.1
Initial HNO_4, %	11.0	11.0
HNO_4 consumed, %	100	99
Initial H_2O_2, %	3.2	3.2
H_2O_2 consumed, %	60	54
Treatment temperature, °C	23	23
Treatment time, h	2.0	2.0
Residue yield, %	52	54
Lignin in residue[c], %	0.1	0.1
TAPPI viscosity, mPa·s	5.9	6.3

[a]Reagent solution:
90% HNO_3, 8.0 g; mixed at 0°C for 30 min, then water added
70% H_2O_2, 2.8 g
Distilled RO water, 19.2 g
Two batches prepared as above and mixed
Overall yield of HNO_4, 60%
[b]1.00 g o.d. basis; wood moisture 6.0%
[c]19.9% lignin in original wood; values are percentage of residue

IV. Delignification of 40–mesh aspen wood with pernitric acid and peroxymonosulfuric acid under equivalent conditions

	Pernitric acid, run 1	*Peroxymonosulfuric acid*
Grams active oxygen per g wood, initial	0.29	0.29
Grams active oxygen per g wood, consumed	0.29	0.064
Molality of HNO_3	1.91	1.91
Liquor to wood ratio	25:1	25:1
Treatment temperature, °C	22	22
Treatment time, min	305	305
Residue yield, %	63	63
Lignin in residue[a], %	5.0	2.1
TAPPI viscosity[b], mPa·s	7	32

[a]19.9% lignin in original wood; values are percentage of residue
[b]Chlorited

dation of the wood carbohydrates. Reactions analogous to the Fenton reaction *(12)*, which produces hydroxyl radicals by the reaction of hydrogen peroxide and metal ions, are probably taking place. Hydroxyl radicals and probably other free radicals result from the reaction of pernitric acid with traces of metal ions present in the wood and in the water used. These extremely reactive free radicals produced by the decomposition of the pernitric acid attack both the lignin and the carbohydrates of the wood causing extensive carbohydrate damage.

Comparing the delignification of aspen wood with peroxymonosulfuric acid with that of pernitric acid can perhaps illustrate this effect of pernitric acid decomposition on carbohydrate degradation. Peroxymonosulfuric acid is extremely stable. For the reaction conditions employed in Run 1 of Table I, peroxymonosulfuric acid decomposition was not detected for more than six days. The reaction conditions of Run 1 were employed in delignification of a sample of the finely divided aspen wood with peroxymonosulfuric acid. The peroxymonosulfuric acid solution was made up by acidifying an aqueous solution of the commercially available potassium salt of peroxymonosulfuric acid (Oxone) with 70% nitric acid to obtain the same molality of acid as employed in Run 1. To equate the oxidizing power of the peroxymonosulfuric acid solution with that of the pernitric acid solution, the content of active oxygen in the solution was the same as that in the pernitric acid solution.

Table IV compares the results of the peroxymonosulfuric acid delignification with the data from Run 1. At the same residue yield, the lignin content of the peroxy-monosulfuric acid delignified residue was less than half that of the pernitric acid delignified residue. The viscosity was more than four times greater. The consumption of peroxymonosulfuric

acid was only 21% of the initial amount added. Both decomposition and reaction with the wood totally consumed the pernitric acid. Therefore, the peroxy-monosulfate delignification was much more efficient in terms of oxidant use and much less degrading to the wood carbohydrates than was the pernitric acid delignification. These results do not prove that the rapid decomposition of pernitric acid is the primary factor in the degradation of the wood carbohydrates. They only lend evidence to support this hypothesis. The relative reactivities of the two peroxides toward the lignin and the carbohydrates of the wood are also important in determining the relative rates of lignin and carbohydrate degradation. If the rapid self–decomposition of pernitric acid could somehow be prevented or inhibited, a more efficient delignification could probably result. Additives have been employed to inhibit the decomposition of hydrogen peroxide and peroxymonosulfuric acid *(13, 14)*. In further work, we will investigate inhibiting the decomposition of pernitric acid through additives.

Conclusions

Dilute aqueous solutions of pernitric acid can effectively delignify finely divided aspen wood. The amount of oxidant consumed is much greater than that for equivalent delignification with peroxymonosulfuric acid, however. This is due in part to the rapid decomposition of pernitric acid at ambient temperature.

Aspen wood residues delignified with pernitric acid have low 0.5% CED viscosities indicating severe damage to the wood carbohydrates. This damage may be mainly a consequence of the production of highly reactive-free radicals resulting from the decomposition of the pernitric acid. If this decomposition could be inhibited, less oxidant might be consumed and greater residue viscosities might result.

Manuals on the storage and handling of hydrogen peroxide warn that strong nitric acid solutions and hydrogen peroxide can react explosively *(15)*. Generation of pernitric acid by quickly adding 70% hydrogen peroxide to 90% nitric acid at ice–bath temperature is therefore a hazardous undertaking. Explosive mixtures easily result. One must exercise extreme care when generating pernitric acid. Use only small quantities of reactants and employ exhaust hoods and safety shields. Dilution of the concentrated mixtures with water negates the explosion hazard.

Experimental

This work used quaking aspen (*Populus tremuloides* Michx.) sapwood from a mature tree. The nitric and sulfuric acids and the sodium hydroxide used were of reagent grade. The 70% hydrogen peroxide and the Oxone used were from E. I. du Pont de Nemours & Co., Wilmington, DE. The peroxide was their ALBONE 70 grade. All chemicals used in analysis were of reagent grade.

The 72% sulfuric acid method employed at the Forest Products Laboratory *(16)* determined the lignin contents of the original wood and delignified residues. This is essentially the Klason lignin procedure.

TAPPI Test Method T 230 om-82 determined the viscosities of the delignified residues. Residues that would not completely dissolve in the CED solution were chlorited using the following method as recommended in TAPPI Suggested Method T 230 su-66:

- Twenty milliliters of distilled water in a 50-mL Erlenmeyer flask were heated to 70°C, and 0.50 g sodium chlorite was added and dissolved. To this solution, 0.50 g of the residue to be delignified was added, and the mixture was shaken. To the slurry, 0.20 mL of glacial acetic acid was added, and the slurry shaken again. The slurry was held in a water bath at 70°C for 5 min and then cooled. After cooling, the chlorited residue was washed thoroughly with distilled water and then filtered and dried in a 105°C oven for 3 min. ◧

Literature cited

1. Poppius, K., Laamanen, L., Sundquist, J., *et al.*, *Paperi ja Puu* 68(2): 87(1986).
2. Anon., *Paperi ja Puu* 72(9): 813(1990).
3. Springer, E. L., *Tappi J.* 73(1): 175(1990).
4. Springer, E. L. and Minor, J. L., U.S. pat. 5,004,523 (Apr. 2, 1991).
5. Minor, J. L. and Springer, E. L., *Paperi ja Puu* 72(10): 967(1990).
6. Minor, J. L. and Springer, E. L., *Proceedings of the 6th International Symposium on Wood and Pulping Chemistry*, Australia Pulp and Paper Industry Technical Association, Melbourne, 1991, p. 389.
7. Springer, E. L., *1989 and 1990 Forest Products Symposium Notes*, TAPPI PRESS, Atlanta, p. 113.
8. Yagodovskaya, T. V., Khadzhi-Ogly, M. R., Nekrasov, L. I., *et al.*, *Russian Journal of Physical Chemistry* 52(1): 52(1978).
9. Kenley, R. A., Trevor, P.L., and Lan, B. Y., *J. Am. Chem. Soc.* 103(9): 2203(1981).
10. Greenspan, F. P. and McKellar, D. G., *Analytical Chemistry* 20(11): 1061(1948).
11. Springer, E. L., unpublished results.
12. Walling, C., *Accounts of Chemical Research* 8(4):125(1975).
13. Colodette, J. L., Rothenberg, S., and Dence, C. W., *J. Paper Sci.* 15(2): J45(1989).
14. Sundquist, J., *Paperi ja Puu* 68(9): 616(1986).
15. Anon., *Hydrogen Peroxide—Storage and Handling*, Technical Manual from E.I. du Pont de Nemours & Co. Inc., Wilmington, 1988, p. 18.
16. Moore, W. E. and Johnson, D. B., *Procedures for chemical analysis of wood and wood products*, USDA, Forest Service, Forest Products Laboratory, Madison, 1967.

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