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Pretreatment of Wastepaper and Pulp Mill Sludge by Aqueous Ammonia and Hydrogen Peroxide

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Abstract

Pretreatment of two different softwood-based lignocellulosic wastes (newsprint and Kraft pulp mill sludge) was investigated. Pretreatment was done by aqueous ammonia and hydrogen peroxide (H_2O_2), two delignifying reagents that are environmentally benign. Three different treatment schemes were employed: aqueous ammonia alone (ammonia recycled percolation [ARP]), mixed stream of aqueous ammonia and H_2O_2, and successive treatment with H_2O_2 and aqueous ammonia. In all cases there was a substantial degree of delignification ranging from 30 to 50%. About half of the hemicellulose sugars were dissolved into the process effluent. Retention of cellulose after pretreatment varied from 85 to 100% for newspaper feedstock and from 77 to 85% for the pulp mill sludge. After treatment with aqueous ammonia alone (ARP), the digestibility of newspaper and the pulp mill sludge was improved only by 5% (from 40 to 45% for the former and from 68 to 73% for the latter), despite a substantial degree of delignification occurring after the ARP process. The lignin content thus did not correlate with the digestibility for these substrates. Simultaneous treatment with H_2O_2 and aqueous ammonia did not bring about any significant improvement in the digestibility over that of the ARP. A successive treatment by H_2O_2 and ARP showed the most promise because it improved the digestibility of the newspaper from 41 to 75%, a level comparable to that of α-cellulose.

Index Entries: Ammonia; hydrogen peroxide; newspaper; pulp mill sludge; pretreatment.

Introduction

During alkaline delignification of biomass, Kraft pulping being one example, lignin is predominantly degraded by cleavage of lignin-hemicellulose

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bonds *(1)*. Delignification brings about changes in the structure of cellulose fiber *(2)*. As an alkaline reagent, ammonia has a number of characteristics suitable for processing of lignocellulosic materials *(3)*. Pursuing this concept, a pretreatment method termed the *ammonia recycled percolation* (ARP) process was developed in our laboratory. This process uses aqueous ammonia as the pretreatment reagent. The reaction is carried out in a flowthrough packed-bed reactor. The process stream is continuously fed into and withdrawn from the reactor. Under this operation mode, the lignin and other extraneous components are separated from the biomass structure, preventing recondensation of lignin. Ammonia is then recovered at the end of the process. This process has been proven to be very effective for pretreatment of hardwood and herbaceous substrates *(4–6)*. In contrast to these types of substrates, the literature on biological conversion of softwood is scarce. Perhaps the lack of such information is because softwood is one of the most difficult substrates to degrade biologically. The softwood-based feedstocks have high lignin content and dense structure between cellulose fiber and lignin. They exhibit extremely low enzymatic digestibility. Hydrogen peroxide is one of the few delignifying reagents that is environmentally benign. Currently, it is widely used in the bleaching process of pulp and the paper industry. Hydrogen peroxide in alkaline conditions promotes rapid oxidative depolymerization of the lignin molecule in lignocellulosic materials *(7,8)*. Hydrogen peroxide has been used in the pretreatment of biomass *(9–15)*. It has also been tested in our laboratory as a supplementary reagent in the ARP system *(5)*. The feedstocks used in these studies, however, have been limited to hardwood and herbaceous feedstocks. The purpose of the present investigation was to find an effective pretreatment method for softwood-based feedstocks, specifically the primary sludge from a Kraft mill and newsprint waste paper. We focused on the conventional ARP and its variations utilizing hydrogen peroxide, concurrently and in succession with aqueous ammonia.

Materials and Methods

Materials

Paper mill sludge was obtained from a Kraft mill (Mead-Beit, Columbus, GA). Newsprint wastepaper feedstock was supplied from Korea Institute of Energy Research, Taejon, Korea. The composition of newspaper feedstock was 53.3 wt% cellulose, 11.2 wt% hemicellulose, and 26.3 wt% klason lignin. The composition of pulp mill sludge was 58.4 wt% cellulose, 12.4 wt% hemicellulose, and 19.72 wt% Klason lignin. The cellulase enzyme Spezyme-CP (lot no. 41-95034-004) was supplied from the National Renewable Energy Laboratory (NREL). The average enzyme activity was 84.7 filter paper units (FPU)/mL.

Experimental Setup and Operation

Figure 1 depicts an experimental apparatus for pretreatment. The system consists of a stock solution reservoir, a dual-channel metering pump,

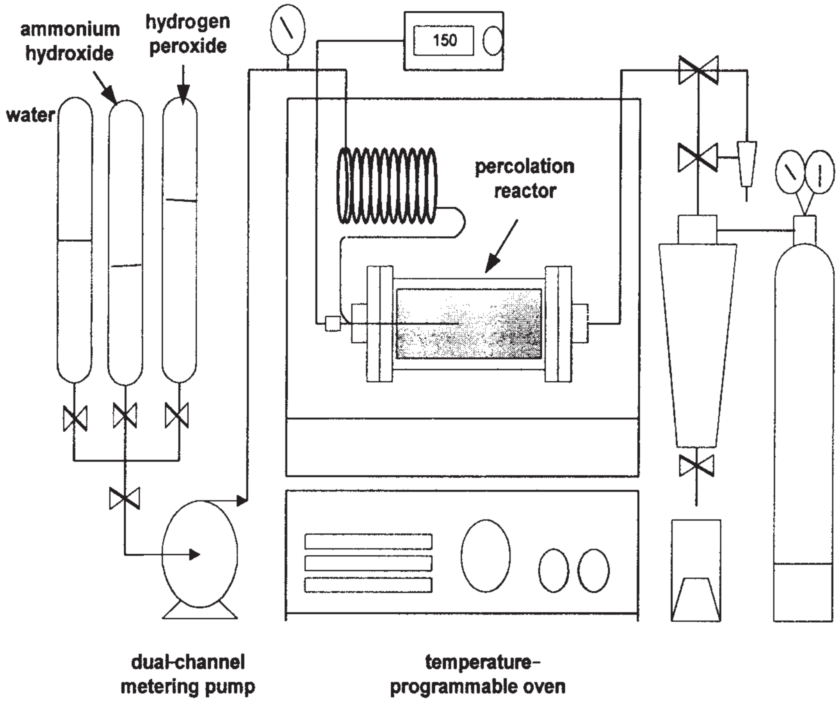

Fig. 1. Schematic of the percolation reactor system.

a temperature-programmable oven, a flowthrough packed-bed (percolation) reactor, and a liquid holding tank that also serves as a back-pressure vessel. The reactor was constructed out of SS316 with a volume of 175 cm^3. The liquid holding tank was connected to a nitrogen cylinder to apply back pressure, preventing evaporation of reactant fluid. For the ARP-hydrogen peroxide (ARP-H) treatment, aqueous ammonia and hydrogen peroxide were pumped simultaneously to the packed-bed reactor through a preheating coil. Alternatively, the treatment was done in two stages: hydrogen peroxide followed by ARP. At the completion of a run, wash water was put through the reactor to remove residual sugar and ammonia trapped in the treated substrates. The wet solids discharged from the reactor were separated into two portions. One was oven-dried at 105°C overnight for measurement of weight loss and further subjected to composition analysis. The other was used in the enzymatic digestibility test.

Digestibility Test

Enzymatic digestibility of pretreatment substrates was performed at 50°C and pH 4.8 (0.05 *M* sodium citrate buffer) on a shake bath agitated at 150 rpm. The cellulase enzyme loading was kept at 60 IFPU/g of cellulose following the NREL standard procedure (LAP-009, 1996). The initial glucan concentration was 1% (w/v). Samples were taken periodically and analyzed for glucose and cellobiose content using high-performance liquid

Table 1
Composition of Newspaper Feedstock and Pulp Mill Sludge After ARP Treatment[a]

		Composition (%)		
Reaction (°C)[b]	Wt% remaining	Cellulose	Hemicellulose	Klason lignin
Untreated				
N	100	53.30	11.23	26.30
P	100	58.36	12.43	19.72
ARP 150				
N	88.90	53.44	6.34	19.77
P	73.36	45.56	5.85	12.96
ARP 170				
N	88.11	53.39	6.22	18.75
P	70.16	45.22	5.44	12.07
ARP 190				
N	88.75	52.69	6.40	19.03
P	70.79	42.42	6.47	13.05
ARP 200				
N	86.98	48.93	6.34	21.33
ARP 220				
N	86.84	48.65	6.63	24.23

[a]Contents of all sugar and Klason lignin are based on untreated oven-dried biomass. Reaction condition: flow rate of ammonia (17 wt%) = 3.2 mL/min.
[b]N, newspaper feedstock; P, pulp mill sludge.

chromatography (HPLC). Glucose and cellobiose content were taken for calculation of the enzymatic digestibility.

Analytical Methods

Solid biomass samples were analyzed for sugars, Klason lignin, acid-soluble lignin, and ash according to the procedures described in the NREL Chemical Analysis & Testing Standard Procedure (nos. 002 and 010). Oligomeric sugars in the liquor and rinsate were converted to monomer using 4% H_2SO_4 hydrolysis at 121°C for 1 h. Sugars were determined by HPLC using a Bio-Rad (Hercules, CA) Aminex HPX-87P column.

Results and Discussion

Ammonia Recycled Percolation

The feedstocks were first put through a series of ARP processes using 17 wt% aqueous ammonia solution. The temperature was varied over the range of 150–220°C. The weight remaining after the treatment averaged to 88% for newspaper and 72% for the pulp mill sludge. The treated solid samples were then analyzed for sugars and Klason lignin. Table 1 summarizes the results. The lignin fraction in the treated biomass decreased as ARP temperature was increased from 150 to 190°C. The cellulose retention

Table 2
Effect of H_2O_2 Concentration on Composition of Biomass Feedstocks on ARP Treatment Supplemented with Hydrogen Peroxide[a]

Concentration of hydrogen peroxide (wt%)[b]	Wt% remaining	Composition (%)		
		Cellulose	Hemicellulose	Klason lignin
Untreated				
N	100	53.30	11.23	26.30
P	100	58.36	12.43	19.72
0				
N	88.11	53.39	6.22	18.75
P	70.16	45.22	5.44	12.07
2.5				
N	85.39	46.14	6.16	20.41
P	84.43	49.11	7.13	14.53
5.0				
N	80.09	45.29	5.69	17.82
P	77.62	46.74	5.98	12.45
7.5				
N	68.93	34.49	4.99	14.50
P	60.45	33.63	4.89	9.86
10.0				
N	52.36	23.71	3.52	10.80
P	48.77	23.57	3.45	7.44

[a]Contents of all sugar and Klason lignin are based on untreated oven-dried biomass. Reaction condition: 170°C, 90 min; flow rate of ammonia (17 wt%) = 3.2 mL/min; flow rate of hydrogen peroxide = 1.0 mL/min.

[b]N, newspaper feedstock; P, pulp mill sludge.

at these temperatures was near 100% for newspaper and 78% for the pulp mill sludge. A further increase in temperature decreased the cellulose fraction of the treated biomass. The hemicellulose content and Klason lignin remained relatively constant over the entire range of the temperature. About 30% of the lignin and 50% of hemicellulose are removed from biomass by the ARP process. The ARP accomplishes 40–60% delignification for hardwood or herbaceous feedstocks *(4–6)*. This again proves our contention that delignification is more difficult for softwood-based biomass than it is for hardwood or herbaceous biomass. Because of the high retention of cellulose and relatively high delignification, 170°C is deemed the optimum operating temperature for the ARP.

ARP-H Treatment

The ARP-H process (ammonia and hydrogen peroxide are put into the reactor simultaneously) was then attempted for the treatment of the aforementioned biomass feedstocks. The concentration of hydrogen peroxide varied from 0 to 10 wt%, keeping ammonia concentration constant at 17 wt% (Table 2). The tendency shown in Table 2 is that H_2O_2 increases the

Table 3
Effect of H_2O_2 Flow Rate Composition of Biomass Feedstocks on ARP Treatment Supplemented with Hydrogen Peroxide[a]

Flow rate (mL/min)[b]	Wt% remaining	Composition (%) Cellulose	Hemicellulose	Klason lignin
Untreated				
N	100	53.30	11.23	26.30
P	100	58.36	12.43	19.72
0.2				
N	85.21	47.12	6.62	20.55
P	72.67	43.57	7.51	13.32
0.5				
N	83.23	50.01	6.04	18.74
P	68.02	54.87	4.41	10.22
0.8				
N	83.20	49.82	6.03	19.66
P	67.45	44.15	4.71	10.33
1.2				
N	80.63	47.32	5.96	18.29
P	67.07	40.49	4.82	10.24

[a]Contents of all sugar and Klason lignin are based on untreated oven-dried biomass. Reaction condition: 170°C, 90 min; flow rate of ammonia (17 wt%) = 3.2 mL/min.
[b]N, newspaper feedstock; P, pulp mill sludge.

overall weight loss and the extent of delignification. Thus, the cellulose fraction within the treated biomass actually increases as the hydrogen peroxide concentration was raised from 2.5 to 5.0 wt%. With the hydrogen peroxide concentrations at 7.5 and 10 wt%, the wt% remaining and cellulose composition decreased dramatically. The extent of delignification was also quite high, in the range of 40–60%. This is a clear indication that H_2O_2, at or above 7.5 wt%, reacts not only with lignin but also attacks cellulose, causing substantial degradation. Based on the data in Table 2, we used hydrogen peroxide at the level of 5.0 wt% in further experiments involving ARP-H.

Further refinement of the ARP-H operation was sought, this time with regard to the hydrogen peroxide throughput (flow rate). Table 3 presents the results of its effect on ARP-H performance. Again taking the wt% remaining and cellulose retention into consideration, the flow rate of 0.5 mL/min was taken to be the optimum. With this flow rate and the concentration of H_2O_2 fixed at 5 wt%, the performance test of ARP-H was conducted by varying the temperature from 150 to 190°C. The results of the ARP-H were similar to those of the ARP. Considering the three main factors collectively (weight loss, delignification, and cellulose retention), we chose 170°C as the optimum temperature for the ARP-H.

Table 4
Composition of Biomass Feedstocks
on Successive Treatment with H_2O_2 and ARP[a]

Reaction condition[b,c]	Wt% remaining	Composition (%)		
		Cellulose	Hemicellulose	Klason lignin
Untreated				
N	100	53.30	11.23	26.30
P	100	58.36	12.43	19.72
H_2O_2 (130°C, 60 min)-ARP				
N	78.18	49.19	4.51	17.61
H_2O_2 (60°C, 60 min)-ARP				
N	87.66	49.33	6.91	23.52
H_2O_2 (60°C, 120 min)-ARP				
N	80.33	45.87	5.61	19.01
P	73.42	48.01	5.35	12.69
H_2O_2 (60°C, 180 min)-ARP				
N	80.29	46.52	5.11	18.35
P	72.61	48.12	5.32	12.87
H_2O_2 (80°C, 60 min)-ARP				
N	87.33	49.20	6.98	23.07
H_2O_2 (80°C, 120 min)-ARP				
N	77.33	48.52	4.53	15.70
P	70.31	46.72	5.00	12.09
H_2O_2 (80°C, 180 min)-ARP				
N	79.10	49.07	4.93	15.64
H_2O_2 (100°C, 60 min)-ARP				
N	82.28	47.58	4.67	21.53

[a]Contents of all sugar and Klason lignin are based on untreated oven-dried biomass.
[b]N, newspaper feedstock; P, pulp mill sludge.
[c]Reaction condition: 170°C, 90 min; flow rate of ammonia (17 wt%) = 3.2 mL/min; flow rate of hydrogen peroxide (5 wt%) = 0.5 mL/min.

Two-Stage Treatment with Hydrogen Peroxide and ARP

An additional variation of the ARP-H process was investigated. In this case, H_2O_2 and aqueous ammonia were put through the percolation reactor in succession applying different temperatures and durations at each stage. In the first stage, 5 wt% aqueous hydrogen peroxide was delivered into the reactor operated at various temperatures with a flow rate of 0.5 mL/min. In the second stage, the regular ARPs were run with 17 wt% ammonia solution at 170°C with 3.2 mL/min of flow. Table 4 summarizes the results.

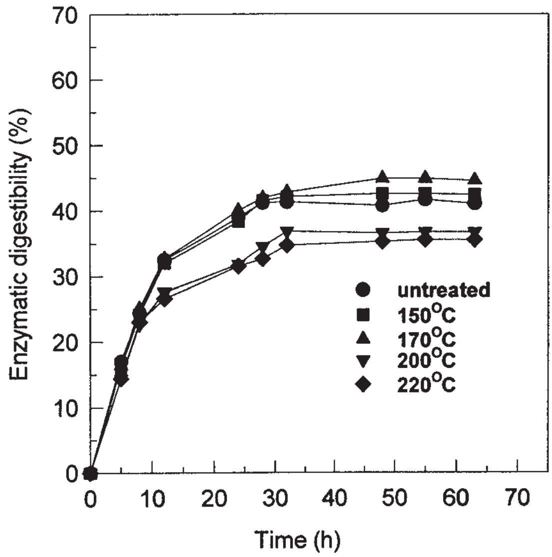

Fig. 2. Enzymatic digestibility of newspaper feedstock after ARP.

The data indicate that the low-temperature hydrogen peroxide runs, especially 60 and 80°C, provide high cellulose retention and a high degree of delignification. For example, with H_2O_2 (80°C, 120 min)-ARP, the cellulose retention is 48.52/53.30 (91%) for newspaper feedstock. The delignification was 40% (from 26.30 to 15.70). For the pulp mill sludge, the results were much different, yielding only 80% of cellulose retention and 39% of delignification. The poor performance indexes for the pulp mill sludge in comparison to the newspaper feedstock was observed in all the ARP runs and its variations.

Enzymatic Digestibility

The data presented to this point dealt with the changes in the composition of biomass brought about by various pretreatments. The composition of biomass is an important factor in the process economics. However, the true yardstick for a pretreatment must come from the direct measurement of digestibility. All the solid samples obtained from the ARP, ARP-H, and two-stage treatments were therefore subjected to the standard enzymatic digestibility test. Figures 2–5 summarize the data. Figures 2 and 3 present the digestibility data after ARP treatment for both substrates. The data indicate that ARP alone is not an efficient pretreatment method for these feedstocks. After ARP treatment, the digestibility of newspaper and the pulp mill sludge was improved only by 5% (from 40 to 45% for the former, and from 68 to 73% for the latter), despite a substantial degree of delignification occurring after the ARP process. Apparently the lignin content is not a prime factor controlling the digestibility for these substrates. The measured digestibility shown here is a drastic departure from hard-

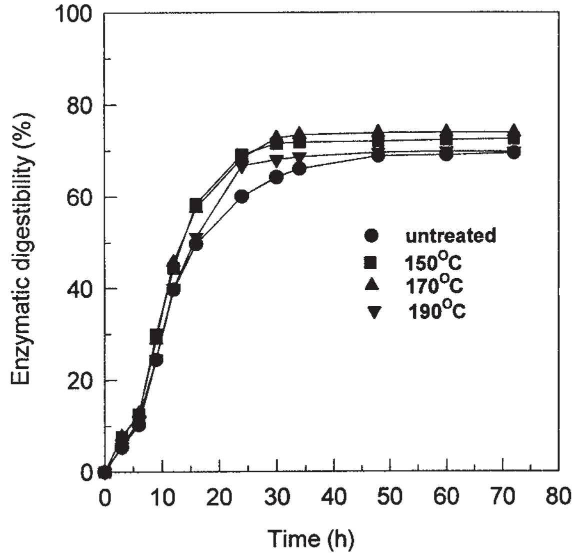

Fig. 3. Enzymatic digestibility of pulp mill sludge after ARP treatment at various temperatures.

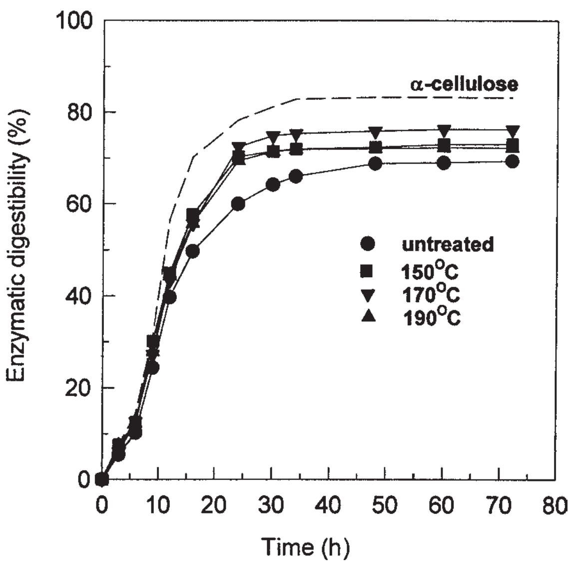

Fig. 4. Enzymatic digestibility of pulp mill sludge after ARP-H.

wood and herbaceous materials in which the digestibilities in the range of 70–90% are easily attainable by ARP *(5,6)*. Figure 4 shows the enzymatic digestibility of pulp mill sludge after ARP-H treatment. After the ARP-H run, the digestibility of pulp mill sludge was only slightly improved over that of ARP, going from 73 to 76%. However, the gain made in the digestibility is offset by the loss of cellulose owing to interaction with H_2O_2.

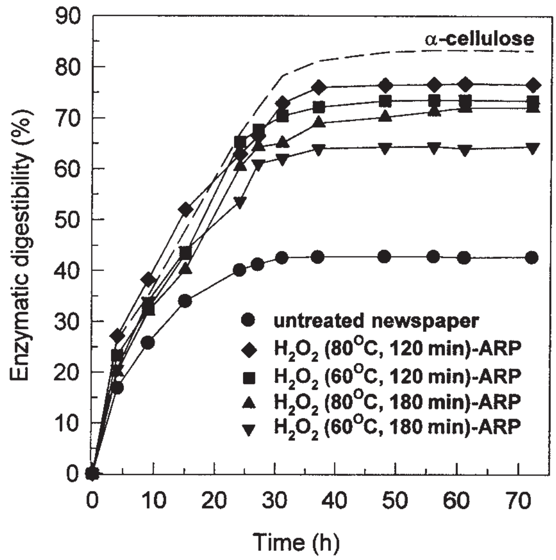

Fig. 5. Enzymatic digestibility of newspaper after successive treatment with hydrogen peroxide and ARP.

Although the absolute value of the digestibility is comparable to that of α-cellulose (83%), the improvement made by ARP or ARP-H is no more than 10% for the pulp mill sludge. Among the various schemes we applied, the one that showed the most promise was the successive treatment by H_2O_2 and ARP. Figure 5 presents the digestibility data for newspaper coming from these series runs. The run that gave the highest digestibility was the one made with H_2O_2, 80°C, 120 min, followed by 90 min of ARP. The digestibility of newspaper feedstock coming from this run was measured to be 75%, a significant improvement over that of the untreated substrate (41%). It shows that delignification by an oxidative agent, H_2O_2, increases the susceptibility to enzymatic hydrolysis of softwood feedstock *(16,17)*. The 75% of digestibility of newspaper feedstock is certainly at a level comparable to that of α-cellulose (83%). Whether the digestibility at this level is acceptable from a process viewpoint is debatable. For the two softwood-based waste materials, however, this is the best one can do at this time with the known pretreatment technology employing environmentally safe pretreatment chemicals. On a positive note, we know that when a biomass substrate is subjected to a simultaneous saccharification and fermentation process, the overall digestibility improves considerably over the enzymatic digestibility.

Acknowledgments

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