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Alkaline Peroxide Mechanical Pulping of Wheat Straw With Enzyme Treatment

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Abstract

Alkaline peroxide mechanical pulping (APMP) of wheat straw with enzyme treatment was studied. Instead of direct enzyme pretreatment on wheat straw, an alternative treatment method was used, in which coarse pulps from refiner defibrated wheat straw rather than wheat straw were pretreated with a crude enzyme containing mainly xylanase, then impregnated with alkaline H_2O_2 solution and further refined. The optimum conditions of enzyme treatment were xylanase dosage of 10–15 IU/g of oven-dried wheat straw, 90 min, 50–60°C, pulp consistency of 5–10%, and initial pH of 5.0, and those for chemical impregnation were 6% NaOH, 70–80°C, 60–90 min, and 4 to 5% H_2O_2. Enzyme treatment improved pulpability of wheat straw by the APMP process, and final pulp quality such as brightness, breaking length, and burst index of pulp. Pulp from the APMP process with enzyme treatment could be bleached to a brightness of 70.5% ISO by two-stage H_2O_2 bleaching sequence with only 4% H_2O_2, and breaking length of the bleach pulp reached 4470 m.

Index Entries: Alkaline peroxide mechanical pulping; enzyme treatment; impregnation; bleaching; wheat straw.

Introduction

Wheat straw has long been used for pulp and paper production and remains one of the major raw materials in many countries such as China. To date, the most common pulping process for straw is based on chemical pulping technology. However, one of the most serious problems associated with straw chemical pulping is the high silica content of the straw, which makes conventional chemical recovery difficult. Alternatively, mechanical pulping seems to be suitable for wheat straw because it is easily disintegrated

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by the mechanical process. The process generates a minimal volume of effluent, thus reducing the environmental impact.

Alkaline peroxide mechanical pulping (APMP) has been a successful pulping method for low-density hardwoods such as aspen and eucalyptus *(1,2)*. Its advantages over the conventional chemical thermomechanical pulping process include good pulp quality, elimination of a bleach plant, and energy savings. The APMP process is based on the incorporation of peroxide bleaching into the chemical impregnation and refining stages, in which bleaching action takes place not only to eliminate alkali darkening of wood chips but to brighten them to certain brightness levels as well. Furthermore, carboxylation of lignin by alkaline peroxide results in easier fiber separation during refining and improved fiber bonding in papermaking. APMP process of agricultural fibers has also been studied and proven successful for kenaf *(3,4)* and bagasse *(5)*. Pan and colleagues *(6–9)* developed an APMP process of wheat straw and successfully applied it to produce wheat straw pulps with acceptable quality for printing-grade papers. However, the wheat straw fibers are difficult to bleach, and at a given peroxide dosage, their achievable brightness level is much lower than that of wood fibers. To produce high-brightness straw pulps, a high dosage of peroxide is necessary, which leads to high production costs. On the other hand, the wheat straw APMP has a yellow hue, which limits its use to low-brightness-grade papers. One possible strategy for solving these problems is biologic treatment of raw materials, a concept known as biomechanical pulping.

Up to now, biomechanical pulping with biologic pretreatment has been investigated for woody and nonwoody materials *(10–17)*. It is well known that inoculation of materials with selected fungal strains results in intensive growth and colonization throughout the chips and straws, which leads to softening and swelling of fiber walls and subsequently to easier fiberization during refining. Fungal pretreatment also results in partial degradation and modification of lignin, cellulose, hemicellulose, or components that link lignin with carbohydrates (lignin-carbohydrate complexes) *(18,19)*. This pretreatment is favorable for fiber separation during refining (thus leading to energy reduction during refining), a decrease in chemicals charge during chemical treatment, and improvement in pulp properties. However, the time for fungal pretreatment is still too long to be economically feasible. Moreover, the normal fungal effect on raw material (wood or straw) would be a simultaneous attack on both the polysaccharides and the lignin, which could lead to pulp yield loss. There is a growing interest in using enzymes instead of microorganism to treat raw materials in order to overcome these problems. Nevertheless, biomechanical pulping of wheat straw with enzymes by the APMP process has not been described in the literature.

Enzymatic hydrolysis of lignocelluloses in vitro depends on the available surface area and average pore size of the substrate *(20)*. In wood rotting and biopulping, the accessibility of lignin and carbohydrates is increased by fungal growth into the interior of wood chips, with a consequent decrease in the diffusion barrier for enzymatic action on wood components. However, the accessibility of native wood (or wood chips) and raw straw to isolated enzymes is very low because the high molecular weight and physical size of enzymes limit their penetration into intact structures of raw materials. Pretreatment such as milling or fiberization increases the accessible surface area, thereby enhancing the action of enzyme. Our preliminary experimental results showed that the efficiency of enzyme pretreatment on wheat straw prior to the APMP process is low. In this article, we report a new biochemical-mechanical-pulping process with enzymes to increase the efficiency of enzyme treatment as well as to improve pulpability of wheat straw by the APMP process. In the process, wheat straw was defibrated first with a high-consistency refiner. Then coarse pulp was treated with hemicellulase and alkaline H_2O_2 in sequence, and further refined. The effects of process variables such as enzyme treatment (e.g., enzyme dosage, treatment time, temperature, and consistency of pulp) and peroxide impregnation (e.g., chemical charge, temperature, time, and H_2O_2 charge) on APMP pulping of wheat straw were investigated, and bleachability of the APMP pulp was evaluated.

Materials and Methods

Wheat Straw and Medium

Wheat straw was collected in Dingtao County, Shandong Province, China, and chopped to 3–5 cm. The supernatant of cultured broth from *Aspergillus niger* An-76 was used as a crude enzyme. The medium contains 2% wheat bran, 0.1% peptone, 0.3% KH_2PO_4, 0.05% $MgSO_4$, and 1% $(NH_4)_2SO_4$, and the initial pH is 6.0. Cultivation was carried out at 30°C for 72 h with a shaking speed of 150 rpm.

Enzyme Assays

Xylanase activity was determined by incubating 0.5 mL of suitably diluted enzyme with 1 mL of 1% xylan (oat spelts xylan; Sigma, St. Louis, MO) in a 0.2 *M*, acetate buffer of pH 4.8 for 30 min at 50°C. The activity was expressed as the equivalent of reducing sugar produced, which was assayed by 3,5-dinitrosalicylic acid reagent *(21)*. Cellulase activity was measured in a similar manner using carboxymethylcellulose as substrate. One unit (IU) was defined as the amount (1 μmol) of xylose or glucose produced by enzymes per minute under the given conditions.

Xylanase activity and cellulase activity of the enzyme An-76 used in the experiments was determined to be 100 and 2.01 IU/mL, respectively, according to the methods described.

Enzyme Treatment

Prior to enzyme treatment, wheat straw was impregnated thoroughly with water and defibrated with a high-consistency refiner (BR30-300CD;

Kumagai Riki Kogyo Co. Ltd., Nerima Tokyo, Japan) to produce coarse mechanical pulps. The clearance of disk in the first and second refining stage was 0.4 and 0.15 mm, respectively. Then the coarse pulps were dewatered through a wire cloth and treated with crude enzyme An-76. The pulp, enzyme solution, and distilled water were mixed thoroughly in polyethylene bags. The bags were immersed in a constant-temperature water bath. The initial pH (5.0) of the pulp slurry was adjusted with acetate buffer (200 m*M*). After enzymatic hydrolysis, the pulps were dewatered through a wire cloth. The control was prepared as previously described, but without enzyme addition.

Preparation of APMP Pulps

The enzyme-treated coarse pulps were pretreated with diethylenetriaminepentracetic acid (DTPA) in polyethylene bags under the following conditions: 5% pulp consistency, 0.3% DTPA (based on oven-dried pulp), 60°C, 30 min, and pH 4.0–5.0. Then the pulps were impregnated with alkaline H_2O_2 at 14% pulp consistency. The chemical-impregnated pulps were further refined in the refiner with disk clearance of 0.1 mm. After refining, the pulps were washed and screened with a laboratory flat screen to remove shives.

Bleaching of APMP Pulps

APMP pulps were bleached in polyethylene bags with P and PP bleaching sequence (P stands for H_2O_2) at 10% pulp consistency. After bleaching, the pulps were washed with tap water.

Analytical Methods

The yields of screened pulps and physical properties of pulps were measured according to the Chinese National Standards *(22)*. The residual H_2O_2 concentration was determined iodometrically *(23)*. The ISO brightness of pulp was measured on a YQ-Z-48A brightness color tester according to TAPPI standards *(24)*.

Results and Discussion

Effect of Enzyme Treatment on APMP Pulping of Wheat Straw

Xylanase Dosage

Pulpability of wheat straw by the APMP pulping process with enzyme treatment was studied using various enzyme dosages. Table 1 shows that the enzyme pretreatment of coarse pulp before further refining resulted in a higher brightness of pulp, a higher physical strength such as breaking length and burst index, a similar tear index, and slightly lower yields of pulp as compared to the control. Pretreatment with a xylanase dosage of 10 IU/g increased the ISO brightness of pulp by 2.2% ISO, the breaking length by 1080 m, and the burst index by 0.4 kPa·m^2/g compared to the control. Enzymatic hydrolysis of coarse pulp can partially remove xylan on

Table 1
Effect of Enzyme Dosage on APMP Pulp Properties[a]

	Xylanase dosage (IU/g)				
	Control	5	10	15	20
Yield (%)	68.21	67.51	66.52	66.46	66.08
ISO brightness (%)	45.2	45.7	47.4	49.8	49.7
Breaking length (m)	3210	4290	4290	3990	3610
Burst index (kPa·m^2/g)	1.3	1.9	1.7	1.8	1.5
Tear index (mN/[m^2·g])	4.4	4.7	4.3	4.3	4.3

[a]Other conditions in enzyme stage: 5% pulp consistency, 50°C, 120 min, pH 5.0. Conditions of chemical impregnation: 8% NaOH, 4% H_2O_2, 70°C, 120 min.

Table 2
Effect of Pretreatment Time on APMP Pulp Properties[a]

Time (min)	Yield (%)	ISO brightness (%)	Breaking length (m)	Burst index (kPa·m^2/g)	Tear index (mN·m^2/g)
60	67.04	46.8	4340	1.8	4.6
90	66.53	47.2	4570	2.2	4.4
120	66.52	47.4	4290	1.7	4.3
150	66.18	47.7	4270	1.8	4.3

[a]Other conditions in enzyme stage: xylanase dosage of 10 IU/g, 5% pulp consistency, 50°C, pH 5.0. Additional conditions are given in Table 1.

the fiber surfaces or from the lignin-carbohydrate complexes (LCC). Therefore, enzyme pretreatment increases diffusivity of chemicals in the subsequent alkaline H_2O_2 impregnation stage. Pretreatment with a crude enzyme solution, which includes xylanase and cellulase activity, can also partially remove some extractives and fines of coarse pulp, which decreased H_2O_2 and NaOH consumption in subsequent chemical impregnation, thus facilitating increased brightness and physical strength of pulp. However, a further increase in enzyme dosage to high levels (e.g., >15 IU/g) decreased physical strength. This could be owing to excessive enzymatic hydrolysis of cellulose. The optimum xylanase dosage was 10–15 IU/g of oven-dried straw.

Pretreatment Time

Table 2 indicates that the ISO brightness of pulp increased slightly with increasing enzymatic pretreatment time. This was attributed to removal of more xylan and improved diffusion and impregnation of chemicals, such as H_2O_2 and NaOH, into coarse pulp, which results in an enhanced bleaching action of H_2O_2 in the subsequent chemical impregnation stage. However, pretreatment times of over 90 min had a negative influence on physical strength of the final pulp, such as breaking length and burst index decreasing at the same enzyme dosage. The optimum time for APMP pulping of wheat straw was 90 min.

Table 3
Effect of Pretreatment Temperature on APMP Pulp Properties[a]

Temperature (°C)	Yield (%)	ISO brightness (%)	Breaking length (m)	Burst index (kPa·m²/g)	Tear index (mN·m²/g)
40	66.91	46.3	4200	1.8	4.5
50	66.52	47.4	4290	1.7	4.3
60	66.67	47.3	4240	1.9	5.1
70	66.95	46.5	4150	1.8	4.6

[a]Other conditions in enzyme stage: xylanase dosage of 10 IU/g, 5% pulp consistency, 120 min, pH 5.0. Additional conditions are given in Table 1.

Table 4
Effect of Pulp Consistency on APMP Pulp Properties[a]

Pulp consistency (%)	Yield (%)	ISO brightness (%)	Breaking length (m)	Burst index (kPa/[m²·g])	Tear index (mN/[m²·g])
3	66.56	46.9	4300	1.9	4.5
5	66.52	47.4	4290	1.7	4.3
10	66.79	48.2	4200	1.6	4.6
15	66.75	46.1	4220	1.6	4.5

[a]Other conditions in enzyme stage: xylanase dosage of 10 IU/g, 50°C, 120 min, pH 5.0. Additional conditions are given in Table 1.

Pretreatment Temperature

It can be seen from Table 3 that increasing pretreatment temperature from 40 to 70°C had a slight influence on the yields of pulp and physical strength. Pretreatment with enzyme at a temperature of 50–60°C resulted in a higher brightness of the final pulp and a slightly higher breaking strength. This could be attributed to high enzyme activity at the temperature range of 50–60°C. A higher or lower pretreatment temperature decreased enzyme activity, thereby decreasing efficiency of the enzyme treatment.

Pulp Consistency

With the same enzyme dosage, an increase in pulp consistency means that the enzyme consistency in the pulp slurry is increasing. This should be beneficial in improving the efficiency of enzyme treatment. However, it was difficult to mix the coarse pulp with enzyme solution at a high consistency of pulp during enzyme treatment, which may have a negative influence on the effectiveness of enzyme treatment. Table 4 shows that pretreatment with enzyme at a high pulp consistency (e.g., 15% pulp consistency) negatively affected the results of APMP of wheat straw, and decreased brightness of the final pulp. Therefore, a suitable consistency of pulp in the enzyme treatment stage was 5–10%.

Table 5
Factors and Levels of Orthogonal Experiment

Level	NaOH charge (%)	Maximum temperature (°C)	Time at maximum temperature (min)	H_2O_2 charge (%)
I	2	60	60	2
II	4	70	90	3
III	6	80	120	4
IV	8	90	150	5

Overall, suitable conditions of enzyme pretreatment in APMP pulping of wheat straw were as follows: xylanase dosage of 10–15 IU/g of oven-dried wheat straw, pretreatment time of 90 min, temperature of 50–60°C, and pulp consistency of 5–10%. The initial pH value was adjusted to 5.0.

Effect of H_2O_2 Impregnation on APMP of Wheat Straw

In the APMP process, impregnation of alkaline H_2O_2 had comparable effects on the final pulp quality, such as the brightness and physical properties of the pulp. The main process variables that influence alkaline H_2O_2 impregnation include alkali charge, maximum temperature, time at maximum temperature, and peroxide charge. To evaluate the effect of process variables in the alkaline peroxide impregnation stage on quality of the final pulp, an orthogonal experiment method was used. The factors and levels of the orthogonal experiment and design of the experiment are given in Tables 5 and 6, respectively. The following conditions were used in the enzyme treatment stage: xylanase dosage of 10 IU/g, 50°C, 90 min, 5% pulp consistency, and pH 5.0. To remove transition metals in the coarse pulps and to minimize the occurrence of metal-catalyzed decomposition of H_2O_2 in alkaline condition, the chelating agent DTPA was used to treat pulps prior to peroxide impregnation. The results of APMP pulping of wheat straw with enzyme treatment under different conditions of alkaline peroxide impregnation are given in Table 7. By the statistical analysis of experiment results, it was found that the NaOH charge changes had an especially significant influence on pulp yield, brightness, tensile index, and burst index; temperature changes affected yield and brightness of pulp; and the H_2O_2 charge affected pulp brightness. Temperature changes had a significant influence on tensile index. The H_2O_2 charge changes had a moderate influence on tensile index and burst index, temperature changes moderately affected burst index, and time changes moderately affected tear index. On the other hand, the NaOH charge changes had little influence on tear index; temperature changes little affected tear index; time changes little affected pulp yield, brightness, tensile index, and burst index; and H_2O_2 charge little affected pulp yield and tear index.

Table 6
Design of Experiment [$L_{16}(4^5)$]

Sample no.	NaOH charge (%)	Temperature (°C)	Time (min)	H_2O_2 charge (%)
1	2	60	60	2
2	2	70	90	3
3	2	80	120	4
4	2	90	150	5
5	4	60	90	4
6	4	70	60	5
7	4	80	150	2
8	4	90	120	3
9	6	60	120	5
10	6	70	150	4
11	6	80	60	3
12	6	90	90	2
13	8	60	150	3
14	8	70	120	2
15	8	80	90	5
16	8	90	60	4

Table 7
Results of APMP Pulping With Enzyme Treatment

Sample no.	Yield (%)	ISO brightness (%)	Tensile index (N·m/g)	Burst index (kPa·m²/g)	Tear index (mN·m²/g)
1	87.92	45.97	3.98	1.0	1.4
2	86.69	46.13	4.27	1.0	1.7
3	84.61	48.83	5.26	1.0	3.2
4	84.24	50.80	6.31	1.0	5.7
5	79.02	47.50	13.46	1.0	6.1
6	77.85	49.50	15.71	1.0	3.4
7	77.29	40.33	19.32	1.2	5.7
8	74.13	42.07	26.85	1.3	3.3
9	77.71	51.57	20.99	1.1	2.8
10	76.31	46.47	30.74	1.4	3.0
11	73.41	45.60	29.80	1.3	3.4
12	69.72	39.00	35.84	1.7	4.9
13	69.72	43.83	47.26	2.0	5.0
14	68.55	40.33	43.61	1.9	3.8
15	65.59	49.60	42.47	1.8	7.2
16	64.82	43.30	48.64	2.0	3.5

Table 8
Bleaching Sequence and Bleaching Results of APMP Pulp and Control Pulp

Sample no.	P_1 stage[a]					P_2 stage[a]			ISO brightness of pulp (%)
	H_2O_2 charge (%)	Temperature (°C)	Time (min)	NaOH charge (%)	Residual H_2O_2 (g/L)	H_2O_2 charge (%)	Temperature (°C)	Time (min)	
1	3	70	120	1	1.58	—	—	—	58.7
2	3	70	150	1	1.59	—	—	—	60.1
3	3	90	120	1	1.29	—	—	—	66.1
4	3	90	150	1	1.10				66.8
5	2	70	120	1	0.81	1	70	120	62.6
6	3	70	120	1	1.46	1	70	120	64.3
7	3	90	150	1	0.99	1	70	120	70.5
Control	3	90	150	1	0.89	1	70	120	65.9

[a]Other conditions in P_1 and P_2 stage: 10% pulp consistency, 2% Na_2SiO_3, 0.05% $MgSO_4$. Brightness of the original pulp: 47.4% ISO for APMP pulp and 45.2% ISO for control pulp.

Overall, in the alkaline peroxide impregnation stage, increasing NaOH charge favored improvement in pulp strength properties but decreased pulp yield. An NaOH charge of >6% decreased pulp brightness, which could be attributed to H_2O_2 decomposition and fiber yellowing at high levels of alkalinity. High-temperature impregnation at the same NaOH charge decreased pulp yields but improved tensile index at a low NaOH charge (e.g., <6%). Therefore, it was necessary to consider all these factors in order to produce pulp with a high yield, high brightness, and high physical strength.

Based on the results, we concluded that the conditions of 6% NaOH, 70–80°C, 60–90 min, and 4 to 5% H_2O_2 were suitable in the alkaline peroxide impregnation stage. However, overall, the yields of APMP pulps of wheat straw were relatively low (<80%) under these conditions.

Bleachability of APMP Pulp of Wheat Straw

To preliminarily evaluate bleachability of APMP pulp of wheat straw, several bleaching experiments of APMP pulp with P and P_1P_2 bleaching sequences were carried out; the results are presented in Table 8. Bleached pulp of 58.7% ISO could be produced by a single H_2O_2 bleaching stage with 3% H_2O_2 (sample 1). Increasing bleaching temperature and time helped to increase the efficiency of bleaching and to produce a higher brightness pulp at the same charge of H_2O_2 (samples 2–4). The APMP pulp could be bleached to an ISO brightness of >70% by two-stage H_2O_2 bleaching sequence with 4% H_2O_2 (about 4.5% ISO higher than control pulp), and the breaking length of the bleached pulp reached 4470 m.

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