A NEW MECHANISM OF BIOPULPING: ATTACHMENT OF ACID GROUPS ON FIBER

O13.2

William R. Kenealy[1], Chris Hunt[2,3], Eric Horn[3] and Carl Houtman[1]

[1] U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, WI.

[2] University of Wisconsin-Madison

[3] Biopulping International, Inc. Madison, WI.

ABSTRACT

We analyzed the physical properties of wood chips incubated with *Ceriporiopsis subvermispora* and cultural parameters of biopulping incubations of *Phanerochaete chrysosporium* and *C. subvermispora.* Dynamic mechanical analyses indicated a reduction in the modulus of elasticity (MOE) and loss modulus of spruce during the time where the biopulping energy savings effect takes place. The data from measurements of the MOE at different moisture contents indicated the fiber saturation point (FSP) of spruce increased from 29% to 42% during biopulping. Chips were made into pulp, which was washed, and the titratable acids attached to the fiber were determined. Titratable acid groups on spruce increased from 96 meq/kg for control pulps to 121 eq/kg for *C. subvermispora* treated spruce pulps. A 25 eq/kg of pulp would be expected to increase the FSP by 14%. Oxalate could be extracted from the biopulps by base in significantly greater amounts than by acid. Oxalate is bound to the pulp, probably through an ester linkage, in amounts that were in excess of the amount needed to explain the increase in FSP. A single esterification of oxalic acid would increase the acid content of the pulp, which should cause an increase in water content and softening of the chips.

INTRODUCTION

Biopulping was originally investigated as a process to use the selective lignin degradation of some white-rot fungi to 'aid in the pulping and subsequent delignification of wood chips. *Phanerochaete chrysosporium* and *Ceriporiopsis subvermispora* have been used in many biopulping trials. While selective lignin degradation was the goal of investigating these fungi, significantly less energy was required to convert treated wood chips into pulp. Biopulping became known for this energy savings effect (ESE) and less for lignin degradation. In addition to energy savings the paper derived from the biopulp often had significant increases in strength.

MATERIALS AND METHODS

Fungal treatment reactors were prepared with 1 kg fresh spruce, pine, aspen or eucalyptus wood chips (19 mm) and treating with steam for 10 min. After cooling, water (to 50% solids, w/w), corn steep liquor (0.5% w/w on dry wood), and inoculum were added and the mixture was incubated. Pulp for titration was refined with a single pass using a 30.5-cm-diameter laboratory atmospheric refiner. Handsheet pulps were refined at atmospheric pressure to 100 mL Canadian standard freeness (CSF) for aspen, one pass the 103 kPa followed by atomosperic refining to 400mL CSF for eucalyptus or 50 mL CSF for pine and spruce. Energy consumption was recorded with a watt meter attached to the refiner motor.

Dynamic mechanical analysis measurements were made at 20°C with 0.02% strain on a 1.9 cm free span (4.0 by 1.3 by 0.3 cm longitudinal) with a DMTA V (Rheometric Scientific, Piscataway, New Jersey). Since DMA in nondestrucive, the change in properties for each sample was measured (n = 5). Elastic and loss moduli by DMA are reported at 1.6 and 4.0 Hz, respectively. A glove box was attached to the DMA instrument to evaluate moisture effects. Saturated salt solutions were used to control relative humidity, equilbrated samples were weighed and tested inside the box. The moisture-strength equation for wood had two unkown

values, FSP and strength at 12% moisture, which were determined by a least squares fit. Coarse pulp was extracted using toluene/ethanol (32:68 w/w ratio). The extracted pulp was alternately soaked and rinsed in 0.1 M HCl (total time 18 h). After rinsing with deionized water, samples were freeze dried. Titration of 1.4 g pulp in 1 L of 0.001 M KCl with 3 ML of 0.1 M KOH was followed over 1 h with pH and conductivity measurements.

Milled wood or pulp samples (0.1 g ± 0.01) were weighed into 15-mL polypropylene centrifuge tubes, extractant (0.1 M NaOH or 0.05 M H_2SO_4, 2L) was added, mixed, and the acidic samples left at room temperature for 96 h, filtered and analyzed for acetate by GC and oxalate by HPLC. The basic samples were heated for 1 h at 65°C, then incubated 96 h at room temperature. Supernatants were acidified, filtered, and analyzed for acetate and oxalate.

RESULTS

Biopulping treatment of spruce resulted in reduction of MOE by 22 and 36%, and loss modulus by 33 and 13% in the tangential and radial directions, respectively. MOE measured at different moisture contents (Figure 1) indicates an increased FSP from 29 to 42%. Extrapolation suggests that MOE would decline 26% (similar to the biopulping result) due to the increase in FSP alone. Increasing FSP by the addition of acid groups to carbohydrates should produce a significant ESE.

The pulp was extracted, washed and the titratable acids determined. On spruce, the control had 96 meq/kg pulp and the *C. subvermispora* treated spruce 121 meq/kg. On aspen and pine the titratable acids were (control/biopulp) 80/112, and 99/129 respectively with a pooled standard deviation of 6.

Oxalate was analyzed along with acetate from control and treated wood chips (Table 1). Oxalate was identified by the retention time on HPLC and confirmed by the removal of the peak with oxalate decarboxylase treatment. The base extraction of oxalate is considered the total oxalate since it extracts esters as well as what is freely soluble. Not shown in Table 1 are data that indicated *G. trabeum*, a brown-rot fungus that does not provide a biopulping effect, had 15 and 9 total meq oxalate /kg at 0 and 14 days on pine respectively. The free oxalic acid for *G. trabeum* on pine was 3 (0 days) and 1 (14 days) meq oxalate /kg.

The extraction of the wood indicated that acetate was recovered in amounts that corresponds to the species of wood used. Figure 2 indicates that for both *C. subvermispora* and *P. chrysosporium* there is a general trend for increased oxalate and decreased acetate extractable from the fiber with time. Oxalate attached to the fiber increases at the same time that the ESE is developed. The energy saved roughly corresponded to the amount of oxalate attached to the fiber.

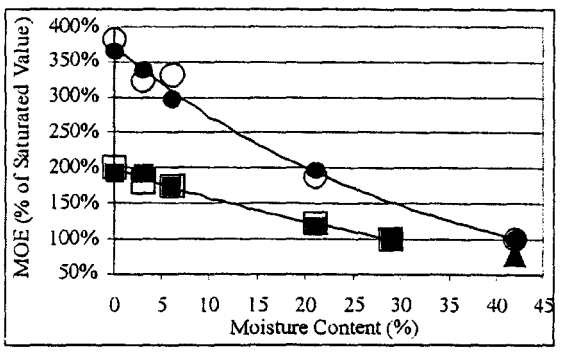

Figure 1. (Left) Spruce tangential and radial MOE as a function of moisture content % of MOE at saturation. Open and closed circles, tangential and radial measurements of *C. subvermispora* treated material. Open and closed squares, tangential and radial measurements of control material. Triangle represents the extrapolation of the untreated control to the moisture content of biopulped material (42%).

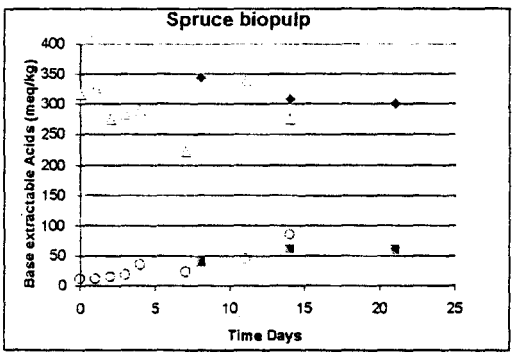

Figure 2. (Right) Spruce biopulp analyzed for base extractable acids. Triangles and diamonds, acetate from *C. subvermispora* and *P. chrysosporium* respectively. Circles and squares, oxalate from *C. subvermispora* and *P. chrysosporium* respectively.

Table 1. Acetate and oxalate extracted from wood samples just inoculated 0 and after 14 days incubation with *C. subvermispora*. Total acid determined by base extraction, free by acid extraction.

Species	Days	n	Oxalate (meq/kg)		Acetate (meq/kg)		Tensile (Nm/g)	Energy saved (%)
			Total	Free	Total	Free		
pine	0	2	12	5	324	29	20.3	34.9
	14	2	+87	+23	+25	+9	+9.0	
spruce	0	10	13	3	324	45	32.1	31.6
	14	10	+66	+17	-31	-3	+6.8	
aspen	0	10	21	ND	923	65	19.2	26.3
	14	10	+59		-58	+5	+8.1	
eucalyptus	0	6	49	6	692	30	6.0	18.8
	14	6	+31	+21	+29	+8	+5.2	
Pooled s.d.			24	12	29	15	0.1	1

ND = not determined, s.d. = standard deviation. Handsheet tensile strength and refiner energy savings (compared to the control) are reported for a representative sample for each wood species.

CONCLUSIONS

The ESE of biopulping is primarily a result of increased FSP, caused by increased fiber bound acid groups. The attachment of oxalate by a single esterification will provide a proton that can dissociate and a concomitant influx of water to balance the osmotic pressure. The method of attachment of oxalate is unknown, but could be due to oxidative means or by esterification and transesterification.

NINTH INTERNATIONAL CONFERENCE ON BIOTECHNOLOGY IN THE PULP AND PAPER INDUSTRY

DURBAN, SOUTH AFRICA
10-14 OCTOBER 2004

EDITED BY
Francois Wolfaardt and Marleen Kock

JOINTLY ORGANISED BY
Durban Institute of Technology
Sappi Forest Products