

## **Oxalic Acid Pretreatment for Mechanical Pulping Greatly Improves Paper Strength while Maintaining Scattering Power and Reducing Shives and Triglycerides**

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### **ABSTRACT**

In this paper we introduce a new technology based on a mild chemical pretreatment process prior to mechanical pulping. Chips are treated with a dilute solution of oxalic acid (OA) for only 10 minute at 130°C, in a typical example. The properties of the pulp produced by this OA process are quite different from those obtained via conventional chemical pretreatments, providing a much more valuable pulp, and at higher yields.

Refining results obtained at the Andritz Pilot Plant in Springfield, Ohio show an outstanding combination of strength improvements, energy savings, and shive and triglycerides reduction, with only a modest loss in brightness. Under suitable conditions the light scattering coefficient of the oxalic-treated treated chips was fully recovered without losing the above benefits. Maintaining light scattering coefficient with this treatment is of great interest, particularly to those mills producing lightweight coated paper (LWC).

Refining results are presented here, along with an evaluation of the process economics for a LWC example case. Based on strength improvements (kraft replacement in the final furnish) and energy savings, the production cost savings are substantial. For the LWC example, at least \$9 million/year net savings before license fees can be realized in an operation producing 372 t/d of OA mechanical pulp for 600 t/d of blended LWC furnish.

Based on this strong economic potential, several mechanical pulp mills have expressed interest in conducting in-mill evaluations. Planning for mill trials is currently underway.

### **INTRODUCTION**

Presently about 25% of the world's wood pulp is produced by mechanical pulping. This volume is expected to increase as raw materials become more difficult to obtain: With twice the yield of chemical pulping processes, mechanical pulping is a practical way to extend these resources.

Mechanical pulping is electrical energy-intensive (a mill producing 300-ton pulp per day spends about \$10 million in electricity cost per year) and yields paper with less strength compared to paper produced from chemical pulping processes. These disadvantages limit the use of mechanical pulps in many grades of paper. In many cases, chemical (kraft) pulp is blended with mechanical pulp to impart strength to the paper produced. However, chemical pulp is expensive and produces large amounts of both air and water pollutants in its processing.

The new OA process modifies the internal bonding in the wood fiber composite structure, producing chips that behave significantly differently during the subsequent refining operation of mechanical pulping. The resulting pulp has substantially better fiber properties, giving much higher strength while at the same time providing energy savings in the refining process.

#### **Development History**

The OA process had its origins with the biopulping research [1-2] conducted at the University of Wisconsin Biotechnology Center and the USDA Forest Service Forest Products Laboratory (FPL), Madison, WI. That research clearly demonstrated the removal of calcium from wood chip cell walls during two-week fungal pretreatment. Addition of calcium (up to 2000 ppm on a dry weight basis) to the wood chips at the time of fungal inoculation completely inhibited biopulping efficacy (Akhtar *et al.*, unpublished). Observed deposition of calcium oxalate on the surface and inside of the wood chips, and the lower pH of the fungus-treated chips, were suggestive that oxalic acid produced by the fungus could be involved in biopulping. Several follow-up experiments were conducted by Akhtar *et al.* wherein pretreatment of southern yellow pine chips with a dilute solution of oxalic acid prior to mechanical pulping resulted in substantial energy savings and fiber strength improvements.

Process development work was conducted in the University of Wisconsin Department of Chemical Engineering, in collaboration with BioPulping International (BPI), Madison, WI, and with the assistance of FPL. A PCT application

on the new technology was filed by the Wisconsin Alumni Research Foundation (WARF). Process development and optimization has continued to date, with process commercialization by OxaTech, Inc., a subsidiary of BPI.

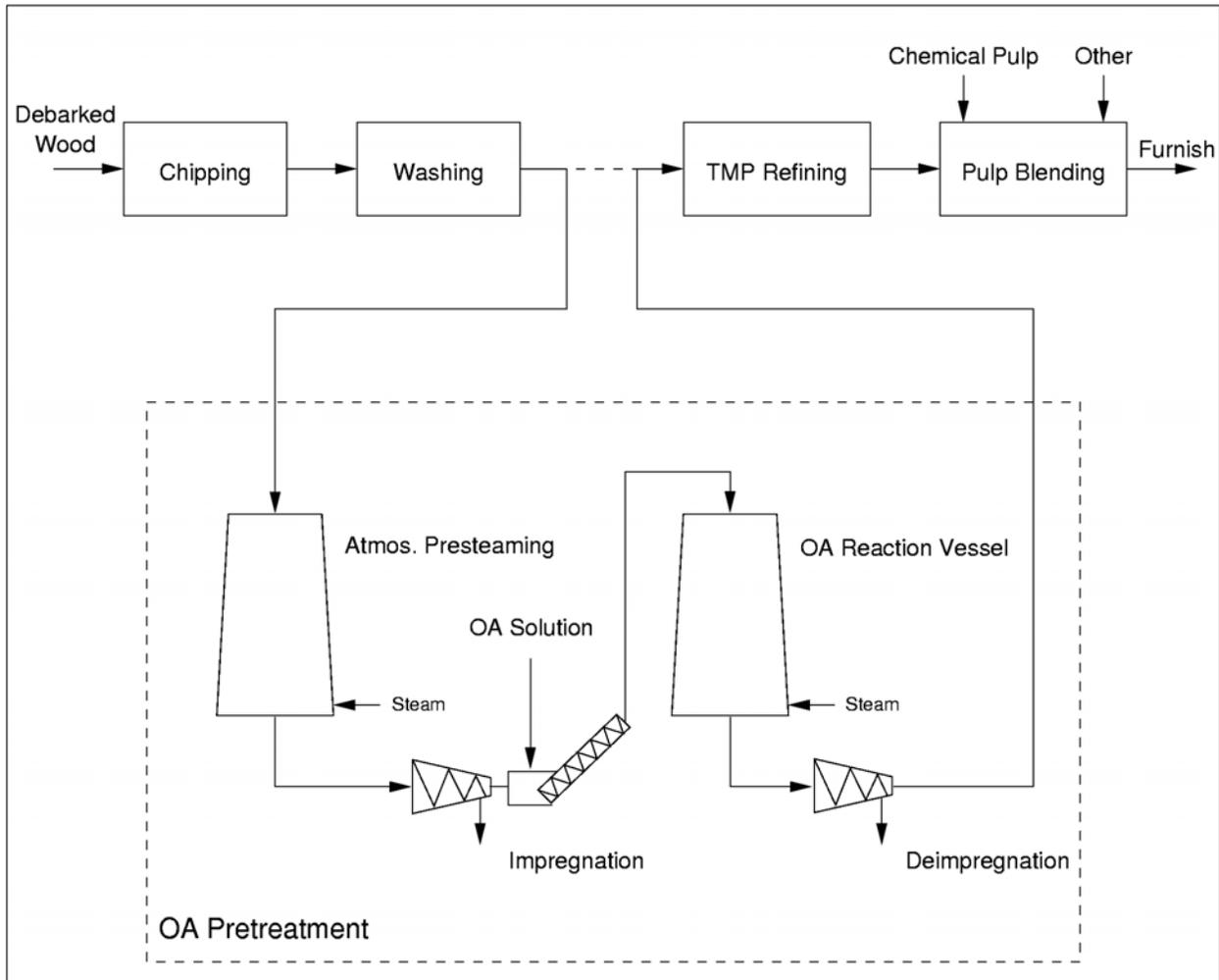


Figure 1. Representative OA process scheme and relationship to TMP line.

#### OA Process Overview

The OA process is incorporated into the mechanical pulping line in a manner similar to that of traditional chemical pretreatments. Figure 1 depicts the general components needed for the process and shows the relation to the existing components of a TMP line. Feed chips are intercepted after washing and screening. The process typically involves presteaming, impregnation, a reaction residence-time vessel, and deimpregnation. Yield loss is approximately 3–3.5% in the case of southern pine.

#### Results of TMP refining testing at Andritz

Southern yellow pine chips were treated with dilute OA solution for 10 minutes at 130°C. The treated chips were subsequently TMP-refined at Andritz to a series of freeness levels. Untreated chips from the same supply batch were refined analogously for comparison purposes. Energy requirements were determined and the pulp properties were analyzed. Table I presents the results for three-pass refining to 40 CSF.

Table I. TMP refining results at 40 freeness.

	Untreated	OA Process Treated
CSF (ml)	40	40
Refining energy (kW·h/t)	3,094	3,027
Tensile Index (N·m/g)	28.5	31.6
Tear Index (mN·m <sup>2</sup> /g)	6.2	7.8
Burst Index (kPa·m <sup>2</sup> /g)	1.49	1.91
Bulk (cm <sup>3</sup> /g)	2.64	2.58
Scattering Coefficient (m <sup>2</sup> /kg)	65.7	65.9
Brightness (% ISO, unbleached)	53.4	52.2
Shive Content (%)	0.40	0.18
Fines (% through 200 mesh)	41.6	37.3

All strength properties are improved substantially. Of particular note are the optical properties of the modified fibers. Scattering is retained, while brightness loss is only about one point, and absorption is also substantially retained. Energy savings are modest for this case, but higher savings might be obtained by modifying the refining conditions. Shive content is halved. Fines are reduced.

#### Pulp Blending – Kraft Replacement

Pulp samples from the above refining tests were blended with commercial unbleached kraft pulp. A 50%/50% blend of untreated mechanical and kraft pulps was prepared as a reference case, and a blend of 60% OA-treated mechanical with 40% kraft was examined in comparison. Handsheet tests for these are shown in Table II.

Strength, scattering, and opacity properties are retained or improved. These results are indicative of the level of kraft replacement that may be obtained in a LWC furnish. The kraft percentage of the furnish can be reduced by 12%, and kraft tonnage can be decreased by around 24%.

#### Pitch Reduction

Initial analyses conducted by Econotech Services, Ltd. with southern pine chips indicate that the most troublesome component of the pitch, the triglyceride content, is reduced by up to 40% as a result of the OA pretreatment. As the triglycerides may contribute to as much as 55% of the total pitch during the peak season, the pretreatment process should afford significant reduction in pitch control costs.

Table II. Handsheet properties of untreated and OA-treated TMP blends with kraft pulp.

	50% Untreated / 50% Kraft	60% OA-Treated / 40% Kraft
Tensile Index (N·m/g)	42.4	43.6
Tear Index (mN·m <sup>2</sup> /g)	9.77	10.07
Burst Index (kPa·m <sup>2</sup> /g)	2.68	2.71
Specific Volume (cm <sup>3</sup> /g)	1.63	1.72
Scattering Coefficient (m <sup>2</sup> /kg)	45.7	50.4
Opacity (%)	89.2	91.2
Brightness (% ISO, unbleached)	65.9	63.3

### Process Economics Example

The primary economic advantage of the OA pretreatment results from the greatly improved strength of the resulting mechanical pulp fibers. Substitution for expensive chemical pulp produces large savings. In addition to strength improvement, some refiner electrical power savings are achieved, and pitch control costs are reduced. These three savings sources are the only ones quantified in the analysis below. Additional benefits may be speculated, but have not been quantified yet. Possibilities include savings from the lower shive production, lower fines impact on the water loop, drainage/drying energy improvements, and improved uniformity of the pulp.

Offsetting expenses associated with the OA process include:

- Bleaching chemical consumption increment
- Oxalic acid supply cost.
- Wood yield loss (<3.5%)
- Steam increment and power for OA process operation
- Labor, maintenance, and overhead for the added process equipment

The following example shows the net effect of the above savings and expense factors. Consider the case of 600 t/d (metric) LWC production incorporating southern pine TMP as described in Table III. The base case furnish blends conventional mechanical pulp and kraft pulp at 300 t/d each. Using the OA process, 372 t/d of treated mechanical pulp may be used, reducing the kraft pulp use to 228 t/d.

Table III. Basis for 600 t/d LWC Example.

TMP:	300 t/d	Wood:	38.5 \$/t
Kraft:	300 t/d	Kraft:	605 \$/t
	Production:	350 d/y	
	Refiner power:	3,094 kW·h/t	
	Electricity cost:	0.04 \$/kW·h	
	TMP yield:	95 %	
	TMP / Kraft	50 / 50 %	

Table IV summarizes the relative production costs for conventional and OA-treated mechanical pulps. OA process operating costs include chemical supply, utilities, incremental water treatment, and labor and maintenance.

Table IV. TMP Pulp Manufacturing Costs (\$/t of TMP)

Cost	Conventional	OA-Treated
Energy:	124	121
Wood:	41	42
Bleach:	25	28
Peak Pitch Control:	3	-
Other Costs:	22	22
OA Treatment:	-	9
Total	215	222

Table V shows the total furnish production costs. The net savings amount to 42 \$/ton of furnish pulp, or about \$9 million/y for the example mill before payment of license fees.

Table V. Total Furnish Manufacturing Costs

Conventional				OA Process			
Pulp	t/d	\$/t	10 <sup>6</sup> \$/y	Pulp	t/d	\$/t	10 <sup>6</sup> \$/y
TMP	300	215	22.6	TMP	372	222	28.9
Kraft	300	605	63.5	Kraft	228	605	48.3
Total	600		86.1	Total	600		77.2

## CONCLUSIONS

The OA pretreatment process for TMP production offers the opportunity for substantial production cost savings in grades that use chemical pulps for reinforcement. The effects obtained with the process differ markedly from conventional chemical pretreatments. By providing a modified TMP with improved strength properties while retaining desirable optical properties, significant reduction in kraft pulp usage is possible. Pitch content is reduced.

### Acknowledgements

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