Obtaining value prior to pulping with diethyl oxalate and oxalic acid

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Pulp and paper are converted to paper products with yields of paper dependent on the wood and the process used. Even with high yield pulps there are conversion losses and with chemical pulps the yields approach 50%. The portions of the wood that do not provide product are either combusted to generate power and steam or incur a cost in waste water treatment. Value prior to pulping is an approach to pulping that tries to recover the carbohydrate components that do not enter the paper product before the pulping process has been started. We describe here an approach that releases hemicellulosic sugars from wood chips (both softwoods and hardwoods). Treatment of wood chips with oxalic acid solutions or diethyl oxalate in a vapor phase deposits oxalic acid within the wood chip where it will hydrolyze the hemicellulose. Solutions of these hydrolysates are readily fermented with *Saccharomyces cerevisiae, Pichia stipitis or Escherichia coli*. The treated wood chips are improved sources for pulp and paper production. The high yield thermomechanical pulps require 30-50% less electrical refiner energy and result in a stronger paper product. Chips treated prior to kraft pulping have similar yields of pulp, but decreased kappa values for the same cooking conditions. The pretreatments described hold promise for the generation of new products from existing manufacturing infrastructure while improving traditional processes.

INTRODUCTION

Pulping technology spans the range from high yield mechanical pulps to intermediate chemical pulps to low yield dissolving pulps. High yield pulps convert most of the wood to pulp but have significant electrical refiner energy costs and are of low strength. Chemical pulps are of higher strength, but typically have greater environmental costs and overall are more costly than mechanical pulps. Quite a range of products can be made from blends of various pulp types and these often rely on chemical pulps for part of the blend to impart greater strength to the product. Cost reduction in producing a pulp product can be brought about by making stronger mechanical pulps, or reducing the energy required for making the pulp.

Concurrent with the drive for cost reduction in pulping is an increased interest in biorefining. Here the desire is to convert the carbohydrate portions of the wood into fermentable sugars. We have been developing a wood chip pretreatment that can provide a spectrum of products from largely pulp to mostly fermentable carbohydrate. Most of the work performed thus far has been to pretreat wood chips prior to producing thermomechanical pulp. The process developed deposits oxalic acid in the wood chip where it will cleave 1hemicellulose into sugars that can be fermented to products like 2ethanol. The 3process also provides a reduction in the electrical refiner energy required to make TMP and results in a stronger TMP product.

MATERIALS AND METHODS

Treatment of wood chips, extraction of carbohydrates, determination of the wood sugars and TMP production and energy savings are all defined in the references. Kraft pulps were conducted on 130g (OD) samples of chips (control or treated) with 3 replicates. Pine cooked at 16%AA, 34%sulfidity, 60min-ramp 70min-cook 177°C, Eucalyptus and aspen cooked at 17%AA, 23%sulfidity, 90min-ramp 90min-cook 165°C. Kappa determinations were by TAPPI (T-236) titration yield numbers were by gravimetric methods. For pre kraft pine chips were treated with 40ml diethyloxalate (DEO)/kg chips at 140°C for 30 minutes. Eucalyptus and pine were treated at 24 ml and 20 ml DEO/kg chips at 140°C for 30 minutes. Oxalic acid (OA) treatments were at 130°C for 10 minutes with impregnation at 0.33% OA dihydrate.

RESULTS

Results from pretreatments for materials used for TMP can be found in the references. The results from kraft pulping studies are shown in Table 1A. For eucalyptus, aspen and pine kappa values and kraft cook yields were determined for multiple small bomb cooks.

The same cooking conditions were used for the all the samples from each species. Table 1 shows the cooking yields are about the same for treated chips as for control chips. The material being used for the cooks thus provides about the same amount of pulp. The kappa numbers were different which indicates the lignin remaining in the pulps is lower and since the yield is the same it probably indicates an increase in cellulosic content.

The content of the carbohydrates extracted from the chips prior to pulping is shown in Table 1B.

1A	Kappa Ave (std dev)	Kraft Yield %	Carbohydrate released (gram/kg wood)						
			1B	Arabinose	Galactose	Glucose	Xylose	Mannose	Total
Aspen	14.8 (0.2)	45.5							
Asp-DEO	11.1 (0.3)	45.2		2.4	1.9	1.7	20.7	1.3	28.9
Asp-OA	12.0 (0.2)	45.5		2.4	1.5	1.2	5.7	0.6	11.9
Eucalyptus	13.9 (0.3)	44.8							
Euc-DEO	10.6 (0.2)	44.5		1.4	2.4	1.4	23.5	1.2	30.7
Euc-OA	11.7 (0.2)	44.6		1.3	2.1	1.0	11.9	0.8	17.7
Pine	31.8 (0.4)	46.9							
Pine-DEO	29.5 (0.3)	47.8		8.5	10.2	10.0	17.8	28.4	75.4
Pine-OA	28.6 (0.2)	47.9		8.2	5.6	5.0	7.6	11.7	38.5

Table 1A. Kappa determination and yield for southern yellow pine, aspen and eucalyptus chips controls and pretreated with DEO or OA. Kappa determination the average of 3 replicates for each of 3 cooks. 1B. Carbohydrate released from treated chips. Represents identified free sugars after an analytical 4% sulfuric acid hydrolysis. Monosaccharide content before analytical hydrolysate is approximately 50% of the total released.

DISCUSSION

The data presented here along with that of the references provides evidence that high quality pulps can be made from wood chips that have been depleted in the hemicellulose content. The hemicellulose is obtained by the oxalic acid treatment as 50% monosaccharides with the remainder sugar derivatives. The hydrolysates have been concentrated by reverse osmosis and are suitable for fermentation.

[1]Kenealy, W., E. Horn, M. W. Davis, R. E. Swaney, and C. J. Houtman. 2007. Vapor phase diethyl oxalate pretreatment of wood chips: Part 2, release of hemicellulosic carbohydrates, *Holzforschung* in press.
[2]Kenealy, W., C. J. Houtman, J. Laplaza, T. W. Jeffries, and E. G. Horn. 2007, *in* Chemical Materials and Energy From Forest Biomass D. S. Argyropoulos, Ed. (Amercian Chemical Society).
[3]Kenealy, W., E. Horn, and C. J. Houtman. 2007 Vapor phase diethyl oxalate pretreatment of wood chips: Part 1, energy savings and improved pulps, *Holzforschung* in press.

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