

Vapor-phase diethyl oxalate pretreatment of wood chips: Part 1. Energy savings and improved pulps

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Abstract

Diethyl oxalate (DEO) was injected into a digester containing wood chips (pine, spruce, or aspen) preheated to 130–140°C and held for 30 min at the same temperature. When mechanical pulps were produced from these pretreated chips, savings in electrical refiner energy could be achieved. For southern yellow pine (*Pinus taeda*), the electrical refiner energy required to produce pulps with Canadian standard freeness (CSF) of 100 ml was 38–55% less than for an untreated control. Energy savings were also observed for aspen (*Populus* spp.) and spruce (*Picea* spp.). DEO-treated pine handsheets showed a 26% improvement in tear index compared with a control at 100 ml CSF. Under the pretreatment conditions described, DEO rapidly vaporizes, reacts with water already present in the chip, and forms an oxalic acid (OA) solution. Reported handsheet properties and energy savings for pine chips treated with a solution of OA are similar to DEO-treated handsheets. It can be concluded that the effect of DEO treatment is due to reactions catalyzed by OA.

Keywords: energy savings; ester; mechanical; oxalate; oxalic; refining; thermomechanical; vapor phase.

Introduction

The pulp and paper industry competes in a global marketplace, where energy and material costs determine profitability. For thermomechanical pulp (TMP) there is a need to reduce energy in the refiner and make stronger paper products (Meyer-Pinson et al. 2004). While strength can be improved by blending with more costly chemical pulps, increasing the intrinsic strength of TMP will result in lower production costs. Biopulping, the treatment of wood chips by white-rot fungi and subsequent chip refining, was envisioned as a method for saving energy and making a stronger paper product (Akhtar et al. 1998).

Recently, we identified a mechanism for biopulping (Hunt et al. 2004). White-rot fungi create or attach carboxylic acid groups (oxalate esters) on the carbohydrates in wood. Since oxalic acid (OA) is a dicarboxylic acid, attachment of one acid group in an ester bond leaves the second carboxylic acid group free. Attachment or creation of carboxylic acid groups increases the influx of water and swelling of wood, which results in energy savings during refining. Acid groups on fiber surfaces can also increase binding between fibers and improve the tensile and burst strength of paper products. The disadvantages of biopulping (2-week incubation time and pulp darkening) have limited its commercial deployment, but several effects of biopulping can be mimicked in the absence of organisms.

OA is excreted by wood-degrading fungi (Shimada et al. 1994; Dutton and Evans 1996), and is thought to lead to hemicellulose degradation and cellulose depolymerization (Green et al. 1991). Oxidative reactions by manganese peroxidase (produced by white-rot fungi) are enhanced by chelation of manganese ions by oxalate, providing greater solubility and oxidative action at a distance from the enzyme (Wariishi et al. 1992; Kuan and Tien 1993; Kishi et al. 1994; Sutherland et al. 1995; Timofeevski and Aust 1997; Zapanta and Tien 1997). Oxidative actions involving oxalate can produce free radicals (Khindaria et al. 1994), which might result in oxalate attachment.

Early studies in biopulping indicated that OA might be suitable for pretreatment of wood chips (Akhtar et al. 2002; Swaney et al. 2003). A process was developed in which pine wood chips were impregnated with a solution of OA, heated, and then refined into pulp (Akhtar et al. 2002; Swaney et al. 2003). This pretreatment saved significant energy in the mechanical refining process and provided stronger paper products than control-refined material. Similar treatments at lower temperatures have been reported for poplar (*Populus trichocarpa*) (Meyer-Pinson et al. 2004). There is also some evidence that OA can help to preserve fiber length, in addition to saving energy in mechanical refining (Vehniainen 2006). The successful design of an OA pretreatment of wood chips coupled with a new hypothesis for the biopulping energy savings indicates that the generation of fiber-attached oxalate esters or OA itself could provide benefits in energy savings and in improved paper products.

Esters can be created by reacting an acid with an alcohol (water is formed as a by-product). Transesterification (the process of exchanging the alkoxy group of an ester) is a way of changing esters (Ma and Hanna 1999; Kaieda et al. 2001; Watanabe et al. 2002; Sheih et al. 2003; Zhang et al. 2003). No fiber-attached oxalate esters were detected in our initial studies of OA-pretreated wood chips. This is not surprising because water is present in large amounts, which shifts the equilibrium towards

deesterification. In an effort to minimize the influence of water present, a new method was developed in which vapor-phase delivery of OA occurs via diethyl oxalate (DEO). This technique reduces the mass transport limitations normally encountered in the treatment of wood with liquid solutions and also promotes transesterification. The studies described here explore the application of DEO to reduce the energy requirement for TMP production and to improve the strength of the resulting paper.

Materials and methods

Commercial chips of southern yellow pine (*P. taeda*), aspen (*Populus* spp.) and spruce (*Picea* spp.) were provided by a paper mill. The chips were frozen soon after preparation and were kept frozen. Chips from different storage containers were mixed together prior to analysis of moisture content and processing. Logs of aspen (*Populus* spp.) and spruce (*Picea* spp.) donated by SENA, Biron Division, Wisconsin Rapids, Wisconsin, were debarked, chipped and screened for fines and then passed through a 22-mm screen. DEO and OA dihydrate were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA).

Treatment of wood chips

Wood chips (2.5 kg, oven-dry) were placed in a 21-l digester and steamed for approximately 10 min. The temperature within the digester was recorded using a HT100 probe (Dickson, Addison, IL, USA). The condensate drain was closed and the vessel brought to steam pressure of 210 kPa until the pressure was stable (5–10 min). A stainless steel pipe with valves at both ends was charged with DEO. From here DEO was injected into the digester using pressurized nitrogen or carbon dioxide. Following injection, the jacket pressure on the vessel was maintained at 240 kPa for 30 min. At the end of the incubation, the condensate port of the digester was opened, and the chips were removed, submersed in water and kept at 4°C for at least 40 h. Control chips were treated in an identical manner, except no chemical was injected. A dried sample of the wood chips was milled to 20 mesh (Wiley mill, Thomas Scientific, Swedesboro, NJ, USA) and analyzed for acetate and oxalate (Hunt et al. 2004). Pine chips were also subjected to the OA pulping pretreatment (Swaney et al. 2003) for analysis of the acetyl and oxalate contents of treated chips.

Drained chips were refined with one pass at 276 kPa using a laboratory pressurized refiner: a 30.5-cm single-disc Sprout-Bauer model #12-1CP, refining plate pattern D2B505, 3041 rev. min⁻¹ (Andritz, Inc., Sprout-Bauer Equipment, Muncy, PA, USA). This treatment was followed by further refining with an atmospheric refiner: a 30.5-cm single disc Sprout-Bauer model #D2202, refining plate pattern C-2976, at 12% consistency. The Canadian standard freeness (CSF) was measured according to Tappi standard (1999) T227 Om-99 after atmospheric refining. Energy consumption was recorded using a watt meter attached to the refiner motors.

Handsheets

Handsheets and measurements were made according to Tappi standard (1995) T205 Sp-95 and Tappi standard (1996a) T220 Sp 96. Burst, tear, and tensile strengths were determined according to Tappi standard (1997) T 403 Om-97, Tappi standard (1998) T 414 Om-98, and Tappi standard (1996b) T 494 Om-96, respectively. Brightness was measured according to Tappi standard (1992) T 525 Om-92.

NMR acquisition

The ¹³C (62.9 MHz) NMR spectra were recorded on a Bruker AVANCE DPX 250 spectrometer (Rheinstetten, Germany) equipped with a 5-mm z-gradient QNP probe at ambient temperature. The sample concentration was 0.5 g in 2.0 ml methanol spiked with d₆-acetone, and the chemical shifts are reported relative to d₆-acetone at 30.08 ppm. A total of 16,000 data points were collected over 250 ppm using Bruker's standard zgpg30 microprogram with a 3.0-s relaxation delay and Waltz-16 decoupling. Spectra were obtained after applying one zero-fill and 3.0-Hz line broadening prior to Fourier transformation. A time-course study was carried out with initial acquisition for 5 min and subsequent scans averaged over 1 h.

The ¹³C spectra of methanolic solutions of OA, methyl oxalate, and dimethyl oxalate exhibited the following chemical shifts: OA, 161.7 ppm; methyl oxalate, 160.2, 160.7 and 53.6 ppm; and dimethyl oxalate, 159.0 and 53.9 ppm. For quantitation, the carbonyl peaks near 160 ppm were integrated.

Results

Treatment of wood chips

After steaming, pine wood chips were exposed to four different treatments: two with 10 and 40 ml DEO kg⁻¹ chips, respectively, and two treatments served as controls; one without chemicals and one with an amount of ethanol equivalent to the ethanol produced by the highest level of DEO treatment (34 ml ethanol kg⁻¹ chips). Reaction temperatures were between 136°C and 142°C and the reaction time was 30 min.

Upon the introduction of DEO into the digester, a short temperature decrease for 2.5 min was recorded. Chips (5 kg) at 50% moisture contain approximately 2.5 kg of water. If all the DEO provided at 40 ml DEO kg⁻¹ chips were uniformly distributed in this amount of water, the concentration of DEO in water would be approximately 0.3 M DEO. After digestion there was no change in the texture or color of the chips taken from different parts of the digester (i.e., there was no stratification), although the DEO was added at the top of the vessel. A slight red color or darkening was observed for spruce and pine after draining the water-immersed chips treated at the highest level of DEO. Aspen chips were significantly darkened by the treatment. The wood chips increased by approximately 7% in weight during the steam treatment. Exposure to DEO did not result in any further weight increase.

Refiner energy

A representative set of refiner energy curves for pine is illustrated in Figure 1. Less energy was required for the primary, secondary and tertiary stages of treatment compared to controls. The energy requirements were dependent on the amount of DEO applied. Interpolation using least-squares fitting to power law functions allowed for estimation of the energy required to obtain pulp of 100 ml CSF for each sample. Figure 2 presents the average specific energy required to make pulp of 100 ml CSF for several DEO treatments and three different wood species. The energy required was considerably less for the DEO-treated materials. A set of pine controls treated with

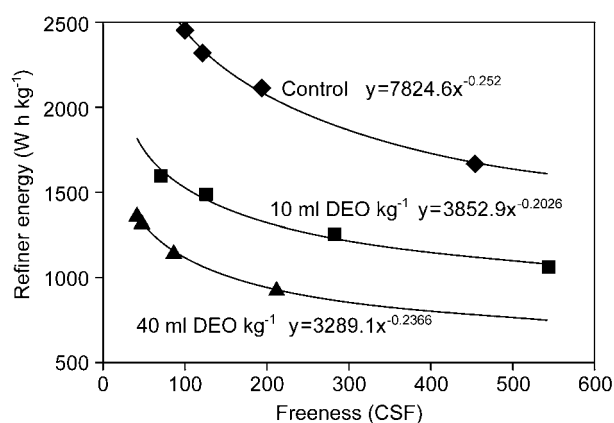


Figure 1 Refiner energy consumption for pine. Results for a representative experiment with pine chips treated with 10 and 40 ml DEO kg⁻¹ and a control. CSF, Canadian standard freeness.

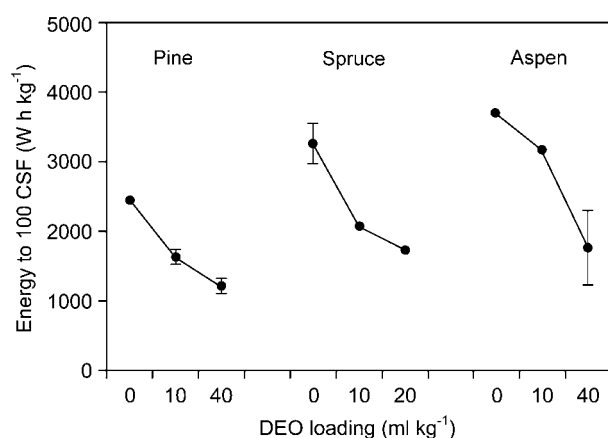


Figure 2 Specific energy required to reach 100 ml CSF for pine, spruce and aspen. The error bars indicate the range of the data.

ethanol resulted in energy demands of 2354 and 2427 W h kg⁻¹ to process pulps to 100 ml CSF. The average energy demand for the controls (without additives) was 2443 W h kg⁻¹.

Commercial spruce chips treated with 20 ml DEO kg⁻¹ at a maximum temperature of 131°C were refined in the same manner and required 1711 W h kg⁻¹ to obtain pulps with 100 ml CSF, compared to 3542 W h kg⁻¹ for the control (max. temp. 130°C). Commercial aspen chips treated with 40 ml DEO kg⁻¹ chips (max. temp. 137°C) also required less energy (2285 W h kg⁻¹) than the unheated control (3671 W h kg⁻¹). These experiments on spruce and aspen were repeated with chips from identified wood after it was observed that the commercial chips were not from a single genus and species. The refining results gave similar energies and the data were included in the averages in Figure 2.

Pulp handsheet properties

The tear indices of pine handsheets presented as a function of freeness (Figure 3) revealed substantial strength improvements for the treatments. Linear fitting resulted in the following data for 100 ml CSF: 2.40 mN m² g⁻¹ for the control, 3.09 mN m² g⁻¹ for 10 ml DEO kg⁻¹ chips, and

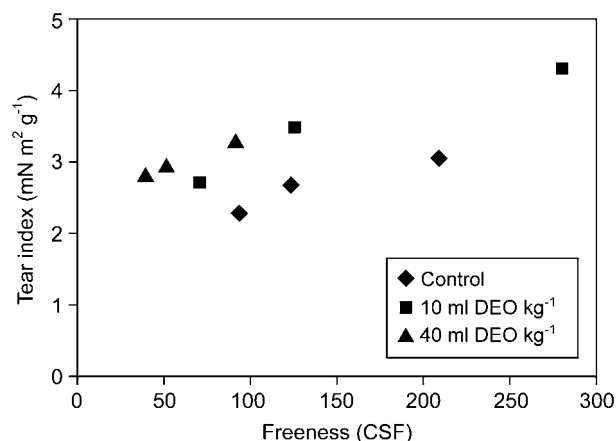


Figure 3 Pine handsheet tear index. Results are from a representative experiment and represent the average of 10 determinations. CSF, Canadian standard freeness.

3.37 mN m² g⁻¹, for 40 ml DEO kg⁻¹ chips. The tensile and burst indices are plotted as functions of handsheet density in Figure 4. The slope of a linear fit for 10 ml DEO kg⁻¹ chips is the lowest compared to 40 ml DEO kg⁻¹ chips and the control. The burst index values for treated chips were higher than for the control. In other experiments the tear, tensile, and burst indexes were comparable to or greater than the controls.

Handsheet properties relating to brightness, scattering, and printing opacity are listed in Table 1. The brightness of treated samples was greater than or equal to that of the control in these experiments. The opacity and scattering coefficients were generally greater than those of the control.

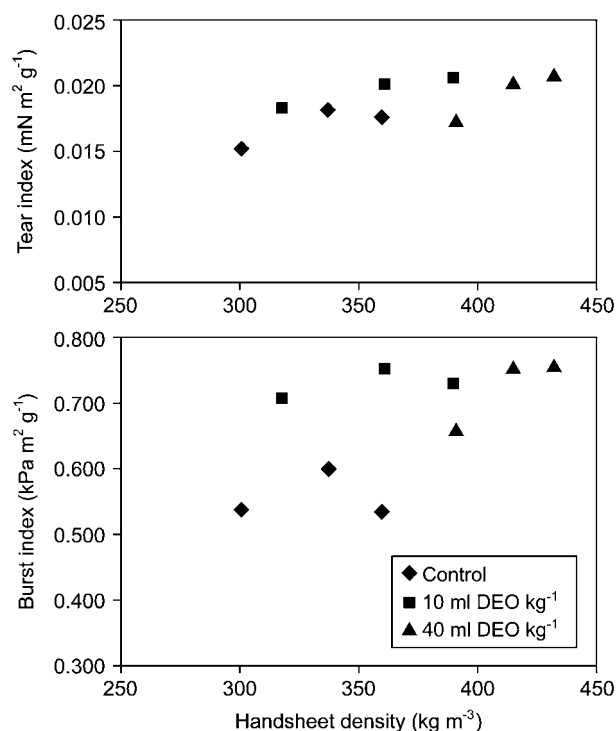


Figure 4 Pine handsheet burst and tensile indices. Results are from a representative experiment and represent the average of 10 determinations.

Table 1 Optical properties of pine handsheets.

Sample	CSF (ml)	ISO brightness (%)	Printing opacity (%)	Scattering coefficient (m ² kg ⁻¹)
Control	210	38.6 (0.1)	94.5 (0.2)	35.7 (0.6)
	124	39.7 (0.4)	96.5 (0.3)	40.0 (1.2)
	94	40.2 (1.3)	96.8 (0.2)	41.5 (1.8)
10 ml DEO kg ⁻¹ chips	281	37.8 (1.0)	96.6 (0.4)	36.3 (1.0)
	126	41.9 (0.7)	97.1 (0.1)	40.9 (0.9)
	71	43.7 (0.1)	97.8 (0.1)	46.1 (0.8)
40 ml DEO kg ⁻¹ chips	92	40.0 (0.3)	98.8 (0.1)	49.1 (0.9)
	52	40.7 (0.2)	99.1 (0.1)	53.3 (1.0)
	40	40.4 (0.2)	99.2 (0.1)	54.4 (1.3)

Brightness, printing opacity, and scattering coefficient are the mean of five determinations (standard deviation shown in parentheses). CSF, Canadian standard freeness.

Table 2 Oxalate and acetate contents of pine wood chips.

Sample	n	Content (μmol g ⁻¹)			
		Oxalate		Acetate	
		Acid	Alkali	Acid	Alkali
Oven-dried	3	1 (0)	2 (0)	38 (21)	427 (157)
Control (no DEO)	6	1 (1)	2 (0)	41 (18)	420 (108)
10 ml DEO kg ⁻¹ chips	6	25 (9)	14 (4)	43 (17)	409 (114)
40 ml DEO kg ⁻¹ chips	6	54 (13)	58 (18)	50 (19)	319 (83)

Data represent the mean (standard deviation) for experiments using different batches of wood chips.

Table 2 shows the acetyl and oxalyl content of treated and untreated pine. The chips were not washed beyond immersion in water, so residual oxalate originating from the treatment was present on the chips. The oxalyl content of the treated chips did not increase significantly when the oxalate was extracted by alkali, indicating that the oxalate was not bound as an ester. The acetyl content increased dramatically upon extraction with alkali, which indicates that the majority of the acetyl groups were bound as esters. The acetyl content of the 40 ml DEO kg⁻¹ chips was less than the content of the other samples, indicating a net loss of acetyl groups during the treatment. The oxalate content of pine chips treated by the method for OA pulping also had similar amounts of OA extracted by acid (41 μmol g⁻¹) and alkali (31 μmol g⁻¹); for acetate, 224 μmol g⁻¹ was extracted by alkali and 42 μmol g⁻¹ by acid.

Chemical studies to estimate diethyl oxalate reactivity

We modeled the esterification/deesterification reaction from the NMR results of seven experiments by minimizing a leastsquares error term with the Solver function of Microsoft Excel. These experiments included three temperatures (23°C, 33°C, and 43°C), three concentrations, and samples with and without sulfuric acid catalysis. Reactions were started with either mixtures of methanol-OA or dimethyl oxalate-water. A reaction model was designed with four bimolecular reactions: esterification of OA, esterification and deesterification of the monomethyl ester, and deesterification of dimethyl ester. Each reaction was assumed to be first-order in each reactant and first-order in hydrogen ion concentration. The hydrogen ion concentration was calculated by accounting for the

concentration of any strong acid added and deprotonation of the various species. A single set of activation energies, pre-exponential factors, and acid dissociation constants were estimated and are shown in Table 3.

The model fit was excellent over a wide range of reaction conditions, which indicates that the assumptions about the reaction mechanism (bimolecular and acid-catalyzed) appear to be correct. Solvent also appears to have an effect, because reactions in water solutions were approximately five-fold faster than reactions in methanol. This is likely explained by stabilization of the charge separation caused by the high dielectric constant of water. This reaction mechanism is also consistent with the conclusions from other esterification studies (Ronnback et al. 1997; Popken et al. 2000; Lilja et al. 2002).

Table 3 Model reaction rates and equilibrium constants for oxalic acid (OA) during esterification/deesterification.

Reaction	Activation energy (kJ mol ⁻¹)	Pre-exponential factor (l ² mol ⁻² h)
Esterification OA	42.6	3.89 × 10 ⁶
Deesterification of methyl oxalate	57.1	4.29 × 10 ⁸
Esterification of methyl oxalate	51.7	3.89 × 10 ⁷
Deesterification of dimethyl oxalate	71.4	1.71 × 10 ¹¹
Equilibrium constant (mol l ⁻¹)		
First proton of OA	4.57 × 10 ⁻³	
Second proton of OA	1.64 × 10 ⁻⁴	
Proton of methyl oxalate	3.78 × 10 ⁻⁵	
Ionization of water	1.00 × 10 ⁻¹²	

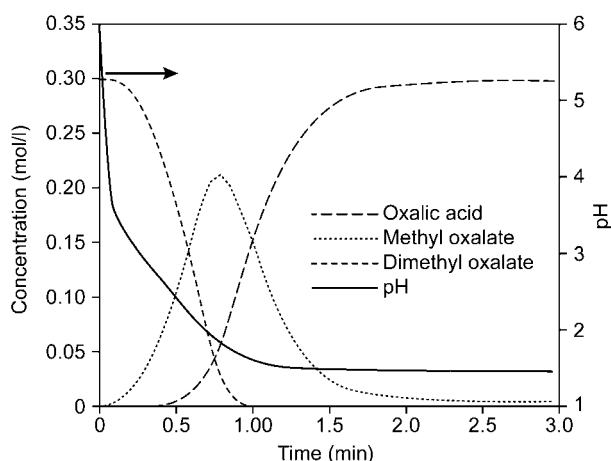


Figure 5 Predicted time course of dimethyl oxalate deesterification at 140°C in water. The predicted change in pH caused by the formation of acid groups as the reaction proceeds is also shown.

We suggest, based on the results of the kinetic study, that diethyl oxalate is rapidly deesterified. In water, the reaction equilibrium is shifted strongly toward OA. Figure 5 shows model predictions for a dimethyl oxalate concentration of 0.3 M in water and a temperature of 140°C. Inspection of this Figure reveals that the majority of dimethyl oxalate is converted to OA within 1.5 min. As deesterification proceeds, the pH of the solution rapidly decreases to 1.5, as illustrated in Figure 5. The rate of this reaction is strongly temperature-dependent. At 140°C, the estimated time to 90% diester conversion is 0.8 min. When the temperature is lowered to 100°C, the conversion time is 8 min, and at 70°C the conversion time is 56 min.

Discussion

The results clearly demonstrate that pine wood chips can be treated with DEO without harming TMP paper and significantly decreasing the energy demand for refining. The optimal DEO concentration for the highest energy savings and best handsheet strength has not been determined here. Increasing the amount of DEO appears to increase the energy savings when the pulp is produced. The temperature and duration of the reaction likely influence the strength and brightness properties of the resulting paper products. Evaluation of the commercial potential of this process will require further study.

OA-treated pine had increased tensile, burst, and tear indices that exceeded the control by 11%, 35%, and 26%, respectively (Swaney et al. 2003). The average increase in tear index (Figure 2) was 26% for both 10 and 40 ml DEO kg⁻¹ chips. Both the burst and tensile indices of the treated chips improved (Figure 3). This indicates that the improvement is likely due to reactions with OA at increased temperatures. The paper strength properties of poplar pulp obtained after OA treatment (at a much lower temperature, 25°C) showed a decrease in tensile index and an increase in tear index, although the differences were small (Meyer-Pinson et al. 2004). OA-treated pine (Swaney et al. 2003) showed significant energy sav-

ings for electrical refining comparable to those observed here. The ethanol-treated pine control included here resulted in no electrical energy savings, indicating that the action by DEO is likely due to OA deposited within the chips.

Pulps produced with lower energy demand and with increased strength properties have tremendous commercial advantages. Savings in refiner energy and reduced amounts for chemical pulps in blends leads to rapid recovery of the investment needed for process changes (Swaney et al. 2003).

DEO-treated aspen and spruce also showed high potential for energy savings. We detected that our commercial spruce chips contained fir (*Abies* spp.) and the aspen chips contained spruce (*Picea* spp.), while the pine chips used in our studies were not mixed with other species. The results for the aspen and spruce commercial chips were repeated with wood chips from defined single species. Similar savings for electrical refiner energy were observed. Increasing the treatment intensity for spruce (either the DEO concentration or the temperature) resulted in pulps with unsatisfactory quality (data not shown). A similar finding was observed for pine pulps produced under harsher conditions.

Under the conditions described here, DEO rapidly vaporizes at 140°C and then hydrolyzes upon water contact. The hydrolysis consumes water and leads to the monoethyl ester, acid and ethanol, then to OA and ethanol in the second hydrolysis. The kinetic model developed for the dimethyl ester of oxalate indicates that all the diester is converted rapidly to OA. Although ester hydrolysis is rapid (Figure 5), vaporization and diffusion of DEO might limit the deposition of OA in the wood chip. The temperature decrease observed after the introduction of DEO into the digester may reflect the volatilization and hydrolysis of DEO.

Hydrolysis of DEO results in rapid acidification of the water. This provides acidic conditions in which an ester could participate in transesterification reactions. However, no evidence of oxalate esterification or transesterification with the fiber was demonstrated. We explain this by a shift in equilibrium towards hydrolysis, as indicated above. Similar negative results have been obtained for oxalate esterification in the case of pine chips treated with OA.

The brightness and opacity of handsheets from DEO pine pulps were improved or at least reached the levels for controls. Accordingly, no additional bleaching would be necessary. Meyer-Pinson et al. (2004) reported that poplar treated with OA showed increased brightness and opacity. On the other hand, decreased brightness was reported for OA-treated pine (Swaney et al. 2003).

Hydrolysis of acetyl groups in fiber is known to occur in acidic treatments. The acid generated from the hydrolysis of acetate esters cleaves other esters and produces an autohydrolysate at higher temperatures. In both OA- and DEO-treated pine, the acetyl content of the residual wood chips was lower. Dilute acid treatment of wood chips cleaves hemicelluloses (Springer 1985). In the process described here, water degrades residual diethyl oxalate and the hemicelluloses are partly removed. Hemi-

cellulose analyses is described in the accompanying paper (Kenealy et al. 2007).

A loss in hemicelluloses might partly explain the decreased energy demand for refining. The loss of arabinose from wood followed by removal or destruction of other components of hemicelluloses has been correlated with wood strength (Green et al. 1991; Winandy and Lebow 2001).

The flash point of DEO is 75°C, which is higher than for many industrial solvents. Precautions were taken to avoid the presence of air (oxygen) in the reactor. This was achieved by steaming prior to DEO introduction. This treatment had the additional advantage of increasing the temperature of the chips. Moreover, the DEO was introduced with nitrogen or carbon dioxide gas to minimize exposure to air. The toxicity of DEO is comparable to that of OA and it should not be ingested or inhaled. The digester contents were quenched with water at the end of the treatment as a precaution to hydrolyze any remaining DEO to OA and ethanol. The model for deesterification indicates that the diester would have completely reacted long before 30 min.

Conclusions

DEO treatment of wood chips prior to TMP significantly reduces the energy demand and does not affect adversely the paper product. In fact, with an optimized level of treatment, handsheet strength and brightness are increased. OA is the active agent in bringing about these effects. There are advantages in DEO treatment compared to dilute acid, since the process has fewer steps (no impregnation and draining steps are necessary) and does not require heating of excess water. A disadvantage is that DEO is more expensive than OA.

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