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Vapor-phase diethyl oxalate pretreatment of wood chips: Part 2. Release of hemicellulosic carbohydrates

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Abstract

Wood chips of pine, spruce, aspen, and maple were treated at 135–140°C with diethyl oxalate (DEO) and analyzed for extractable and residual carbohydrates. Under these conditions, DEO hydrolyzes to ethanol and oxalic acid (OA). The amount and identity of carbohydrates released from the chips were species-dependent. For all wood species, increasing the amount of chemical, time, or temperature resulted in an increment in carbohydrates released. Approximately 50% (by wt) of extracted carbohydrates were monosaccharides. In addition, acetic acid was detected in the water extracts. When extracts were subsequently alkaline-treated, more acetate was released, indicating the presence of acetyl esters. The composition of water extracts and of wood chips after treatment indicates that these treatments primarily affect hemicelluloses. In summary, treatment of wood chips with DEO or OA releases carbohydrates suitable for fermentation, with no evidence of cellulose degradation.

Keywords: biorefining; ester; hardwood; hemicelluloses; oxalic acid; oxalate; softwood.

Introduction

With the shortage of fossil energy resources, the interest in converting biomass to fuels and chemicals is increasing (Ragauskas et al. 2006a,b). The process of converting biomass to simple chemical compounds is called biorefining (Kamm and Kamm 2004). One biorefining variant is "value prior to pulping" (VPP) (Thorp and Raymond 2004), which involves the separation of non-cellulosic carbohydrates from wood chips before traditional chemical or mechanical pulping (Raymond and Closset 2004). VPP is distinguished from attempts to recover carbohydrates from pulping black liquor in that carbohydrates are less degraded and separation is less difficult. VPP optimization requires a balance between potential yield loss, paper property changes and capital investments and any increased revenue from marketing a by-product. Implementation of this process could also increase the price of fiber for other purposes (Kenny 2006).

Many processes have been proposed for extracting carbohydrates from wood (Kenealy et al. 2006). Dilute acid pretreatments with sulfuric acid or sulfur dioxide have produced fermentable carbohydrates and pulp (Richter 1956; Clark and Mackie 1987; Boussaid et al. 2000; Soderstrom et al. 2003; Mosier et al. 2005). It has been reported that hot water extraction, or autohydrolysis, is useful in generating a soluble carbohydrate extract. However, the effects on paper products have not been reported (Thorp and Raymond 2004).

Oxalic acid (OA), a strong dicarboxylic acid with pK_a values of 1.23 and 4.19, has potential for VPP (Akhtar et al. 2002; Meyer-Pinson et al. 2004; Kenealy et al. 2006; Vehniainen 2006). OA can degrade hemicelluloses (Green et al. 1991) and can also damage cellulose over prolonged periods of time (Green et al. 1992). OA can liberate xylose from oak (*Quercus* spp.) or beech (*Fagus* spp.) wood shavings in reasonable yields, allowing purification of the xylose from the extraction liquor (Steiner and Lindlar 1971). OA or its derivatives may be useful in VPP provided that conditions can be optimized so that there is little damage to the paper product.

We have developed processes to treat wood chips with diethyl oxalate (DEO) (Kenealy et al. 2007) or OA (Swaney et al. 2003) at elevated temperatures. With water and heat, DEO is hydrolyzed to ethanol and OA. In the case of DEO as reactant, OA is delivered with minimal water. TMP-type products made from OA- or DEO-treated wood are as strong as controls (Akhtar et al. 2002; Swaney et al. 2003; Kenealy et al. 2006, 2007).

The present study examined aqueous extraction of carbohydrates after DEO treatment of softwood (southern yellow pine and spruce) and hardwood (aspen and maple) chips. By characterization of the composition of the extracts, we assessed the potential of these pretreatments for production of fermentable carbohydrate resources.

Materials and methods

Southern yellow pine (*Pinus taeda*) chips were provided by a commercial mill. The chips were frozen until needed for treatments. Logs of aspen (*Populus* spp.) and spruce (*Picea* spp.) were donated by SENA, Biron Division, Wisconsin Rapids, WI. Maple (soft maple, *Acer saccharinum*) logs were provided by Weyerhaeuser, Rothschild, WI. The logs were debarked by hand, chipped (19 mm), and screened to remove pieces >38 mm and <6 mm. Only chips that passed through a 22-mm screen were investigated. Chips were placed in plastic bags and stored frozen. DEO and OA dihydrate were purchased from Sigma-Aldrich Chemical Company (St. Louis, MO, USA).

Treatment of wood chips

The reactor configuration has been described previously (Kenealy et al. 2007). Wood chips were treated with 10–40 ml DEO kg^{-1} wood, followed by extraction with water. In addition, chips were processed without added chemicals as controls. Pine chips were treated with 3 g l^{-1} OA (10 min, 130°C) as a positive control (Swaney et al. 2003). Pine chips were also processed with 34 ml ethanol kg^{-1} wood as a control, because hydrolysis of one DEO molecule will give two ethanol molecules. The aqueous-extracted wood chips were sampled, freeze-dried and milled for analysis.

Chemical analyses

Extraction and analysis of acetate (by GC) and oxalate (by HPLC) from milled wood samples were performed according to Hunt et al. (2004). Accurate determination of acetic acid remaining in treated wood chips was not possible because the chips had to be dried prior to milling. Acetyl esters in aqueous extracts were converted to sodium acetate by mixing samples with 0.1 M NaOH, followed by incubation for 1 h at 65°C. Samples were centrifuged in a microcentrifuge tube at 21,000×*g* for 10 min at room temperature, and the supernatants were acidified with 0.25% H_2SO_4. Acidified supernatants were centrifuged and the resulting supernatant was filtered prior to analysis. All HLPC/GC samples were filtered through a 2-ml Whatman (Clifton, NJ, USA) 0.45-μm UNIFILTER® hydrophilic PVDF microplate into a GC/HPLC sample vial (Kenealy and Destree 2005).

The carbohydrate and Klason lignin compositions of wood samples were determined following a two-step acid hydrolysis procedure (Davis 1998). Klason lignin contents were determined by filtration and gravimetric measurement of the residues. Carbohydrate contents were determined by high-performance anion exchange chromatography using pulsed amperometric detection (HPAEC/PAD) (Davis 1998). The HPAEC/PAD system consisted of an AS50 autosampler, a GS50 quaternary-gradient high-pressure pump, and an ED50 pulsed amperometric detector (Dionex Corporation, Sunnyvale, CA, USA). Fucose was used as an internal standard in all cases. Following column conditioning with 0.30 M $NaC_2O_2H_3$ and 0.40 M NaOH, carbohydrates were separated on Carbo-Pac PA1 guard and analytical columns (Dionex) by elution with water at 1.10 ml min^{-1}. Carbohydrates in hydrolyzed wood samples were determined by injection of 10 μl of wood hydrolyzate in 1.25% H_2SO_4 and separated at 18°C. Monosaccharides in wood extracts were determined by injection of 25 μl of extract and separated at 25°C. The total carbohydrate content of extracts (monosaccharides, polysaccharides, and any carbohydrate derivatives with acid-labile moieties) was determined following hydrolysis in 4% (w/w) H_2SO_4 for 1 h at 120°C. In this case, 25 μl of extract hydrolyzates in 4.0% H_2SO_4 was injected and separated at 18°C.

Analysis of time and temperature data

The digester was not equipped to maintain a constant temperature, and estimation of the temperature from the steam pressure was not possible after the DEO was injected. The temperature within the digester was recorded using a HT100 probe (Dickson, Addison, IL, USA). Pine treatments with 40 ml DEO kg^{-1} wood were conducted for different times and temperatures to generate a range of time-temperature integral values. To compare different temperature and time treatments, an integrated rate expression approach was taken. The method is similar to the H-factor calculation used for controlling kraft pulping processes (Vroom 1957). An Arrhenius rate expression, with activation energy of 96 kJ mol^{-1} and pre-exponential factor of 2.54×10^{13}, was integrated with respect to time. The values of the constants in this rate expression were chosen so that the integral value provided the best least-squares match to total carbohydrate removal for five pine control samples.

We chose the time-temperature integral method over the *P* factor (Overend and Chornet 1987), based on previous work (Brasch and Free 1965). The authors used the equation $P=t\exp(T-100)/B$, where *t* is time (min), *T* is temperature (°C), and *B* is a constant with a value of 14.75. The best least-squares fit to the data in this study was $B=14.45$. While the *P* factor method could be used to compare treatment conditions, our time-temperature integral method provides corrections that are more easily related to a reaction rate model.

Results and discussion

Carbohydrates from wood

Amounts of carbohydrates released from pine, spruce, aspen, and maple chips following treatment with increasing quantities of DEO are listed in Table 1. In control samples that experienced only heat (0 ml DEO), the major carbohydrates released were arabinose (pine), arabinose and galactose (spruce), xylose (aspen), and glucose (maple). Treatment of pine chips with ethanol gave similar results to heat treatment (arabinose 3.8 ± 1.0 g kg^{-1} wood, galactose 1.0 ± 0.2 g kg^{-1} wood, glucose 1.1 ± 0.2 g kg^{-1} wood, xylose 0.5 ± 0.2 g kg^{-1} wood, and mannose 0.8 ± 0.3 g kg^{-1} wood; $n=2$). As the amount of DEO was increased, a general trend for increased carbohydrate release was observed. Sugars released from the softwoods increased rapidly with increasing DEO, but leveled off at the highest DEO concentration. Xylose was the predominant sugar released from hardwoods; it continued to increase with DEO up to the highest level tested (40 ml kg^{-1}).

Amounts of monosaccharides and oligosaccharides removed by aqueous extraction are illustrated in Figure 1. Results of OA treatment of pine are also shown for comparative purposes. The profile and amounts of total carbohydrates released from pine and spruce are quite similar. Mannose was the predominant carbohydrate released. The amount of glucose released was 30% of that of mannose. Although arabinose and galactose are minor components in wood, representing less than 4% of the wood mass in the species tested, they comprise a significant proportion of the carbohydrates extracted in this study. Total carbohydrates extracted (corrected for water of hydrolysis) following DEO treatment represented 6.6%, 5.7%, 5.8%, and 4.4% (wt/wt) of the pine, spruce, aspen, and maple chips, respectively.

Total carbohydrate released following OA treatment of pine was less than half of that released by DEO treatment. However, the carbohydrate profile, including the mannose/glucose ratio, was similar. For OA treatment, more carbohydrate (7% of that in the extract) was found in the condensate collected from heating. Negligible carbohydrates were present in the drained impregnation solution. The OA concentration measured in the OA extracts was $<30\%$ of the concentration measured in the pine-DEO treatment shown in Figure 1.

Figure 1 illustrates the proportion of monosaccharide extracted. The anhydroarabinose in hemicelluloses was released from all of the treated woods mostly as (mono-

Table 1 Aqueous extracts of DEO-treated wood chips.

Wood species	DEO (ml kg^{-1} wood)	Content (g kg^{-1} dry wood)				
		Arabinose	Galactose	Glucose	Xylose	Mannose
Pine	0	3.7±0.2	1.3±0.3	0.7±0.1	0.4±0.0	0.9±0.1
	10	8.0±1.5	4.6±1.1	3.3±1.6	5.8±3.0	10.2±5.7
	20	10.2±1.4	8.3±1.9	6.6±3.7	12.5±7.0	22.4±14.3
	30	10.3±1.1	8.0±1.2	5.4±2.3	10.1±3.8	16.7±8.2
	40	11.3±0.7	10.9±0.7	8.3±1.8	15.7±2.9	27.9±7.1
Spruce	0	2.3±0.3	2.6±0.8	1.2±0.1	0.1±0.0	0.8±0.1
	10	6.8±0.2	4.7±0.6	2.9±0.6	2.5±0.3	6.4±0.9
	20	9.5±1.1	7.3±0.6	5.2±0.3	6.1±0.0	15.7±1.8
	30	11.4±1.7	10.2±0.8	7.8±0.0	10.6±0.9	26.2±0.9
	40	11.5±1.3	10.1±1.0	7.8±0.3	10.4±0.9	24.9±0.5
Aspen	0	1.7±1.6	1.3±0.2	2.5±0.4	3.0±2.0	1.8±2.0
	10	1.0±0.5	1.0±0.9	1.3±1.4	4.4±1.0	0.5±0.2
	20	2.4±0.8	2.1±0.1	2.4±0.4	20.2±14.6	1.5±1.1
	30	2.7±0.0	2.8±0.3	3.1±0.2	18.8±4.5	1.0±0.0
	40	3.4±0.2	3.6±0.6	4.1±1.1	52.4±15.2	2.8±0.4
Maple	0	0.6±0.1	0.8±0.1	5.9±0.6	0.1±0.0	1.1±0.2
	10	3.0±0.4	1.3±0.1	8.0±0.5	5.2±2.0	1.4±0.0
	20	4.5±2.1	1.8±0.4	9.8±0.5	12.7±8.6	1.9±0.1
	30	5.7±0.8	2.3±0.1	10.6±1.4	21.9±6.6	2.8±0.3
	40	6.4±0.8	2.6±0.0	11.2±1.3	27.1±4.0	2.7±0.2

Data represent the mean±SD for two determinations of aqueous extracts after secondary hydrolysis, except for pine treated with 0 ml DEO kg^{-1} wood (n=4) and pine treated with 10, 30 and 40 ml DEO kg^{-1} wood and aspen treated with 40 ml DEO kg^{-1} wood (n=3). All chips were heated at 135–140°C for 30 min after injection of DEO (or nitrogen for the controls) into the vessel.

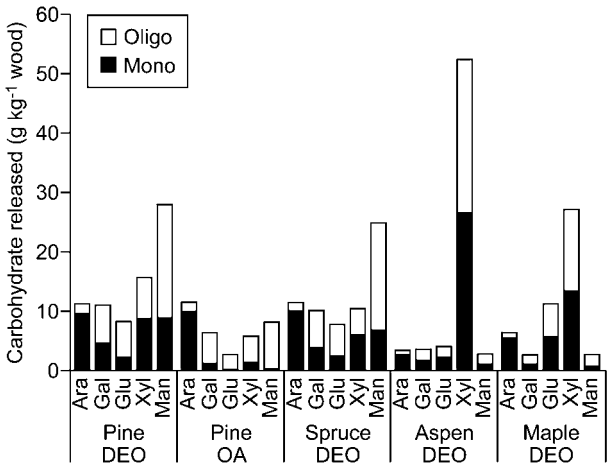

Figure 1 Major wood carbohydrates released from pine, spruce, aspen, and maple wood chips treated with 40 ml DEO kg^{-1} wood and by the oxalate pulping method for pine (OA). Data represent the mean monosaccharide and oligosaccharide contents of aqueous extracts. The number of determinations are the same as given in Table 1 for DEO treatments and n=6 for the OA process.

meric) arabinose. This finding is related to the fact that arabinose is generally part of terminal carbohydrate residues on hemicelluloses (Timell 1965). Xylan appeared in the hydrolyzate as up to 50% xylose. The data for all DEO treatments are summarized in Table 2. A slight trend for increasing monosaccharide with increasing DEO was observed (data not shown). Because the reaction was less intense, extracts from OA-treated pine chips had lower monosaccharide contents.

The composition and extent to which the carbohydrates in extracts are monomeric is important from the perspective of fermentation. Monosaccharides are readily fermented. Carbohydrates released by DEO treatment are approximately 50 wt.% monosaccharides suited to fermentation without additional treatment. However, additional treatment to hydrolyze oligo- and polysaccharides or developing fermentative organisms that can metabolize such larger fragments would be required for complete fermentation. More experiments are needed to determine whether increasing the intensity of DEO treatment could elevate the yields of monomers.

Lignin and glucan contents of pine, spruce, aspen and maple chips were increased by treatment and extraction (Figure 2). In general, mannan and xylan contents

Table 2 Percentage carbohydrate as monosaccharide in aqueous extracts.

Wood species	Proportion as monosaccharide (%)				
	Arabinose	Galactose	Glucose	Xylose	Mannose
Pine	87±8	42±12	26±11	57±13	31±12
Spruce	84±7	32±8	30±3	54±4	22±4
Aspen	65±15	36±15	53±7	47±6	27±15
Maple	75±12	34±11	51±2	49±3	19±12

Data represent the mean±SD of the percentage monosaccharide for all the DEO treatment conditions (n≥8).

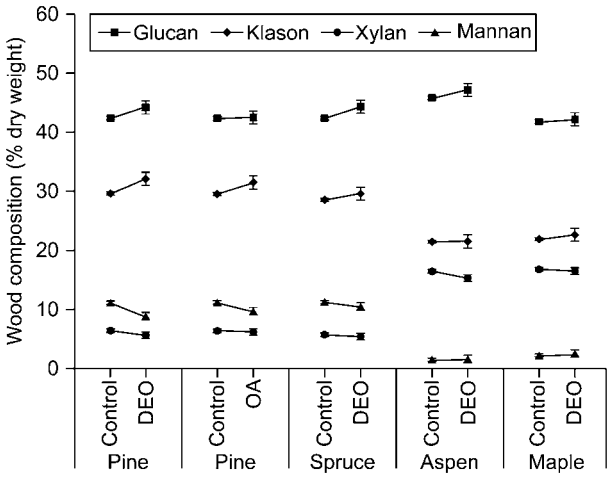

Figure 2 Composition of wood chip components before and after treatment and extraction. Control indicates the mean composition of freeze-dried and oven-dried untreated chips; DEO represents the mean composition of the chips treated with 40 ml DEO kg^{-1} wood; and OA represents the mean composition of OA-treated pine chips. Error bars represent pooled standard deviations. Since the controls appeared to exhibit different variance from the treatments, one pool was over the controls and one over the treatments.

decreased upon treatment, although the low levels of mannan in the hardwoods were not significantly reduced. Arabinan and galactan contents were even more substantially depleted (data not shown). Similar changes were observed for OA treatment of pine. The total composition identified for all samples in Figure 1 averaged 88% of the dry weight. The composition of ethanol-treated pine control samples was most similar to other control samples (n = 2), with 29.6 ± 0.1% lignin, 41.3 ± 0.4% glucan, 7.0 ± 0.2% xylan, and 10.6 ± 0.3% mannan. Comparison of the results for ethanol-treated pine with those for the DEO and OA treatments indicates that hydrolysis is due to OA and not to ethanol.

Based on the composition of the carbohydrates liberated, the hydrolysis is highly specific for hemicelluloses. The ratio of glucose/galactose/mannose liberated from DEO-treated chips (40 ml kg^{-1} treatment) was 1.0:1.4:3.2 for pine and 1.0:1.4:2.9 for spruce. Analysis of these ratios implies that the glucose component is predominantly derived from galactoglucomannan (Jacobs and Dahlman 2001). Small amounts of arabinose and xylose are likely the result of hydrolysis of arabinoglucuronoxylan.

The predominant carbohydrate released from aspen was xylose. In addition, the amount of acetate liberated was two-fold greater than that observed for pine or spruce. The amount of glucose released can be attributed to the glucuronoxylan typical of hardwoods (Jacobs and Dahlman 2001). There is no evidence of cellulose degradation. The glucose released from maple was greater than that predicted by composition of its typical glucuronoxylan. However, this is attributable to the presence of significant amounts of "free" sucrose in this wood. Sucrose is rapidly and quantitatively hydrolyzed to glucose and fructose under the test conditions employed. With the exception of maple, the average glucose content in the extracts was approximately 10–12% of the carbohydrates identified.

In summary, cellulose does not appear to be a major contributor to the glucose released because: (1) the sugar composition of extracts is consistent with the composition of hemicelluloses; (2) the glucan content of treated chips increases with treatment intensity; and (3) TMP strength remains the same or increases with treatment (Kenealy et al. 2007).

Analysis of acid content of extracts

There was a trend for increasing total acetate present in extracts with increasing DEO (Figure 3). This trend was more pronounced for hardwood species. Acetate content increased after treatment with alkali. Accordingly, acetyl esters were also present in the aqueous extracts, although most of the acetate was present as acetic acid. Untreated wood chips contained 13, 19, 42 and 51 g acetate kg^{-1} wood for pine, spruce, aspen and maple, which accounts for 38%, 23%, 27%, and 16% of the initial amount of acetate present in the woods, respectively.

As expected, the amount of OA recovered was dependent on the amount of DEO applied (data not shown). OA measurement results are similar for acid- and alkaline-treated wood sample measurements, indicating that no oxalate esters were formed during the DEO treatment and that no unhydrolyzed DEO remained in the extracts. Regardless of the amount of DEO applied, 72% of the OA equivalents were recovered.

Extended treatments

The release of carbohydrates and acetate from DEO-treated pine is presented as a function of the time-temperature integral in Figure 4. More intense treatments, involving either a longer time or elevated temperature, lead to higher values of the time-temperature integral. This value represents the amount of total carbohydrate

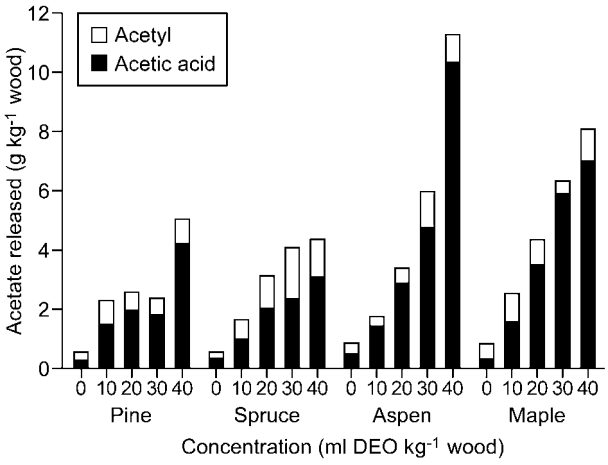

Figure 3 Total acetate extracted from wood. Data represent the mean for the indicated levels of DEO used (ml kg^{-1} chips) for the wood species. The lower portion of the bars represents the yield determined by direct analysis of the extract. The upper portion of the bars show the increase in detectable acetate after saponification.

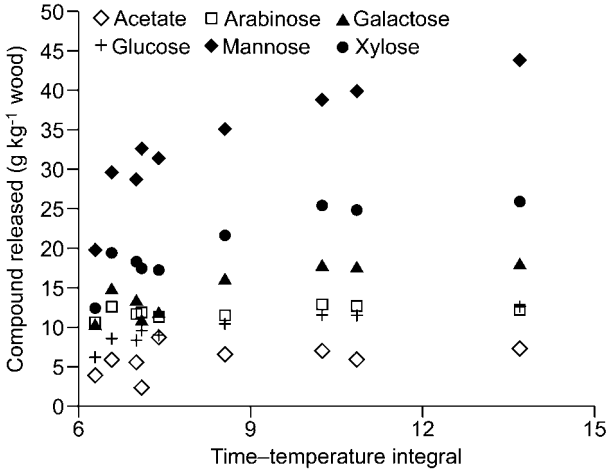

Figure 4 Release of pine wood components with increasing temperature-time integral. Data are from nine experiments using 40 ml DEO kg^{-1} wood.

(gm kg^{-1} wood) that would be expected from treatments of pine by temperature alone and without chemical. In general, all components tend to increase with the integral, indicating that the time-temperature integral may provide a useful estimate of the treatment intensity.

In pine, the intensity of DEO treatments that bring about substantial arabinose release also provides refiner energy savings and increased handsheet strength properties (Kenealy et al. 2007). The correlation of arabinose liberation with refiner energy savings is consistent with the findings of Winandy and Lebow (2001), who reported a loss of wood strength when arabinose content decreases.

Process advantages

The DEO process described here needs only water within the chips as solvent. Thus, even small amounts of DEO are enough to generate concentrations of OA able to hydrolyze hemicelluloses within chips. In addition, the low amount of water does not dilute the acetic acid produced by hydrolysis of the acetyl groups on hemicelluloses. DEO treatment is similar to the treatment of chips with sulfur dioxide (Richter 1956; Clark and Mackie 1987; Boussaid et al. 2000, 2001; Soderstrom et al. 2003; Mosier et al. 2005). Sulfur dioxide can be supplied as a gas, which forms sulfurous acid within the wood chips. In contrast, direct application of acid solutions requires excess water, resulting in a less efficient process and dilution of the acetic acid liberated.

All of the equipment required is similar to that currently used in paper mills. Process improvements such as hot extraction, countercurrent design and intensity optimization should enhance the extraction of hemicelluloses and would provide chips ready for pulping. Furthermore, pre-fermentation treatments such as enzymatic hydrolysis could also increase the yield of monomers. Finally, acetic acid can potentially be separated and recovered from the sugars (Eriksson 1997; Kates 2005). This separation would both remove a potential inhibitor of fermentation and provide an additional product stream. The DEO process described here promises to make a positive contribution to the overall economics of TMP paper production.

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