Reducing troublesome pitch in pulp mills by lipolytic enzymes

Kurt Fischer and Kurt Messner

Institut für Biochemische Technologie, Abteilung für Mykologie, Technische Universität Wien, Getreidemarkt 9, A-1060 Vienna, Austria

ABSTRACT *Unbleached sulfite pulp was treated with enzyme to reduce the content of chlorinated triglycerides, which are reported to be the cause of pitch deposits formed during paper manufacturing. The enzyme hydrolyzed 86% of the triglycerides within 2 h, and the liberated fatty acids in the pitch were extracted with a sodium hydroxide solution. Pitch fractions with and without triglycerides and free fatty acids were chlorinated with chlorine water to simulate chlorination during the bleaching process.*

Chlorinated pitch without triglycerides and free fatty acids was less adhesive than pitch containing free fatty acids or pitch that was not treated with enzyme. The results demonstrate that (a) triglycerides content in pulp is a major contributor to pitch adhesiveness and (b) enzyme treatment followed by sodium hydroxide extraction reduces pitch adhesiveness and may be used to decrease pitch deposits formed during paper manufacturing.

KEYWORDS
Chlorine compounds
Enzymes
Fatty acids
Paper machines
Pitch
Pitch control
Pulp mills

Pitch deposited on exposed parts of the paper machine, such as on the machine wire or on the air foils, can degrade product quality and can impair the production process. Any treatment that reduces the amount of pitch formation could lead to savings in downtime and production costs.

In untreated wood, pitch is located in parenchyma cells and on the surfaces of the fibers (*1*). The composition of pitch determines the amount of deposits, and the composition varies depending on the season and the type of wood. Thus, pitch problems only appear during certain months of winter and spring, and some sorts of wood are better suited than others for pulp manufacturing. High pitch content renders some types of wood unusable for pulp manufacturing.

The presence of triglycerides appears to account for the differences in pitch deposit formation in the use of different types of wood. Deposit-forming pitch always contains much higher concentrations of triglycerides than pitch that forms no deposits (*2*).

The formation of pitch deposits begins during the bleaching process with chlorine, in which the double bonds of the pitch triglycerides are chlorinated (*3*). The chlorinated pitch is then released from the fibers, and it accumulates in the water used for paper manufacturing. Through a largely unknown mechanism, these chlorinated triglycerides form pitch deposits.

Until now, no successful method has been developed to remove these sticky chlorinated triglycerides from the pitch, although the addition of emulsifying agents such as talc has yielded some success (*4*). Therefore, we have assessed a method of triglyceride removal on the laboratory scale that utilizes the hydrolysis of the triglycerides by lipases and the removal of the liberated fatty acids with sodium hydroxide solution.

Experimental procedure

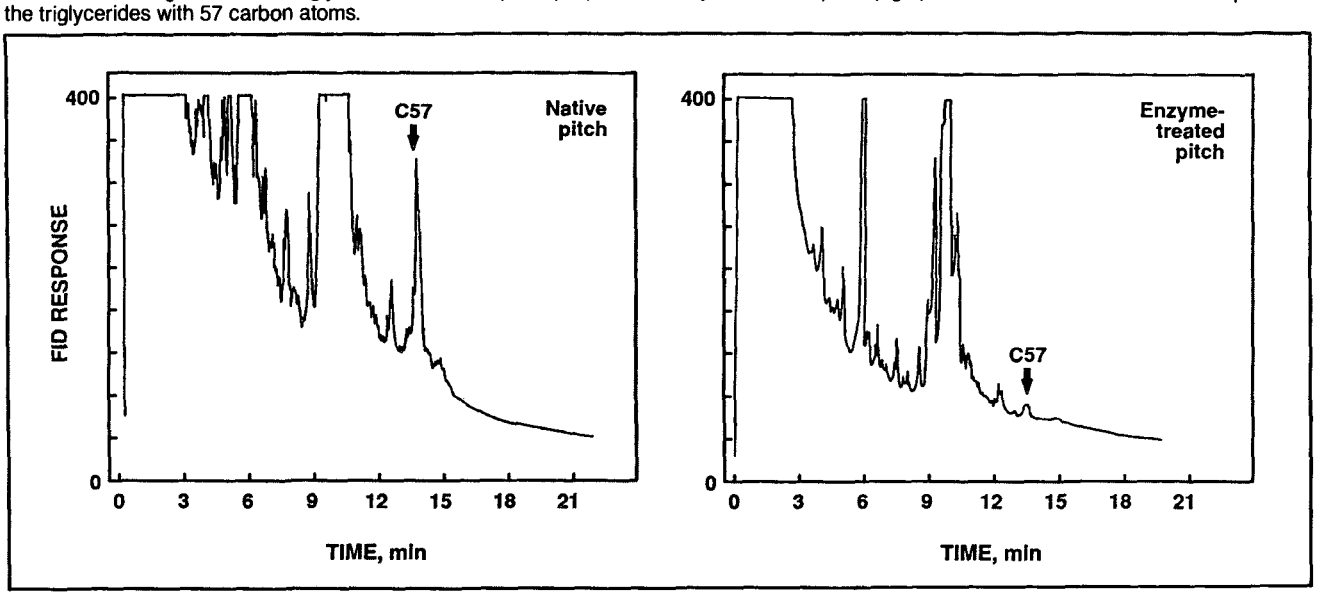
Unbleached softwood sulfite pulp was treated with enzyme to hydrolyze pitch triglycerides. The reduction of the triglycerides was determined by gas chromatography (GC). Fatty acids were removed by extraction with a sodium hydroxide solution to show the difference in the physical properties of fractions with and without glycerides and fatty acids. The fractions were chlorinated with chlorine water to simulate the bleaching process with chlorine. The success of the chlorination was determined by NMR spectroscopy.

Materials and methods

Materials

Bleached and unbleached softwood sulfite pulps were obtained from

1. Gas chromatograms of the triglycerides in native pitch (left) and in enzyme-treated pitch (right). The label "C-57" indicates the peak for the triglycerides with 57 carbon atoms.



I. Experimental specifications of Resinase A

Activity, units/mL	50,000
Temperature, °C	20-50
pH range	6-11
Contact times*	30 min to 2 h

*Manufacturer recommended contact times. We used incubation times up to 3 h to ensure that no further hydrolysis occured.

II. Hydrolysis of the triglycerides (C-57)

Pitch	Triglycerides, mg/g	Reduction, %
Native	0.420	...
Treated		
1 h	0.088	79
2 h	0.059	86
3 h	0.059	86

Mg per g of dry-weight pulp.

III. Recovered fractions of pitch

Fraction	Pitch recovered mg	%
Fatty acid	172	42
No fatty acid	238	58

IV. Adhesiveness of the chlorinated pitch samples

	Adhesiveness, mN/mm
Fatty acid fraction	14
Native pitch without free fatty acids	10
No fatty acid fraction	7

Leykam AG, Austria. The lipase Resinase A was provided by NOVO Enzyme Process Division (Bagsvaerd, Denmark). The enzyme is a dark brown liquid of fungal origin. The experimental specifications are listed in **Table I.**

Hydrolysis of triglycerides

Wet unbleached sulfite pulp (200 g wet; 32% dry weight = 64 g dry) was suspended in 2 L of 0.025 M tris-HCl buffer (tris-hydroxymethylaminomethane) containing 0.025*M* $CaCl_2$ at pH 7.7 and 37°C, forming a consistency of 2.9%. The temperature was adjusted to 37°C in a water bath, and 4 mL of Resinase A solution was added. The suspension was incubated for 3 h, during which it was constantly stirred at 400 min^{-1}. Samples for gas chromatography were taken after 1, 2, and 3 h.

Extraction of fatty acids

After incubation, the pulp was filtered by suction and extracted with acetone for 12 h. The solvent was removed by distillation on a rotary evaporator, and the pitch was dissolved in dichloromethane. The solution was dried with sodium sulfate, and the dichloromethane was removed by distillation. The pitch was dissolved in diethyl ether and was extracted with three 100 mL portions of 0.1*M* NaOH solution in a separation funnel. The combined ether layers were dried over sodium sulfate, and the solvent was evaporated to yield the fraction of pitch that contained little or no fatty acids.

The sodium hydroxide layers were acidified with hydrochloric acid and were extracted with three 100-mL portions of diethyl ether. The ether solution was dried over sodium sulfate, and the solvent was removed on a rotary evaporator. The fraction of pitch produced in this manner contained most of the fatty acids liberated by hydrolysis (the fatty acid fraction).

Native pitch was extracted in the same way but without the addition of

enzyme to produce native pitch that contained no free fatty acids.

Chlorination of the pitch samples

Pitch samples included the fatty acid fraction, the pitch fraction without triglycerides and free fatty acids, and native pitch without free fatty acids. A 50-mg portion of each sample was added to 2 L of a 0.5% solution of chlorine in water in a separation funnel. The mixture was shaken briefly every 5 min for 1 h. The funnel was flushed with sulfur dioxide until the mixture appeared colorless and emitted a slight odor of SO_2.

The solution was filtered and washed with 500 mL of water. The filtrate was extracted 4 times with dichloromethane. The combined organic layers were dried over sodium sulfate, and the solvent was evaporated.

GC analyses of hydrolyzed triglycerides

Pitch samples of about 50 mg were dissolved in 10 mL of dichloromethane for analysis. GC analyses were performed on a Carlo Erba 6000 Vega equipped with a split/splitless injector, FID, and a 3-m analytical column (DB-5). (The "split/splitless" injector is a special injection system that allows you to split up the sample and bring only a part of it to the analytical column, to prevent the column from being overloaded.)

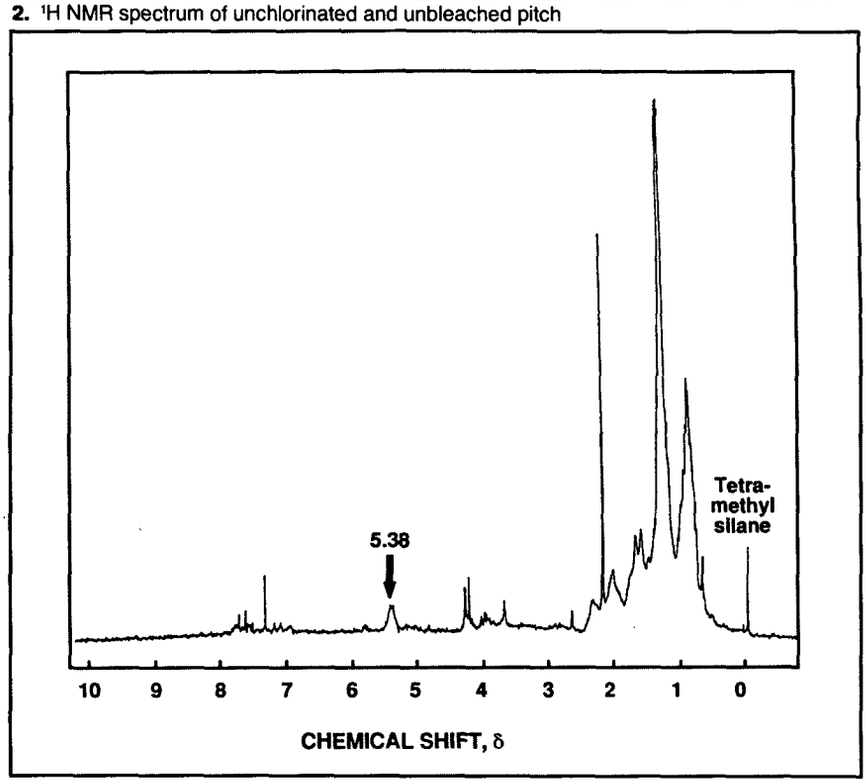
The carrier gas was helium, injected under 100 kPa at 320°C, split 5/ 26 mL/s. The temperature program was: 2 min at 250°C, from 250°C to 300°C at 10°C/min, from 300°C to 340°C at 5°C/min, 10 min at 340°C. The FID temperature was 340°C (*5*).

Standard substances of trilinolein, triolein, and tristearin (Sigma Chemical Co., St. Louis, MO) were used to identify the triglyceride peak "C-57." The peak was calibrated using tristearin as standard substance.

NMR analysis of the chlorinated samples

To demonstrate the completeness of the chlorination, the pitch samples were analyzed by an NMR spectrometer (Jeol FX 90 Q FT-NMR, 90 MHz). Bleached pulp was extracted and analyzed in the same way to compare the results.

2. ^{1}H NMR spectrum of unchlorinated and unbleached pitch



Enzyme activities

Enzyme activity was assayed using a Mettler DL-21 titrator. Olive oil (1%, Sigma Chemical Co.) in 0.025*M* $CaCl_2$ (*6*) was used as the substrate. The enzyme activity was calculated from the sodium hydroxide solution needed to neutralize the liberated acids (*7*). One unit is the amount of enzyme that liberates 1 μmole of titrable fatty acids per minute at 37°C and pH 7.7.

The purpose of the activity assay was to confirm the data of enzyme activity supplied by the manufacturer in the specifications. The assay would allow us to detect any decomposition of the enzyme that occurs during storage. In receiving the enzyme samples, we could confirm the 50,000 units per milliliter.

Adhesiveness

Adhesiveness was measured following the German standards DIN 53 281 and DIN 53 283 for testing adhesives, using a Zwick 1484 universal material testing machine. Pitch was placed between two aluminum plates covering an area of 12 mm × 12 mm and was compressed with 1 kg. The force necessary to separate the plates was measured.

Results

Hydrolysis and alkaline extraction

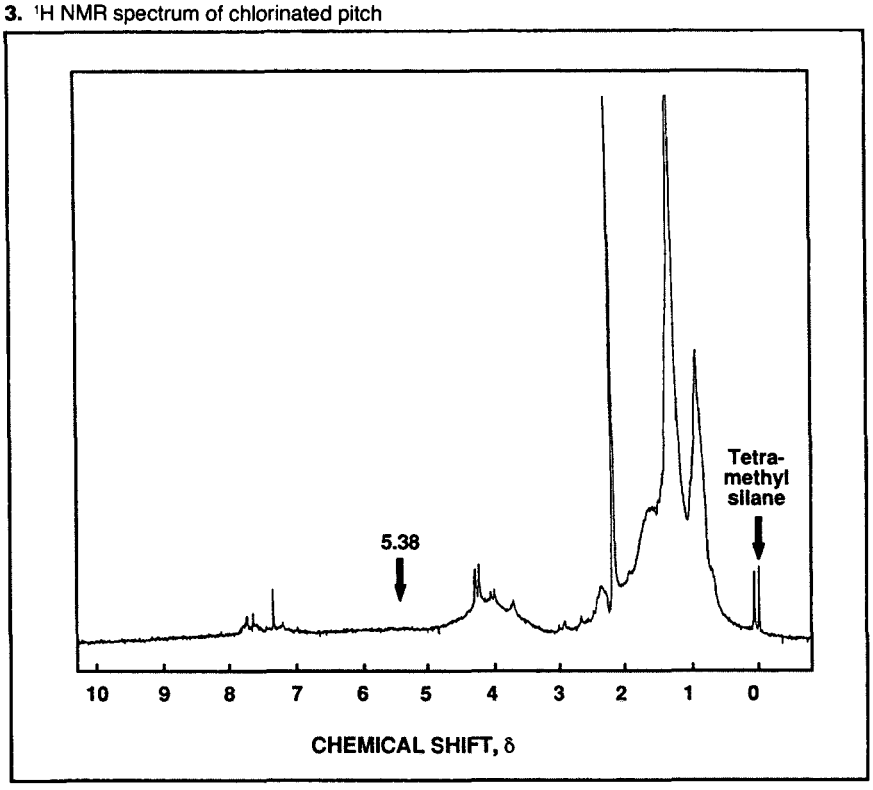
Figure 1 (left) shows the chromatogram of native pitch. All triglycerides containing 57 carbon atoms are evidenced by the same peak ("C-57"). This peak indicated all triglycerides with three C-18 fatty acids. Tristearin, triolein, and trilinolein were used to identify the C-57 peak.

Only the area of Peak C-57 was used to calculate hydrolysis because this peak includes most of the unsaturated fatty acids (oleic acid, linoleic acid, and linolenic acid). The chromatogram of treated pitch in **Fig. 1 (right)** exhibits a much smaller C-57 peak, indicating a reduction in triglyceride content. The results of the GC analyses are shown in **Table II.**

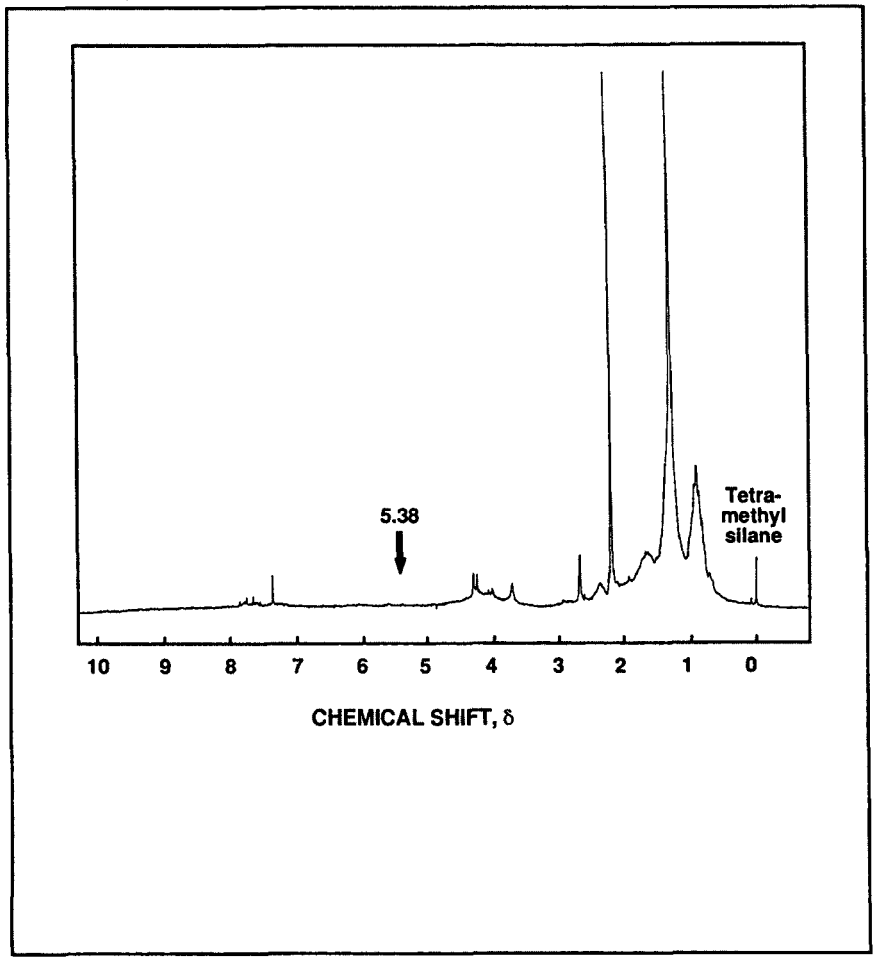
Approximately 86% of the C-57 triglycerides in the pitch was hydrolyzed by the lipase within 2 h. This result indicates that the pitch is accessible to the enzyme and that the triglycerides may be degraded in an acceptable length of time.

The extraction of 200 g of wet pulp yielded 0.474 mg of a viscous, brown pitch. The physical properties did not change during the fractionation with the sodium hydroxide solution. The weights of the fractions are shown in **Table III.**

3. ^{1}H NMR spectrum of chlorinated pitch



4. ^{1}H NMR spectrum of bleached pitch



Chlorination and change in physical properties

After chlorination, the adhesiveness of all fractions increased. (The adhesiveness of the unchlorinated pitch was too low to be measured with this method, so no values can be presented.) The fraction without fatty acids was less viscid than the nonhydrolyzed pitch and much less viscid than the fraction containing the acids (**Table IV**). This is the most important result of the study because it demonstrates that the use of the enzyme reduced the tendency of the pitch to form the adhesive substances of pitch.

NMR spectroscopy

The completeness of the chlorination was detected by NMR spectroscopy. The olefinic hydrogen atoms showed a resonance at 5.38 ppm (**Fig. 2**). This resonance did not appear in the spectra of the chlorinated pitch (**Fig. 3**) and bleached pitch (**Fig. 4**). These results show that in both samples no double bonds were present in the fatty acids. Therefore, the process of bleaching was simulated well by this method of chlorination.

Conclusions

Within 2 h, the enzyme hydrolyzed 86% of the C-57 triglycerides in the pitch containing the most important unsaturated fatty acids. This result indicates that the triglycerides in the pitch can be reached by enzymes. Also, the presence of pulp fibers does not greatly influence the activity of the enzyme and the hydrolysis.

We found that the chlorination of the pitch with chlorine water is an appropriate method of simulating the chlorination during the bleaching process with chlorine. The completeness of the chlorination was demonstrated by NMR spectroscopy.

The lower adhesiveness of the samples without chlorinated triglycerides and fatty acids demonstrates the importance of these substances in the formation of pitch deposits. It shows that the triglycerides are a major source of the formation of sticky substances in the pitch. By removing the triglycerides, the adhesiveness of the pulp can be reduced.

The fatty acids liberated by the enzyme treatment may themselves cause pitch deposits. To avoid this problem, the fatty acids can be ex-

tracted with a sodium hydroxide solution.

The results of this study demonstrate that the application of lipase in the pulping process will improve the properties of the resins by lowering their adhesiveness. How well this procedure can be applied in reducing the problem of pitch deposits will have to be tested on a larger scale in pulp mills.□

Literature cited

1. Kamutzky, W., Wochenbl. Papierfabr. 20: 753(1983).
2. Allen, L. H., Trend (Pointe Claire, Can.) 26: 4(1977).
3. Esterbauer, H., Papier 34: 37(1983).
4. Dreisbach, D. D. and Michalopoulos, D. L., Tappi J. 72(6): 129(1989).
5. Puchinger, L. and Stachelberger, H., Phyton (Austria) 29: 233(1989).
6. Oi, S., Ymazyki, O., Sawada, A., and Satomura, Y., Agr. Biol. Chem. 33: 729(1969).
7. Peled, N. and Krenz, M. C., Anal. Biochem. 112: 219(1981).

The authors wish to thank Leopold Puchinger, Institut für Angewandte Botanik, Technische Mikroskopie und Organische Rohstofflehre, for performing the GC analyses and Johannes Froehlich, Institut für Organische Chemie, Technische Universität Wien, for chlorination and NMR spectroscopy.

Adhesiveness was measured at the TGM, Technologisches Gewerbemuseum Wien, Versuchsanstalt für Kunststofftechnik. We are grateful to Leykam Muerztaler AG for the financial support of this project.

Received for review Oct. 30, 1990.

Accepted Aug. 27, 1991.