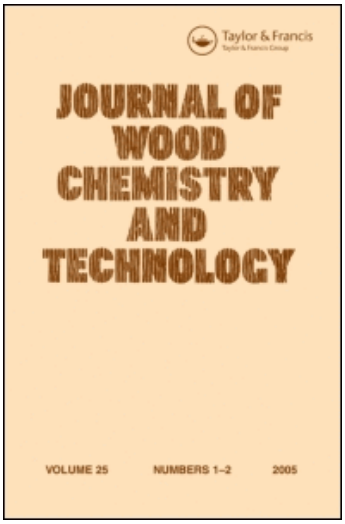

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VARIATION IN THE COMPOSITION OF WOOD EXTRACTIVES FROM *Eucalyptus globulus* DURING SEASONING

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ABSTRACT

The variation in the content of extractives from *Eucalyptus globulus* wood has been studied during a three-month seasoning experiment. The decrease in the total acetone extract (by over 56%) after seasoning is well correlated to a parallel reduction on the colloidal pitch measured in black liquors. The composition of lipophilic extractives during the seasoning period has been studied by gas chromatography and gas chromatography-mass spectrometry. Sterols, sterol esters, triglycerides, fatty acids and steroid ketones were the main lipophilic compounds among *E. globulus* wood extractives. Significative variations in the content of these compounds were observed during seasoning.

INTRODUCTION

The term *resin* is often used as a collective name for those lipophilic wood extractives, that are soluble in nonpolar organic solvents but insoluble in water.[1]

Wood resin causes significant technical and economic troubles in the pulp and paper manufacture due to the formation of viscous lumps (the so-called *pitch*) that accumulate on equipment and dark deposits in pulp and paper.[2] During pulping or refining, the canals and parenchyma rays in wood can be ruptured, releasing and dispersing wood resin that forms colloidal pitch particles. Then they can coalesce into larger droplets of pitch, which may deposit on the surface of fibers or equipment, or remain suspended to be discharged in effluents or waste waters.[2]

Traditionally, pitch deposits in pulping processes have been reduced by debarking and seasoning logs and wood chips.[3-9] It is well known that storing a felled log will reduce the resin content of the wood and bring about changes in the nature of the resin.[10,11] Therefore, storage of wood can reduce pitch problems considerably, depending on the storage conditions. Reduction of resin content occurs markedly faster when the wood is stored in the form of chips, instead of logs, since oxidation processes proceed more freely and faster in chip form.[1,2,12,13] On the other hand, it is generally recognized that prolonged wood storage can also result in negative effects, such as reduced pulp yield and low pulp quality.[1] Hence, the advantages of wood seasoning in minimizing pitch problems must be weighted against the loss of pulp quality which might be sustained through such storage.[12]

There are several papers reporting the variation in the composition of extractives from different softwoods and hardwoods during seasoning.[8,14-17] However, little work has been done so far concerning eucalypt wood,[18] which is extensively used for paper pulp manufacture in several countries, including Spain, Portugal, and Brazil. Among the different *Eucalyptus* species, the wood of *Eucalyptus globulus* is the most economically-important raw material for paper-pulp production in southwest Europe. In this paper, we study the variation in the composition of extractives from *E. globulus* wood, with special emphasis in the lipophilic compounds, during a three-month seasoning experiment. Both gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) were used to analyze the extracts.

TABLE 1

Variation of the Total Acetone Extract and Lipophilic and Polar Fractions (%) from *E. globulus* Wood and Colloidal Pitch in Black Liquors during Seasoning. The percentage of degradation is shown in parenthesis

	Control	1 month	2 months	3 months
acetone extract	1.52	1.01 (34)	0.85 (44)	0.67 (56)
lipophilics	0.26	0.26 (0)	0.18 (31)	0.16 (38)
polars	1.26	0.75 (40)	0.67 (47)	0.51 (60)
colloidal pitch (10^6 particles/cm^3 at 1%)	57.0	40.8 (28)	14.2 (75)	11.5 (80)

RESULTS AND DISCUSSION

Several seasoning experiments were carried out at different periods of the year at the ENCE kraft pulp mill (Pontevedra, Spain) using *E. globulus* wood chips with different content of extractives. In all cases, the colloidal pitch in black liquor underwent a significant decrease with the storage time of wood. Table 1 shows the variation in the content of the total acetone extract and the lipophilic and polar fractions from *E. globulus* wood as well as the variation of colloidal pitch in black liquors during a three-month wood seasoning experiment carried out from April to July, 1997. A drastic reduction in colloidal pitch (80%) was observed. Likewise, the total acetone extract decreased by 56%, while the polar and lipophilic moieties were reduced by 60 and 38% respectively. A good correlation between the decrease in *E. globulus* wood acetone extract and the reduction of colloidal pitch in black liquors existed.

During kraft cooking nearly all the phenols and polyphenols in the polar fraction of a wood extract are dissolved.[18] However, some of the lipophilic constituents may survive the kraft pulping and bleaching processes and, hence, may be found in pulp and pulp-mill deposits.[2,19] Sterols, waxes, sterol esters and steroid ketones have been

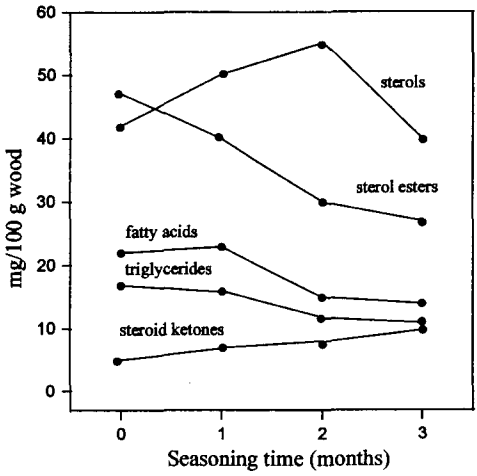

FIGURE 1. Variation in the content of lipophilic extractives from *E. globulus* wood during seasoning.

found in pitch deposits from eucalypt pulps and pulp-mills, and high amounts of fatty acid salts have also been found in mill deposits.[19]

Sterol esters, sterols, fatty acids, triglycerides and steroid ketones are the major lipophilic groups present in fresh *E. globulus* wood, accounting for 47, 42, 22, 17 and 5 mg/100 g wood, respectively. Sterol esters and sterols are mainly constituted by sitosterol. The variation in the composition of lipophilic extractives from *E. globulus* wood during the three-month seasoning experiment is shown in Figure 1.

After the first month of seasoning, the content on lipophilic extractives was not modified (Table 1); however, the composition of the different constituents was altered. The most significant variarion was the reduction in the content of sterol esters by 15%. This decrease was approximately balanced with a corresponding increase of free sterols and steroid ketones, the latter being attributed to the oxidation of sterols. Triglycerides were reduced by 6% and the content in free fatty acids increased very slightly, this increase being attributed to the hydrolysis of sterified fatty acids.

During the second month of seasoning, the decrease in the sterol esters content persisted (36%). A parallel increase in the content of free sterols (31%) and steroid ketones (60%) was also observed. The increase of free sterols could be due to the fact that the hydrolysis of sterol esters took place faster than the degradation of the sterol moiety. The triglyceride content continued to decrease by 29% during the second month of seasoning. The decrease in the content of sterol esters and triglycerides was not balanced by a corresponding increase of fatty acids, but an over-all loss of fatty acids of 32% occurred.

During the third month of seasoning, the decrease in the content of sterol esters, triglycerides and fatty acids continued, although at a lower rate that in the previous month; the steroid ketones further increased. During this month, the content in free sterols decreased markedly, contrary to previous months, probably due to the biological degradation of the sterol moiety.

After the three-month seasoning experiment, sterol esters, triglycerides, fatty acids and sterols were significantly removed by 42, 35, 36, and 31 %, respectively, whereas steroid ketones increased by over 100%, but they remained a minor fraction. It is clear that seasoning of *E. globulus* wood chips decreases the content of those lipophilic wood extractives responsible for pitch deposition. However, natural seasoning increases the risk of stain and decay. Wood weight loss during seasoning was also measured and was estimated at 1.2% monthly. Thus, it could be concluded that when pitch problems are found in market pulps, as a consequence of a high extractive level in the wood, outside chips storage for a maximum of two months would be justified. Nevertheless, the loss of pulp strength and brightness and increased wood storage costs associated with long storage must be weighted against the loss of pulp production and quality due to higher pitch deposition using fresh wood.

EXPERIMENTAL

Wood Samples

Samples were collected from *Eucalyptus globulus* grown in Pontevedra (North

Spain). The trees were cut at an age of 12-14 years, debarked, and chipped. The chips were stored outside from April 1997 to July 1997 and sampled monthly.

Wood Extraction

Wood chips, previously ground to sawdust, were Soxhlet-extracted with acetone for 6 h. The dried extract weight constitutes the "acetone extract" value given in Table 1. The amounts of lipophilics in the extracts were determined by redissolving the acetone extract in chloroform and evaporated under nitrogen to dryness. The amounts of polars corresponded to the chloroform insoluble residue.

Colloidal Pitch Measurement

A hemacytometer[20] was used to measure pitch particle concentration in the black liquor from Kraft cooking of eucalypt wood.

Gas Chromatography (GC)

A Hewlett Packard HP 5890 gas chromatograph equipped with a split-splitless injector and a flame ionization detector (FID) was used. The injector and the detector temperatures were set at 300°C and 350°C respectively. The samples (1 μL) were injected in the splitless mode. Helium was used as the carrier gas at a rate of 2 mL min^{-1}. The capillary column used was a high temperature, polyimide coated fused silica tubing DB5-HT (5 m x 0.25 mm I.D., 0.1 μm film thickness; J&W Scientific), specially processed for a extended temperature of 400°C. The oven was temperature-programmed from 100°C (1 min) to 350°C (3 min) at 15°C/min. A mixture of standard compounds (palmitic acid, sitosterol, cholesteryl oleate, and triheptadecanoin) was used to elaborate a calibration curve for the quantitation of wood extractives with a concentration range between 0.1 and 1 mg/mL. The correlation coefficient was higher than 0.99 in all the cases. All peaks were quantified by peak area.

Gas Chromatography-Mass Spectrometry (GC-MS)

The GC-MS analyses were performed on a Varian Star 3400 gas chromatograph with an ion trap detector (Varian Saturn 2000) using a high temperature capillary column (DB-5HT, 15 m x 0.25 mm I.D., 0.1 μm film thickness; J&W Scientific). Helium was used as the carrier gas. The samples (1 μL) were injected with an autoinjector (Varian 8200) directly onto the column using a SPI (Septum-equipped Programmable Injector) system. The temperature of the injector during the injection was 120°C, and 0.1 min after the injection was programmed to 380°C at a rate of 200°C/min and hold 10 min. The oven was temperature-programmed from 120°C (1 min) to 380°C (5 min) at 10°C/min. The temperatures of the ion trap and the transfer line were set at 200°C and 300°C respectively. Compounds were identified by computer comparison of the mass spectra with those in the Wiley and Nist libraries, by mass fragmentography and, when possible, by comparison with standard compounds.

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