Studies on the delignification of spruce wood by organosolv pulping using SEM-EDXA and TEM

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Summary. Samples of spruce wood derived from various stages of organosolv pulping were studied by SEM-EDXA and TEM. During the first stage (methanol-water) the lignin content of the secondary walls decreased slowly, whereas in the compound middle lamellae only the reactivity of lignin increased. During the subsequent stage (methanol-NaOH) the delignification proceeded fast in both layers but the residual lignin content in the compound middle lamellae remained higher than in the secondary walls.

Introduction

The study of delignification on an ultrastructural scale results in very important informations on the progress of a pulping process. In recent years, two methods proved most appropriate for the quantification of lignin in the various cell wall layers: UV microscopy combined with microdensitometry (Fergus et al. 1969; Scott et al. 1969) and SEM-EDXA following the bromination of lignin (Saka et al. 1978).

Apart from particular questions such as the distribution of guaiacyl and syringyl lignins (Fergus, Goring 1970; Gromov et al. 1977), lignin distribution in compression wood (Fukazawa 1974), lignin concentration of the tertiary wall or S3 layer (Scott, Goring 1970), mechanical pulps and steam-exploded wood (Gardner et al. 1982; Bruun, Lindroos 1983; Donaldson et al. 1988) have been studied applying the above mentioned methods.

Particular interest has also been accorded to various pulping processes and the topochemistry of delignification. Thus kraft, soda, soda-anthraquinone, soda-oxygen, chlorite and sulfite pulping have been studied (Procter et al. 1967; Fergus, Goring 1969; Wood et al. 1972; Saka et al. 1978, 1982; Greune, Fengel 1988).

Environment compatible processes such as organosolv pulping were not yet investigated on this score. In connection with studies on lignin from the Organocell process (Lindner, Wegener 1988 a, b) we had the opportunity to pursue the delignification in a two-stage cooking of spruce wood.

Material and methods

Air dried chips of spruce wood (Picea abies Karst.) were delignified with methanol-alkali according to the Organocell process in a 201 digester (Lindner, Wegener
Samples were collected after the first stage (methanol-water, 190 °C, 40 min) during the second stage (methanol-NaOH, 170 °C, 20 min) and after the second stage (methanol-NaOH, 170 °C, 40 min). Furthermore another delignification (second stage only) was carried out.

The chips were subdivided into small rods (1 mm × 1 mm × 8 mm) with a razor blade and then thoroughly washed with distilled water. After drying overnight at 70 °C the rods were brominated according to Saka et al. (1978). After a careful removal of surplus bromine by extraction with chloroform and removal of residual chloroform by heating (70 °C) and repeated evaporation the samples were embedded in a low-viscosity epoxy resin (Spurr 1969). The embedded samples were cut into 1 μm sections for EDXA with an ultramicrotome (LKB Nova). The sections were collected on nylon grids covered with formvar film, and the grids mounted on carbon supports.

Spot analyses of cell corners (CC), the compound middle lamellae (ML) and the secondary walls (SW) were carried out. Each section was moreover analyzed for chlorine content of the embedding medium which is a standard value for the correction of section thickness. Conditions for the analysis in the SEM (Leitz-AMR 1200B equipped with a Kevex 2000) were: voltage 25 kV, current 130–140 A, diaphragm 300 μm, spot 4, inclination angle of the sample 0 °. Details of calculation are described elsewhere (Greune, Fengel 1988). Moreover sequential analyses consisting of 60–160 syncron runs resulted in concentration profiles of bromine in the cell walls.

For observations in the TEM (Zeiss EM 10C) the samples were prestained with uranyl acetate or KMnO₄ before embedding. After cutting (300–400 nm in thickness) the sections were poststained with lead citrate.

Results

Because of the scattering of electrons within the cell walls the information obtained by X-ray energy comprises a large area compared to spot size. Thus the material of the compound middle lamella is exclusively analyzed in the cell corners (CC) only, whereas the analysis of the compound middle lamella (ML) also includes the material of the secondary wall 1 and probably parts of the secondary wall 2. Analysis of the secondary wall (SW) carried out in the middle of S2, however, comprises only material of this layer. The results of the various analyses have to be viewed under this aspect.

The graphic representation of results of the X-ray analysis showing the relative bromine concentration in the upper part and the percentage of lignin in the lower part is shown in Fig. 1. During the first stage (methanol-water) only about 10% of the original lignin is removed from the ML and SW area whereas the lignin content of the cell corners increases slightly (Fig. 1, left). The increase results from a higher percentage of bromine linked by lignin which can be interpreted by an increase of lignin reactivity. During the second stage (methanol-NaOH) a continuous removal of lignin can be observed in all wall layers. At the end of the process the ML and SW areas contain about 40% of the original lignin. In the real compound middle lamella represented by the cell corners (CC) remain about half of the original lignin. A one-stage cooking with methanol-NaOH results in a slightly improved delignification of the secondary walls but in a higher lignin content in the compound middle lamellae compared to the two-stage cooking (Fig. 1, right).