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Eija Bergelin^a; Bjarne Holmbom^a

^a Process Chemistry Centre, Laboratory of Wood and Paper Chemistry, Åbo Akademi University, Turku/Åbo, Finland

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Reactions and Distribution of Birch Extractives in Kraft Pulp Oxygen Delignification

Eija Bergelin and Bjarne Holmbom

Åbo Akademi University, Process Chemistry Centre,
Laboratory of Wood and Paper Chemistry, Turku/Åbo, Finland

Abstract: Extractives composition and distribution was examined around the oxygen delignification stage in a birch kraft pulp mill. Pulp suspensions were divided into different fractions with a dynamic drainage jar device to obtain fibers (+100 mesh), large fines (100–200 mesh), and small fines (200–400 mesh) fractions as well as the colloidal and dissolved fractions. The fractions were extracted and the resin components analyzed by gas chromatography. No significant oxidation reactions of wood resin were found to occur in oxygen delignification. Major removal of resin was achieved in the subsequent washer, where resin is removed with dissolved, colloidal, and fines fractions. Overall deresination in the subsequent washer was 58%.

Keywords: Kraft pulping, birch, oxygen delignification, wood resin, extractives, betulinol

INTRODUCTION

Analysis of extractives is important for quality control in the pulp industry. High levels of extractives affect fiber properties and pulp quality negatively. Wood resin carried over to the bleach plant will react with the bleaching chemicals to various degrees depending on their chemical structure and on the bleaching agent used.^[1] The components that survive the bleaching processes can remain as extractives in the pulp and are detrimental to product quality. Large amounts of extractives in pulps used for food packaging may give taste and odor to the foodstuffs. Yellowing may also be in part caused by oxidation reactions of extractives. Wood resin, that is, lipophilic extractives, can cause problems also in papermaking processes. Deposits from resin adhere to different parts

Address correspondence to Eija Bergelin and Bjarne Holmbom, Process Chemistry Centre, c/o Laboratory of Wood and Paper Chemistry, Åbo Akademi University, Porthaninkatu 3, FI-20500 Turku/Åbo, Finland. E-mail: eija.bergelin@abo.fi or bjarne.holmbom@abo.fi

of the paper machine or may appear as dirt spots in the paper. This can cause interruptions in paper production and decreases paper product quality. There is also a connection between buildup of deposits in the pulp mills and the need of re-circulating process waters to meet the demand of environmental protection. Typical places of deposition of birch extractives is in storage towers and in washer areas.^[2]

Oxygen delignification can be regarded as a continuation of cooking, or as the first stage of bleaching.^[3] Today it is a standard stage in production of bleached chemical pulp. In the oxygen delignification stage the pulp is treated with oxygen in a pressurized vessel at elevated temperature and alkaline conditions. The delignification varies in the range 40–70% depending on the wood raw material and whether one or two reactors in series are used. Unbleached kraft (sulfate) pulp has a lignin content of 3–5% (kappa number around 20 for birch and for softwood around 35), which after oxygen delignification can be decreased to about 1.5%, corresponding to a kappa number of 8–12.

Extractives that are soluble in organic solvents with low polarity are called lipophilic extractives. Wood extractives consist of a large variety of low-molar-mass components, usually representing a minor fraction of the wood. They are defined by their solubility in organic solvents or water.^[4] Polar solvents extract hydrophilic salts, sugars, starch, and phenolics. Usually when wood resin in general causes problems, such as deposits during pulping, bleaching, and papermaking, the term pitch is used.^[5] The amount and composition of wood resin varies considerably depending on the wood species. Birch wood contains 2–2.5% wood resin, which is mainly composed of triglycerides (fat) and fatty acid esters of sterols and so-called betulaprenols.^[6,7] Birch wood also contains triterpenyl alcohols (triterpenols), such as lupeol and methyl betulinate. Furthermore, the outer bark of birch contains 25–30% betulinol that also enters pulp and paper production as bark residues.^[8] *Betula pendula* and *Betula pubescens* are the species mainly used in the Nordic chemical pulping industry. Deresination is considerably more difficult in kraft pulping of birch wood than of softwoods. Consequently, the unbleached birch pulp contains relatively large quantities of extractives, usually 0.5–1% of the pulp.^[5] Resin acids, present in softwoods, are not found in birch wood. In birch kraft pulp mills, it is also a common practice to add tall oil or tall oil rosin, containing resin acids, to the cook to improve pulp deresination, why resin acids also are extracted from birch kraft pulps. Betulinol exists as dispersed particles because it does not melt at process temperatures; its melting point is 248–250°C. It is hydrophobic and sparingly soluble in water. Because solubilization of resin requires melting, betulinol is not solubilized during kraft cooking.^[9] Consequently, betulinol is commonly found in deposits in birch kraft pulp mills and in paper mills using birch kraft pulp.

In an earlier work the deresination and extractives behavior was investigated through material balances along the bleaching line.^[10] This work focused on the oxygen delignification stage. A new approach to evaluate wood resin

behavior in pulping was tested. The pulp suspensions were fractionated according to fiber/particle size and the extractives content and composition in each fraction was analyzed.

MATERIALS AND METHODS

Pulp Samples

Samples of unbleached birch kraft pulp, oxygen-delignified pulp (sampled directly after the oxygen delignification), and pulp after the diffuser washer were taken out at three occasions in a Finnish pulp mill when the production was normal. The pulp consistencies were 16% for the unbleached pulp, 10% for the O-bleached pulp, and 6% for the diffuser washer pulp and the pH values were about 11, 9, and 8, respectively. All samples were stored at 4°C until fractionation and analysis. The kappa number was 20 after the digester and 12 after the oxygen delignification. The oxygen stage conditions were as follows, temperature 99°C, time 60 min, pH 11, O₂ charge 21.0 kg/adt, and the diffuser washer time span was 30 min.

Experimental Procedures

The extractives distribution in the pulp suspensions was analyzed by extracting the fractions of fibers, large and small fines, colloidal particles, and dissolved substances. The experimental procedures and analyses are outlined in Figure 1. Total extractives were also determined by gas chromatography (GC) for the pulp samples. Dry contents of the samples were measured with a moisture analyzer (MA30).

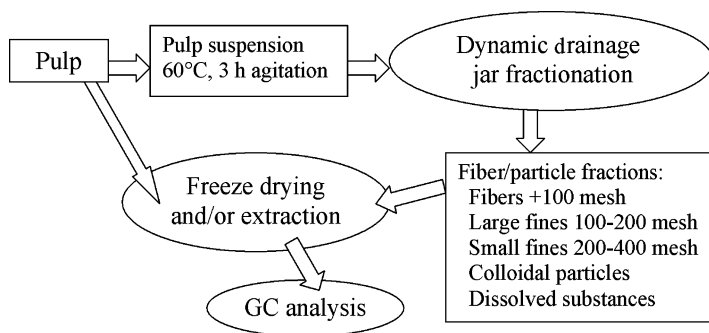


Figure 1. Outline of the experimental procedures for preparation of pulp suspensions for fractionation and analysis.

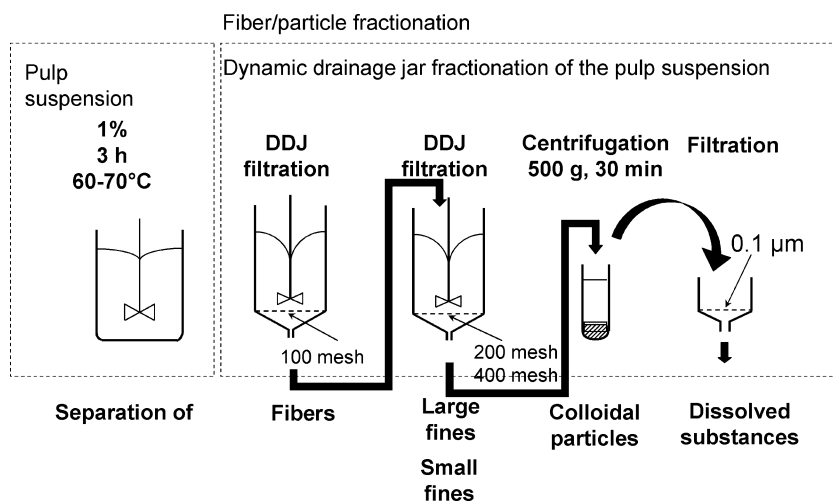


Figure 2. Outline of the pulp fractionation procedure.

Preparation of Pulp Suspensions

An amount corresponding to 20 g o.d (oven dry) pulp was added to distilled water to obtain a 1% suspension (Figure 2). The pulp suspension was then stirred (150 rpm) for 3 h at 60°C to reach adsorption/desorption equilibrium prior to fractionation. The fractionation was done by using a dynamic drainage jar device (DDJ). Long fibers were separated by filtration with a 100-mesh wire (opening 150 μm), large fines with a 200-mesh wire (opening 75 μm), and small fines fraction with a 400-mesh wire (opening 38 μm). The remaining effluent was centrifuged at 1600 rpm for 2 h and the colloidal fraction was separated from the supernatant (containing dissolved substances) by filtration with a 0.1-μm filter. At the end, five fractions: fibers and fines (+100-mesh, 100–200 mesh, and 200–400 mesh), colloidal particles, and dissolved substances for each sample were obtained. Table 1 shows the relative amounts of the fractions. All samples were stored at 4°C before freeze-drying and analysis.

Table 1. Relative amounts of the pulp sample fractions

	Unbleached pulp (%)	Oxygen-delignified pulp (%)	Diffuser-washed pulp (%)
Fiber fraction	95	95	94
Large fines fraction	1	1	0.1
Small fines fraction	0.2	0.2	0.2
Colloidal particles	0.4	0.2	0.2

Extraction Methods and Analysis by Gas Chromatography

Pulp samples and the fiber fractions were freeze-dried and then extracted in an Accelerated Solvent Extractor (Dionex ASE-200) with acetone:water 95:5 by vol. The extraction was performed at 2000 psi pressure and 100°C with two 5 min extraction cycles. The extract volumes were adjusted to 50 ml with acetone and 5-ml aliquots were taken for GC-analysis.

Reflux extraction was used for the fines fractions and the colloidal particles. Reflux extraction was performed with 95 ml acetone, 5 ml distilled water, and 1 ml acetic acid for 4 h. After extraction, the extract solutions were filtered and concentrated by evaporation. The supernatants after centrifugation were extracted using liquid-liquid extraction with MTBE at pH 3.^[11]

After evaporation, the samples were further dried in a vacuum oven for 15 min. After drying, the sample aliquots were silylated by adding 80 μ L N,O-bis-trimethylsilyl-trifluoroacetamide (BSTFA), 40 μ L trimethyl chlorosilane (TMCS), and 20 μ L pyridine and kept in an oven at 70°C for 45 min. The silylated samples were transferred to GC vials and analyzed by GC and GC-MS. Heneicosanoic acid, cholesterol, cholesteryl heptadecanoate, and 1,3-dipalmitoyl-2-oleoylglycerol were used as internal standard compounds. Individual fatty acids, resin acids, and unsaponifiable neutral components (mainly sterols and triterpenols) were analyzed by GC using a HP-1 column (25 m, 0.20 mm i.d.) and FID detection. The initial temperature was 150°C and the temperature gradient 7°C/min. The injection temperature was 230°C and detector temperature 290°C. Fatty and resin acids were quantified against the heneicosanoic acid standard and unsaponifiable components against cholesterol. No response factors were used. Steryl esters and triglycerides were determined by GC on a short column (HP-1, 5 m, 0.53 mm i.d., film thickness 0.15) against the cholesteryl heptadecanoate and the 1,3-dipalmitoyl-2-oleoylglycerol standard peaks, respectively.^[11] GC-MS analyses were performed to verify the identity of certain GC peaks.

RESULTS AND DISCUSSION

Fractionation of pulp according to fiber and particle size can provide information about the pulp extractives distribution. Pulp extractives behavior is closely related to its physical distribution in pulp. Extractives inside parenchyma cells is less accessible for bleaching reagents than extractives on the surfaces of fiber material or extractives that dissolves in the process.

The pulp samples taken around the oxygen delignification were fractionated and analysed for resin content. The reactions that occur in oxygen delignification are mainly aimed at lignin degradation. Lignin degradation is seen in Figure 3 as a change in the components marked as others for the fiber fraction (100 mesh). This diverse component group consists of

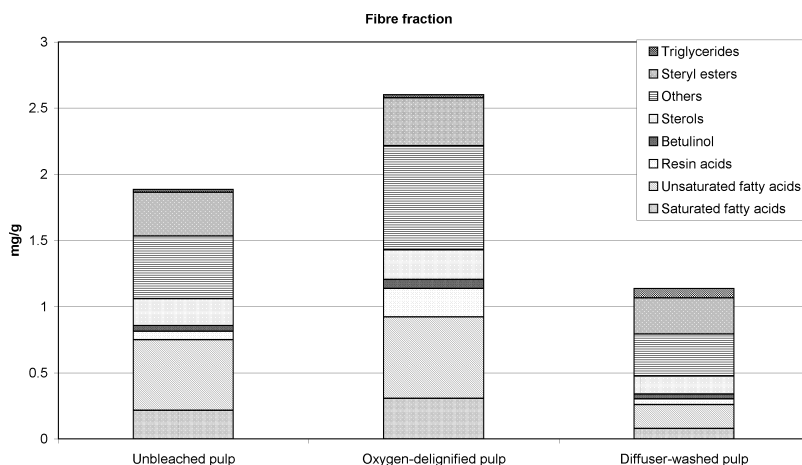


Figure 3. Extractives in the fiber fraction (100 mesh) of unbleached, oxygen-delignified, and diffuser-washed pulp.

triterpenols (excluding betulinol), betulaprenols, and non- or medium polar lignin and hemicellulose degradation products and other phenolic compounds. These components are not native but modified non-extract components relevant in observing the occurring lignin degradation reactions in the oxygen delignification. The increase of these compounds was from 0.12 mg/g in the unbleached fiber fraction to 0.4 mg/g in the oxygen delignified fiber fraction.

It has been stated earlier^[12] that unsaturated resin can react during oxygen delignification. However, this study verifies that there is little oxidation of resin in the mill conditions of oxygen delignification. The unsaturated fatty acids in the fiber fraction were at the same level, 0.53 g/kg and 0.63 g/kg, respectively. After the diffuser washer, the level of unsaturated fatty acids in the fiber fraction was down to 0.18 g/kg. Also, the unsaturated sitosterol known to react further on in the bleaching process, amounted for 0.10 g/kg for both fraction samples.^[10] The linoleic acid/oleic acid ratio changes if oxidation reactions occur but the ratio was 1.8 and 2.0 over the oxygen delignification. For sitosterol/sitostanol the ratio was also unchanged (3.7). Furthermore, no oxidized sterols that appear due to reactions with oxygen were detected after the oxygen delignification stage. Even the oxidation-sensitive betulaprenols were little affected during oxygen delignification. Extensive removal by washing after oxygen delignification was noted by Freire et al.^[13] for *Eucalyptus globulus* kraft pulps. Fernando et al.^[14] also found that the physical distribution of resin inside parenchyma cells greatly affected the removal of extractives. Micelle formation is possible in the physicochemical environment in the washing stage after oxygen delignification, and thus removal of parenchyma cell resin can

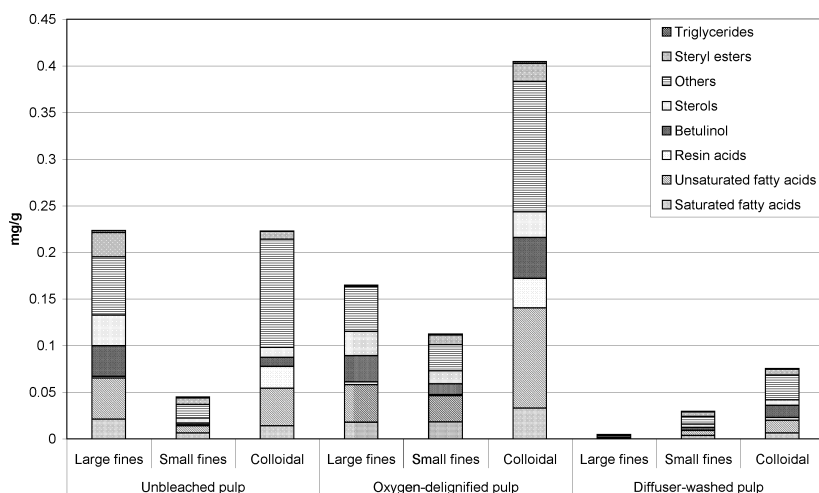


Figure 4. Extractives in the fines fractions (200 mesh and 400 mesh) and the colloidal fractions of pulps.

occur through solubilization of the resin, which here was seen as removal of especially fatty acids and sterols.

Resin on fiber surfaces that can be removed easily in the subsequent washing consists mainly of saturated and unsaturated fatty acids and smaller amounts of sterols (Figure 3). Because betulinol originates from birch outer bark, it is also mostly found on fiber surfaces in the process. The betulinol amount decreased over the oxygen delignification stage due to redistribution of betulinol from the fiber fraction to the fines, colloidal, and dissolved fractions (Figure 4). The decrease in the betulinol content in the diffuser washer occurs then by removal of these fractions.

Compounds originating from lignin degradation were also found on the fiber surfaces, but were easily removed in the diffuser washer, reducing the amount by more than half. The removal of saturated and unsaturated fatty acids was quite effective in the diffuser washer; the saturated fatty acids decreased from 0.21 mg/g to 0.08 mg/g from the fiber fraction and the unsaturated were reduced from 0.53 mg/g to 0.18 mg/g.

There was some redistribution of resin to the small fines fraction (Figure 4), and an increase was seen for the colloidal fraction for the oxygen-delignified pulp, which in the subsequent washer stage is beneficial for the deresination.

The resin in the fines and colloidal fractions are often a major reason for deposition, due to agglomeration of colloidal resin. For the pulp sampled after the diffuser washer, significant amounts of resin had been removed in the washing stage through removal of these fractions. However, when comparing

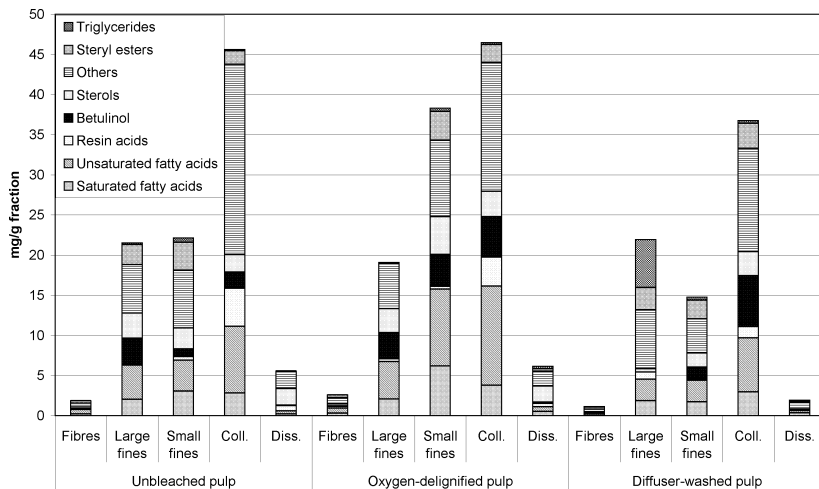


Figure 5. Extractives content in the pulp fractions on total dry matter basis.

the extractives content analyzed and calculated against the fraction weight, it was seen that even if the residual fraction itself was smaller, the extractives content was only slightly decreased (Figure 5).

When the results are calculated against the weight of each fraction, the resin content looks somewhat different for the fractions (Figure 5). Betulinol was removed in the washing stage mainly by removal of the fines and colloidal fractions, but fiber bound betulinol was only removed to a low extent. This is also why a redistribution of resin into the fines fractions, or an increase in the resin content in these fractions also easily causes deposition. Components that were easily dissolved in the process showed a decrease over the whole oxygen delignification stage.

The dissolved components were removed to a large extent in the washing. The components from lignin degradation were partly precipitated onto the fibres but were degraded further or redistributed and then removed in the subsequent washing. The decrease in the resin acid level can be due resin acids reactions in the water phase.

CONCLUSION

Oxidation reactions of wood resin do not occur to any significant extent in the oxygen delignification. Extractives is mainly removed in the subsequent washer where it is beneficial for the resin to be distributed into the fractions that are removed in the washing, namely dissolved, colloidal, and the fines fractions. Total deresination in the subsequent washer was 58%. Betulinol is removed

in the oxygen delignification stage through distribution to fines, colloidal, and dissolved fractions.

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