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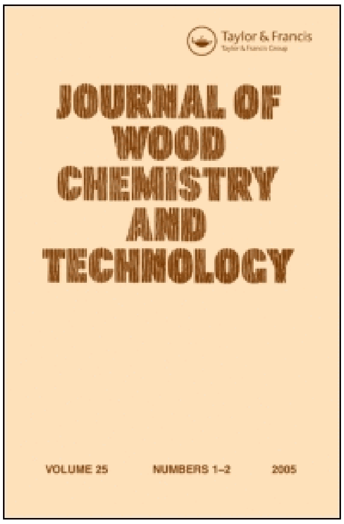

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CHEMICAL CHARACTERIZATION OF BEECH CONDENSATE

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ABSTRACT

Beech (*Fagus sylvatica* L.) condensate from a steaming operation was collected and analyzed. The condensate exhibited a low pH, and contained carbohydrates and phenolic compounds. A total of five phenolic acids and aldehydes (syringic acid, vanillic acid, *p*-hydroxybenzoic acid, syringaldehyde, vanillin) were identified. TLC of the carbohydrates showed the presence of glucose, galactose, xylose, mannose and/or arabinose in the condensate. Fructose, saccharose, raffinose and stachyose were also identified. The COD, BOD5, pH, conductivity and suspended solids (TSS) were determined. The chemical oxygen demand (COD) in the beech condensate

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varied from 2016 to 1393O mg/L. This value is two to three fold higher than the corresponding biological oxygen demand (BOD_5).

INTRODUCTION

Wood surface color is an important feature in wood marketing. Several products, such as furniture, are preferred with a dark color in Europe. To achieve the darker color, lumber, logs, and veneers are often steamed or heat treated in a vat to darken the color of the sapwood in beech, walnut and sometime cherry. However, disposal of the condensate from steaming or hot water treatment represents a hazard to the environment.[1] During the steaming of wood products, some of the hemicelluloses are hydrolysed and/or become soluble at temperatures between 100 to 240°C.[2,3] The increased acidity during steaming treatment also alters the lignin.[4,5] The objective of this work was to characterize the chemicals in the condensate from steam treating beech wood.

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EXPERIMENTAL

Material

A completely sealed chamber measuring ($11 \times 5.5 \times 3.5$ m) (made by Thanry) with steel walls and a rail system was used to steam the wood. This chamber was loaded with 20 m^3 of beech heartwood and sapwood, then steamed for 48 h at 100°C. About 500 mL of condensate was collected in a glass bottle every hour and immediately stored at 4°C.

Water Quality Analyses

The condensates were analyzed for chemical oxygen demand (COD) using the potassium bichromate method[6] and for the 5-day biological oxygen demand (BOD_5).[7] The electrical conductivity was measured with a conductivimeter/resistivimeter from Tacussel (model CDRV 62 E 571). Total suspended solids were measured by filtration.

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Identification of Sugars and Total Phenols

About 10 mL of each sample was filtered under vacuum through a Whatman glass microfiber filter with an average pore size of 1.5 μm. Total phenols were determined in all samples by the Folin-Ciocalteu assay with (+)-catechin as a standard.[8] Total sugars were determined by the phenol/sulfuric acid method with glucose as a standard.[9]

Thin Layer Chromatographic Analyses

Carbohydrates

About 200 mL of condensate was centrifuged at 4000 *g* for 5 min and passed through a PVPP (polyvinyl-polypyrrolidone) column to remove colored substances and lyophilized. Lyophilized samples were dissolved in 1 mL methanol and 10 μL were spotted on silica gel 60 plate from Merck, Darmstadt, FRG. The plates were developed three times in a chloroform/acetic acid/water (6 : 7 : 1, v/v/v) solution. Spots were visualized by spraying with a 2% naphthoresorcinol solution in acetone and 9% orthophosphoric acid (5 : 1, v/v) followed by heating in an oven at 105°C for 10 min.[10] The sugars were determined by comparing the R_f with standards of glucose, galactose, xylose, mannose, fructose, arabinose, saccharose, stachyose and raffinose.

Phenolic Acids

About 3 mg of lyophilized samples obtained by ethyl acetate extraction of the condensate after acidification to pH 2 were separated by TLC using butan-1-ol : acetic acid : water, 4 : 1 : 5 (v/v/v). Ultraviolet light at 280 nm was used to visualize spots before and after spraying with ammonia. Diazotized *p*-nitroaniline was freshly prepared by mixing 2 mL of 5 mg/mL *p*-nitroaniline, 8 mL of 200 mg/mL sodium acetate and 5 drops of 50 mg/mL sodium nitrite. This reagent is known to produce color with a number of phenols. Sodium carbonate 15% (w/w) was then sprayed to help visualize phenolic compounds.[11] Most spots were identified by comparing the R_f with available standards such as syringic acid, vanillic acid and *p*-hydroxybenzoic acid.

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Aldehydes

Aldehydes were separated by TLC using petroleum ether/isoamyl alcohol/acetic acid (100 : 16 : 0.25, v/v/v). The spots were visualized by spraying 2,4-dinitrophenylhydrazine, and identified by comparing the R_f with available authentic standards such as syringaldehyde, vanillin and benzaldehyde.

Alkaline Nitrobenzene Oxidation

About 1 L of condensate collected after 35–44 h steaming was hydrolyzed with 4 mL of 2 M NaOH at 30°C for 24 h. After the alkaline hydrolysis, the mixture was acidified to pH 2 with 2 N HCl and then extracted three times with *n*-hexane. The aqueous phase was extracted with ethyl acetate by a liquid–liquid phase extraction. The residual fraction was evaporated and about 50 mg were placed in a 10 mL stainless steel pressure vessel with 4 mL of 2 M sodium hydroxide and 0.25 mL nitrobenzene. The vessel was kept in an oil bath at 170°C for 3 h.[12]

Derivatization and Gas Chromatography

Ethyl acetate extracts were dissolved in 200 μL of pyridine, and an aliquot of 20 μL was placed in a vial. An equal volume of [*bis* (trimethylsilyl) trifluoroacetamide] BSTFA and 1% trimethylchlorosilane were added to the vial. The contents were mixed and placed in a 60°C heating block for 15 min.

A Hewlett-Packard ChromPack CP 9001 gas chromatograph fitted with a Flame Ionization Detector was used. The injection port and detector were maintained at 250°C. A focused silica capillary column with a temperature program set from 180 to 250°C at 3.5°C/min was used for the separation. Nitrogen carrier gas was used at a flow rate of 10 mL/min. Peak identifications were performed by comparing the retention time of unknown compounds to available standards. The standards included syringic acid, vanillic acid, *p*-hydroxybenzoic acid, syringaldehyde, vanillin and benzaldehyde.

Multi-element Determination

Two gram of lyophilized condensate was dissolved in water for ICP measurement (Jobin Yvon, JY 238, France) to determine Fe, Ca, Mg, and Mn.

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RESULTS AND DISCUSSION

Characterization of Condensate

Table 1 lists the range of the analysed properties from the condensate. The total volume of condensate generated was estimated at 4.5 m^3. The BOD$_5$ level ranged from 755 to 5000 mg/L. This level is significantly higher than the 150 mg/L national level allowed in France. That the BOD$_5$ variation from 755 to 5000 mg/L may be explained by the variability of water soluble extracts produced during progression of steaming. The chemical oxygen demand (COD) in the beech condensate varied from 2016 to 1393O mg/L. This value is two to three fold higher than the corresponding biological oxygen demand (BOD$_5$). Figure 1 gives the COD and

Table 1. Characterization of Condensates from Beech Wood (*Fagus sylvatica* L.)

Wood volume (m^3)	18,97
Wastewater volume (m^3)	4,5
Volume collected (m^3/h)	0.06–0.86
pH	4.0–4.4
Conductivity (µs/cm)	1,04–2,02
COD (mg/L)	2016–13 930
BOD$_5$ (mg/L)	755–5000
TSS (mg/L)	222–420

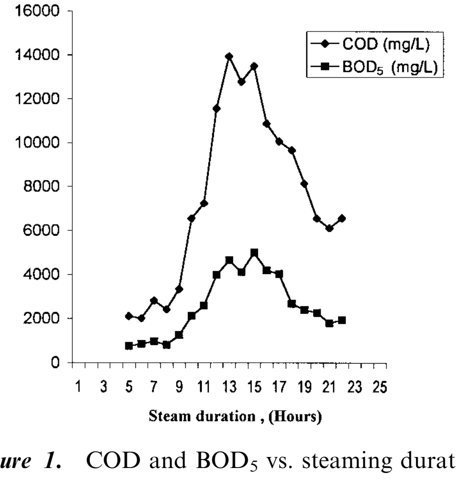

Figure 1. COD and BOD$_5$ vs. steaming duration.

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BOD_5 levels over time during steaming treatment. The condensates were acidic, pH values vs. duration listed in Figure 2.

The electrical conductivity of the condensate varied from 1.000 to 2.000 μs (Figure 3). The electrical conductivity is attributed to the mineral acidic compounds and probable contamination from the steaming chamber. These included Fe, Mg, Mn, Ca from the wood or the steaming chamber. The mineral substances present in beech condensate are low. The values obtained were 2.8 mg of calcium per gram of lyophilized condensate, iron (0.3 mg/g), manganese (0.2 mg/g) and magnesium (0.6 mg/g).

The total suspended solids (TSS) in the condensate ranged from 222 to 420 mg/L (Table 1), and were higher than the level allowed in France. The total suspended solids may come from the loose fibers, and/or from the

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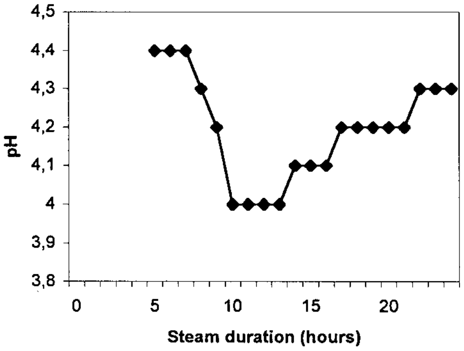

Figure 2. Conductivity vs. steaming duration.

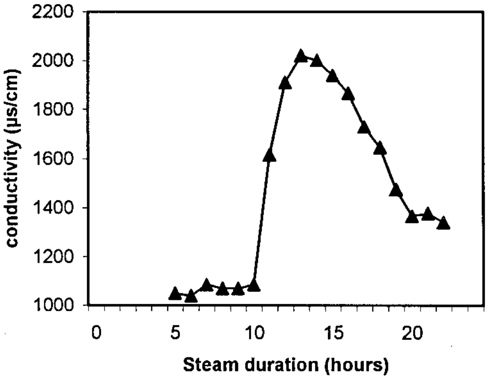

Figure 3. Carbohydrates content vs. steaming duration.

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steaming process degrading some of the wood structural components to give a more friable surface.

Quantitative Analysis of Condensate

Figure 4 shows the content of carbohydrate in the beech condensate as a function of the steaming duration. Figure 4 clearly suggests that the amount of carbohydrates in the condensate reaches a maximum after 6 to 8 h steaming, then decreases to about 250 mg/L before increasing again to 120–150 mg/L after 40 h. The initial yellow-colored condensate between 0 to 4 h and after 35 h can also be attributed to the presence of phenolic acids and benzaldehydes and dehydrated sugar compounds from wood. Figure 5 represents the content of phenol compounds.

Qualitative Analysis

The TLC chromatography of carbohydrates showed the presence of glucose, galactose, xylose, mannose and/or arabinose in the condensate. Fructose, saccharose, raffinose and stachyose were also identified. These findings are in accordance with published work.[13]

The identification of xylose, arabinose and mannose in the condensate between 35 to 44 h steaming confirms the presence of hemicelluloses. Derived sugars in agreement with the literature.[14,15]

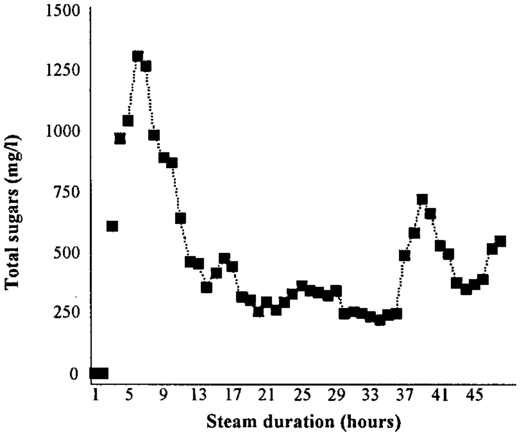

Figure 4. Condensate pH vs. steaming treatment.

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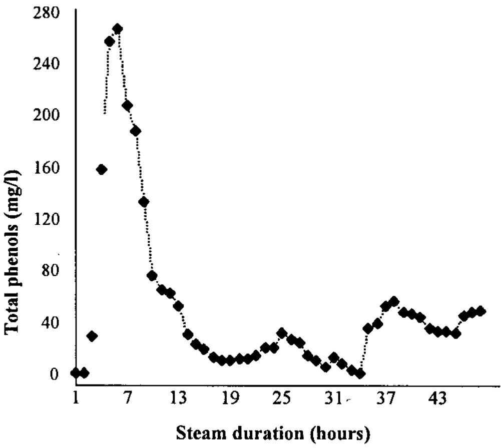

Figure 5. Total phenol content vs. steaming duration.

A previous study reported a relatively high contribution of phenols and carbohydrates in the value of COD. This trend was confirmed in this work with the relatively high value of COD between 4 to 13 h of steaming. Some chemical compounds were identified by GC. A total of 5 compounds (syringic acid, vanillic acid, *p*-hydroxybenzoic acid, syringaldehyde, vanillin) were eluted and identified as phenolic acids and aldehydes. Gas chromatograms showed good resolution of authentic aldehyde and acid products. Alkaline nitrobenzene oxidation of lignin was used to cleave the C6-C3 and C6-C1 constituents of lignin.[16] Syringic and vanillic acid and their aldehydes were identified, as previously described in Ref. [17]. Another plausible explanation, is the conversion of *p*-hydroxybenzaldehyde into its acid form, which is undetectable by the GC method used in this study.[12]

The lignin–carbohydrate complexes were identified in the second stage from 35 to 44 h of steaming treatment. Vanillic acid and syringic acid were identified. This result is similar to those obtained in Ref. [18]. Xylose was identified in the aqueous residual fraction after alkaline hydrolysis. This result showed the presence of a hemicellulosic fraction.

CONCLUSIONS

Characterization of the condensate from steam treating beech wood, indicated that carbohydrates and phenolic compounds were the major

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compounds formed during the first 13 h of treatment. A maximum discharge occurred during the first 13 h of steaming treatment.

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