Characterization and Treatment of the Condensate Generated from Steaming of Beech Timber prior to Kiln-Drying

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ABSTRACT

During steaming of timber, the hydrothermal treatment with saturated water vapor at elevated temperatures leads to numerous decomposition reactions within the wood. Condensate samples were collected from industrial kilns with direct and indirect steaming systems. Their composition was analyzed to determine the concentration of organic compounds like acids and carbohydrates as well as COD and BOD parameters. Aerobic and anaerobic biological treatment tests were carried out to examine the biodegradability of the condensate ingredients. Both methods exhibited high elimination rates of the organic components.

INTRODUCTION

Hydrothermal treatment techniques in wood processing are of major interest in wood engineering research. Besides kiln drying, the steaming of logs or timber is a process widely used in the forest industry to improve wood quality and achieve certain properties for easier processing. In Europe, the most common steamed species is beech, which covers about 20 percent of the forest area in Germany. Steaming for color is the most important reason for treating beech timber. Condensates of this process are the main subject of the investigation reported here. For the production of veneer, logs are steamed or cooked to soften the wood and allow smoother cutting. The mentioned desired wood modifications also bring about undesirable by-products, which are accumulated in the generated condensate. The objective was therefore to analyze the condensate composition and to investigate techniques for a possible onsite pretreatment before discharge. Results of both qualitative and quantitative characterization of industrial condensate samples as well as biological treatment tests will be presented in this paper.

Steaming of timber takes place in steam kilns or combined steam-dry kilns at atmospheric pressure and temperatures between 80 and 100°C. Some kilns are also equipped for pressure steaming and higher temperatures. Steam generation can be either direct by injection of live steam or indirect by evaporation from a heated water pool in the kiln floor. In the kilns with direct steam systems the condensate is collected in a water trench in the floor and continuously drained from the chamber. In the case of indirect steaming the condensate flows back into the heated water pool and can be re-used for steam generation.

As agreed in literature, steaming is an autohydrolysis process because of the naturally acid conditions and the influence of water and steam (Korte 1991). Hydrolysis is believed to cause several parallel and subsequent or overlapping chemical reactions breaking lignin-carbohydrate bonds and liberating hemicelluloses (Kubinsky and Ifju 1973). Water-soluble hydrolysis products and other substances are leached out by water condensing from steam and accumulated in the condensate. Numerous investigations about the chemical changes during steaming inside the treated wood have been carried out (Yilgor 2001). However, only a few publications have focused on the composition of steaming effluents.

Early work was carried out by Plath and Plath (1955) using paper chromatography on condensate from direct steaming of round beech logs. Laurová and Bucko (1998) analyzed condensate from direct high
pressure steaming of beech timber. Lipid compounds in condensate from cooking of birch logs were identified by Ma et al. (1999). Bujanovic, Danon and Kolin (2000) investigated condensate from direct/indirect steaming and cooking of beech timber by spectroscopy. In the most recent study Irmouli (2002) and co-workers carried out a study on condensate from direct steaming of beech timber. While most of the above authors mentioned the necessity for treatment of condensates before discharge, only Ma et al. (1999) have carried out a biodegradation test.

MATERIALS AND METHODS

Condensate Samples

Condensate samples from 8 different industrial steaming kilns in Germany were analyzed. Among those, 16 samples were taken from direct steaming and 5 from indirect steaming processes of beech timber (fagus silvatica). Kiln and timber volumes were 20...330 m³ and 7...100 m³ respectively. Steam temperatures took values between 80 and 135 °C, steaming times ranged from 8 to 104 hours. Provided condensate samples of 1...2 l were stored at 4 °C and analyzed within 24 hours or kept at -18 °C for later use. For all performed biodegradation tests condensate from direct steaming of beech was used.

Analysis of Condensates

Bulk parameters

Chemical oxygen demand COD, biochemical oxygen demand BOD₅, total phosphorus, total nitrogen, total phenols and total/inorganic carbon (TC/TIC) were determined photometrically with standard test kits (LCK, ISIS 6000; Dr.Lange, Germany). The condensate acidity was measured using a pH-Meter model 761 from Knick (Berlin, Germany). Conductivity was determined with the help of a conductivity meter LF 537 from WTW (Weilheim, Germany). Basic and acidic buffer capacities were obtained by titration with 0.01 n sulfuric acid (pH = 3) and 0.01 n sodium hydroxide solution (pH = 7) respectively. Total amount of solids was determined by drying a sample of 5 g at 110 °C. As a measure of the condensate's toxicity the light inhibition of luminescent bacteria was utilized (DIN 38412L34/341) employing a Dr.Lange LUMIStox 300 measuring system.

Concentration of organic compounds

The organic substances (formaldehyde, saccharides, formic acid) were analyzed using High Performance Liquid Chromatography (Merck HPLC-equipment) applying respective standards for the identification and quantification of the investigated compounds. Organic acids from acetic acid (C2) up to capric acid (C10) as well as aldehydes and other organic compounds were determined by Gas Chromatography (HP 5890 with autosampler). To aid and confirm identification of selected compounds solid phase microextraction (SPME) was employed.

Condensate Treatment

Acidity and dissolved oxygen concentration during the biodegradation tests were measured with a pH-meter pH96 and a DO-meter Oxi96 (WTW Germany) respectively. Dry weight percentage of the sludge-wastewater mix was determined as the total amount of suspended solids (MLSS), which was calculated from the mass difference of drying residues from filtered and unfiltered samples of 10 ml at 105 °C. Activated sludge (TSS ≈ 3 g/l) from a local municipal waste water treatment plant (Dresden-Kaditz) was used as a source of inoculum.

To evaluate possible inhibitory effects by the condensate, the Zahn-Wellens method (ISO 9888) was applied in a preliminary investigation of the aerobic biodegradability of the condensate's organic compounds. Two dilutions of the direct steaming condensate (COD = 1000; 1320 mg/l) were tested in duplicate. Besides, one blank vessel (inoculum alone) and another vessel containing 3 g/l glucose solution as a reference substance were used. The vessels were agitated and aerated at 20...25 °C in the dark until no further degradation was detected. The biodegradation
process was monitored by determination of COD in filtered samples corrected with blank controls.

In the subsequent experiments, the sequencing batch reactor (SBR) process was tested as a possible treatment technique in a laboratory-scale apparatus. The SBR was chosen because of its flexibility to adjust to varying amounts and concentrations of different wastewater types (Wilderer et al. 1997). Glass fermentation vessels with stirring systems were used to run two parallel SB reactors (A, B) (Figure 1) with a reactor volume of 5 liters each, at 20…25 °C. Using direct steaming condensate, the COD of influent was increased from 3500 up to 6400 mg/l. In the final week of a total test duration of about 2 months pre-concentrated condensate (COD = 42,000 mg/l) was added to investigate the degradation of undiluted indirect steaming effluent. The diluted condensate was mixed with mineral solution to ensure an optimum ratio of nutrients. Operational conditions of the SBR were as follows:

- 24 hours/cycle, 1 cycle/day, 4 liters of fill and withdraw per cycle
- Fill: feed under mixed and aerated conditions over 7 hours (in 40 minute periods every 2 hours)
- React: starting with fill event and lasting 23 hours
- Settle & Decant: 1 hour

Every withdrawn charge of treated effluent was analyzed with regard to temperature, DO concentration, acidity, MLSS and filtered COD. Biodegradation was monitored by the determined COD concentrations in influent and treated effluent.

In addition to the aerobic bioremediation methods, the anaerobic biodegradability of the steaming condensate was investigated applying a test based on EN ISO 11734. The test substance was incubated with digesting sludge at 35±2 °C. The increase in headspace pressure in the vessels resulting from generation of carbon dioxide and methane by anaerobic microorganisms was detected and recorded by piezoresistive sensor-storage units in the vessel heads (Sensomat-Scientific AL 350 by Aqualytic Langen, Germany). At the end of the test, after sludge sedimentation, the parameters TIC, TC, COD, and BOD₅ of the supernatant liquor were determined.

### RESULTS AND DISCUSSION

#### Condensate Characteristics

All condensates exhibited various shades of brown or reddish brown color with visible suspended particles.

### Table 1. Characteristics of condensate from direct and indirect steaming of beech timber

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Direct Steaming</th>
<th>Indirect Steaming</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD [g/l]</td>
<td>0.925 ..18.6</td>
<td>26.2......149</td>
</tr>
<tr>
<td>BOD₅ [g/l]</td>
<td>0.230 ..7.60</td>
<td>7.70......35.7</td>
</tr>
<tr>
<td>pH</td>
<td>4.0 ......5.7</td>
<td>4.3........5.0</td>
</tr>
<tr>
<td>Acidic / [mmol/l]</td>
<td>0.9 ......21.6</td>
<td>33.3....74.3</td>
</tr>
<tr>
<td>Basic buffer capacity</td>
<td>2.2 ......20.0</td>
<td>20.4..128.8</td>
</tr>
<tr>
<td>Conductivity [mS/cm]</td>
<td>0.3 ......12.1</td>
<td>3.3........12.4</td>
</tr>
<tr>
<td>Total P [mg/l]</td>
<td>10 ........46</td>
<td></td>
</tr>
<tr>
<td>Total N [mg/l]</td>
<td>14 ......119</td>
<td>145........243</td>
</tr>
<tr>
<td>Total solids [m-%]</td>
<td>0.04 ......1.60</td>
<td>1.91...11.80</td>
</tr>
<tr>
<td>Total phenols [mg/l]</td>
<td>9 ........279</td>
<td>217......552</td>
</tr>
<tr>
<td>Toxicity (light inhibition) [%]</td>
<td>64 .......99.9</td>
<td>68.......99.9</td>
</tr>
<tr>
<td>Saccharides [mg/l]</td>
<td>105 ....2958</td>
<td>474.......977</td>
</tr>
<tr>
<td>Organic Acids [mg/l]</td>
<td>96 ......1805</td>
<td>608.....4638</td>
</tr>
</tbody>
</table>

Cumulative condensate parameters for direct and indirect steaming effluents are summed up in Table 1.

**Bulk parameters**

The condensates from steaming can be labeled mildly acidic. Acidity did not change notably with acid concentration. This is explained by the presence of weak organic acids and salts forming a buffer system in the range of pH = 4.5…5.5. While the measured acidic buffer capacity increased with rising acid concentration, the basic buffer capacity was proportional to the condensate’s conductivity. The parameters TP, TN, and TS characterized the condensate as a possible nutrient solution in the case of a biological treatment, for which a ratio of BOD₅:N:P = 100:5:1 should be obeyed.

The average values of 8880 mg/l and 2850 mg/l for chemical COD and biochemical oxygen demand BOD₅ confirm the data previously reported in the literature (Irmouli et al. 2002, Laurová and Bucko 1998) for direct steaming effluents. The higher maximum values are a result of pressure steaming treatment at temperatures above 100 °C. Condensates of the indirect steaming process contain about ten times higher amounts of oxidizable substances, because - as mentioned before - condensate is re-used and thus concentrated over one or more kiln charges.

**Concentration of organic compounds**

The presence of saccharides is a result of the hydrolytic degradation of hemicelluloses, during which polysaccharides are depolymerized to oligosaccharides and monomeric sugar units (Plath 1955). This process is
accelerated by the liberated acetic acid, which is formed from the acetyl groups of hemicelluloses (Garrote 1999). The sugars rhamnose, xylose, glucose, saccharose and for 2 samples mannose were identified. Mannose was not found in condensate from indirect steaming. In contrast to other parameters, direct steaming produced a higher sugar concentration in condensate than indirect steaming. The presence of xylose can be attributed to the high xylan contents in beech (Fengel 1989).

The increase of acid content in the condensate is mainly due to acetic acid, which was in the range of 87...1525 mg/l and 608...4205 mg/l for direct and indirect steaming respectively. Besides acetic acid, formic acid was identified in direct steaming effluent. It is formed mainly at higher temperatures as a result of the splitting of furfural and considerably enhances hydrolytic degradation processes (Runkel 1951). In addition, small amounts of propionic and butyric acid and, in the case of indirect steaming, valeric acid could by detected. Overall acid concentration in condensate of indirect steaming was almost fourfold the value of direct steaming.

The existence of phenols in the condensate can partly be traced back to water-soluble lignin fragments, which are preferably liberated under acidic conditions at elevated temperatures. In addition, soluble native phenolic compounds present in wood tissue may be extracted by steam or hot water treatment (Burtin et al. 2000). Measured phenols concentration for direct steaming condensate was between 9 and 279 mg/l, which agrees with the values reported by Irmouli et al. (2002). Formaldehyde is released from degradation of hemicelluloses, which also leads to the formation of furfural. Furthermore, the treatment of lignin with acids leads to the liberation of formaldehyde (Schaefer and Roffael 2000). Detected formaldehyde concentrations were between 0.2 and 2.9 mg/l in all tested condensates. Effluent from indirect steaming contained higher amounts of phenols and aldehydes than direct steaming effluent.

Toxicity

The measured toxicities (light inhibition of luminescent bacteria) ranged from 64 % to practically 100 % and were still as high as 90 % for 4 diluted (1:10) samples. The data reflected the influence of steaming technique with higher values for more concentrated samples of indirect steaming. However, the determined toxicity is strictly applicable only to the used bacteria type and can be different with regard to other organisms, e.g. those present in activated sludge.

Variation of Condensate Characteristics with Process Parameters

Direct steaming

To compare condensates from different kilns, the concentration was based on the dry wood mass using average condensate rates. Effluent rates per kiln ranged between 0.05 and 0.5 m³/h. The average amount of condensate per dry wood for direct steaming at atmospheric pressure was 8 ml/h/kgdrw corresponding to about 5 kg/h steam per m³ of wood.

An evaluation of condensate samples for different steaming times showed for most concentration parameters a maximum after the heat up period and a successive decrease towards the end of the process. This corresponded with a lightening of the sample color from a dark reddish brown to a less turbid light-brown. Figure 2 displays the COD rates per dry wood mass released with the condensates from direct steaming as a function of steaming time and steaming temperature (t = 11...28 h).

For the period with the highest emission (11...28 h), COD emission rates increased with rising process temperature (Figure 2). For high temperature levels (reached during pressure steaming), the amount of released oxidizable substances doubled compared to steaming at “normal” temperatures around 100 °C. This
relationship seems plausible considering the before-mentioned enhancement of hydrolytic and extractive processes at elevated temperatures and was also reported for round logs by Plath (1955).

**Indirect steaming**

As the condensate flows back into the heated water pool, the extracted substances are concentrated over the steaming time as in an evaporation process. For the incoming condensate the relationship between composition and steaming time or temperature can be assumed similar to that of direct steaming. The condensate is collected inside the kiln and drained only at the end of the process. Hence, the change in effluent composition with the number of steamed kiln charges is of interest for the discharge. COD and BOD₅ values after the first steamed timber charge were about 28,000 and 10,000 mg/l respectively and doubled after the second charge. After the seventh batch COD and BOD₅ levels reached 7 and 3.5 times the value of the first charge. This indicates the degradation of biochemically accessible substances, which is also manifested by the decrease of the effluent’s sugar contents. The successive concentration of the condensate is further documented by the growth of solids content from 2 to almost 12 mass percent. This occurs in connection with an increasing electrical conductivity and basic buffer capacity and a slower rise in acid concentration leading to a slightly higher pH value.

**Condensate Treatment**

Despite the inhibitory effects on luminescent bacteria, the Zahn-Wellens test demonstrated a good biodegradability of the condensate using activated sludge. No distinct adaptation phase could be recorded, degradation started immediately. Inhibitory effects as found for cultures of luminescent bacteria and pseudomonas could not be confirmed, presumably owing to the higher capacity of the biomass. The COD values decreased within the test duration of 92 hours from 1330 / 990 mg/l to 170 / 110 mg/l resulting - after correction with the parallel blank control - in eliminated COD values of 97 % and 93 % for the high and low dilution respectively. The biodegradation was also affected by the solution's acidity, which changed from a mildly acidic to a slightly basic value. Organic acids were rapidly eliminated. After 3 hours acidic acid was no longer present in the supernatant. The reference compound was removed by 95 % confirming the functional capability of the sludge.

In the subsequent experiments the SBR technology could be tested successfully in a laboratory apparatus as a possible treatment technique for the steaming effluents. As shown in Figure 3, in all test cycles a good effluent quality was obtained. The COD of the filtered withdrawn supernatant was always below 175 mg/l after the 23 hour reaction phase. With increasing test duration this concentration decreased, possibly due to sludge adaptation. Effluent BOD₅ values were at a low level of 9…17 mg/l. MLSS values were kept within a relatively high range of 3…4 g/l because of a strong growth of biomass. This caused the sludge loading to be in the range of 0.03…0.08 gBOD₅/(gMLSS⋅d) for both reactors indicating a low food to biomass ratio. The biomass had good settling characteristics and separated well within the clarifying period leaving a clear yet still light-brown supernatant with a very low suspended solids content. During a cycle, degradation processes led from acidic (pH ≈ 6) at the beginning to basic conditions (pH ≈ 8) at the end. At the same time dissolved oxygen concentration increased from very low values during the filling period to a level of 6…9 mg/l for most of the reaction phase.

No clear relationship between effluent COD values and sludge loading for the studied range could be established. However, as shown in Figure 3, lower average COD values were achieved for a lower sludge loading. Sufficient elimination rates could be obtained though at overall low sludge loading rates. COD and BOD₅ values of treated effluent were largely below 150 mg/l and 20 mg/l respectively, achieving the effluent limitations for a direct discharge. Considering the low BOD₅ levels, the residual COD is likely to consist of refractory organic compounds such as lignins (Franta 1997). Figure 3 also displays the relative removed influent COD for different ratios of food to biomass documenting the good degree of elimination.

![Figure 3. COD of treated effluent (---) and COD elimination of reactor A (x), B(+) as a function of sludge loading](image-url)
Degradation ranges for reactors A and B were 95.9...99.7 % and 95.0...99.7 % respectively. The highest relative COD elimination levels were reached at the highest sludge loading rates investigated. A single analysis of phenols for a cycle revealed a degradation of 97 %, from 58 mg/l in the influent to 2 mg/l in the effluent.

As a result of the anaerobic treatment test, the biodegradation according to EN ISO 11734 was calculated from the amount of converted carbon in the headspace and net inorganic carbon formation in the liquid phase in excess over the blank control values. During the test 44...56 % of the carbon added with the condensate was degraded. The COD elimination was between 70 % and 80 %.

CONCLUSION

The main classes of organic compounds of the mildly acidic steaming condensate samples were saccharides from the hydrolytic degradation of hemicelluloses, organic acid liberated by de-acetylation of hemicelluloses, aldehydes, and phenols. Compared to direct steaming, condensates of the indirect steaming process contained about ten times higher quantities of oxidizable substances due to the evaporation inside the kiln. During direct steaming the largest amount of compounds was liberated after the heat up period during the first 20 hours. A rising process temperature led to an increased release of oxidizable substances. Though tests with luminescent bacteria showed inhibitory effects for condensate samples, bioremediation experiments with activated and digesting sludge did not confirm these results. Both aerobic and anaerobic treatment tests demonstrated a good biodegradability. SBR technology was found to be suitable for treating the condensate reaching effluent levels for a direct discharge.

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