Comparison of VOC Emissions from Natural Wood and Heat Treated Wood

Usporedba emisije hlapljivih organskih spojeva iz prirodnog drva i toplinski obrađenog drva

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ABSTRACT • This paper describes the emissions of Volatile Organic Compounds (VOC) emitted by solid Spruce (Picea abies) and Poplar (Populus alba) wood treated at 200 °C and 180 °C. The emissions of VOC from heat treated wood and air-dried (natural) wood were compared with GC-MS analysis. The focus was on the influence of temperature, on the quality and quantity of volatile organic compounds, especially on the amount of emitted phenol and furfural. Furfural and phenol are typical chemicals produced as a result of thermal degradation of wood components. The emission was analyzed as a function of time after heat-treatment. The influence of the finishing with waterborne lacquer on VOC emission was also investigated.

The results of this research have shown that heat treated wood emitted more VOC-components of furfural and phenol than untreated wood (natural wood). The amount of emitted VOC declines with increasing the time between wood modification and measurement of VOC emissions emitted by tested samples. Heat treated wood finished by waterborne lacquer emitted a very high concentration of Butoxy-ethanol. The finished surface does not decrease the amount of emissions escaping from heat-treated spruce and poplar wood.

Keywords: VOC emissions, spruce, poplar, heat-treated wood, gas chromatography

SAŽETAK • U radu su predstavljeni rezultati istraživanja emisije hlapljivih organskih spojeva (VOC) iz cjevovitog drva smreke (Picea abies) i drva topole (Populus alba), toplinski obrađenog pri 180 i 200 °C. Emisije VOC-a iz toplinski obrađenog drva i iz prosušenoga neobrađenog (prirodnog) drva uspoređene su primjenom GC-MS analize. Naglasak istraživanja bio je na utjecaju temperature na kvalitetu i količinu hlapljivih organskih spojeva, posebice na količinu emitiranog fenola i furfurala. Furfural i fenol tipični su kemijski spojevi koji nastaju toplinskom degradacijom drvnih komponenta. Emisija VOC-a analizirana je u ovisnosti o vremenu nakon toplinske obrade. Istraživan je i utjecaj završne obrade drva prema značajnoj na bazi vode na emisiju VOC-a. Rezultati istraživanja pokazali su da toplinski obrađeno drevo emitira više VOC komponenta furfurala i fenola nego neobrađeno (prirodno) drvo. Količina emitiranog VOC-a smanji se s porastom vremenskog razmaka između toplinske obrade drvnih uzoraka i mjerenja emisije VOC-a. Toplinski obrađeno drvo koje je završno obrađeno

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1 INTRODUCTION

Heat-treatment of timber is used to modify the properties of wood to resist dimensional changes in different humidity (Westin et al., 2001), to achieve better heat insulation, improved decay and weather resistance, reduced deformations due to changes of equilibrium moisture content and new shades of colour as an alternative to tropical hardwood.

The heat treatment process involves exposing wood to elevated temperatures from 160 to 260 °C (Militz, 2002). The temperature and duration of heat treatment generally vary from 180 to 280 °C and 15 min. to 24 h depending on the process, wood species, sample size, moisture content of the sample and the desired mechanical properties, resistance to biological attack and dimensional stability of the final product (Militz, 2002; Kamdem et al., 2002; Sanderman and Augustin, 1964).

Heat-treated wood is an eco-friendly alternative to impregnated wood materials, and heat treated wood can be used for garden, kitchen and sauna furniture, cladding on wooden buildings, bathroom cabinets, floor material, musical instruments, ceilings, inner and outer bricks, doors and window joinery and a variety of other outdoor and indoor wood applications (Syrjanen and Oy, 2001).

The main constituents of wood are cellulose, hemicelluloses, and lignin, which are accompanied by minor amounts of extractives and inorganic compounds. The volatile organic compounds (VOCs) emitted from wood during the drying process have been well investigated (Lavery and Milota, 2000; Milota, 2000), also as a function of temperature (Banerjee et al., 1998; Su et al., 1999; Wu and Milota, 1999) and humidity (Banerjee et al., 1998; Wu and Milota, 1999). The chemical changes occurring during the actual heat-treatment were also analysed (Kotilainen, 2000). Currently, there are already some reports on VOCs emitted from heat-treated wood. Since heat-treated wood materials and products are used indoors, safety and impact of these new materials on the indoor air quality should be determined. This is especially important, as it has been found that the soluble extracts of heat-treated maritime pine and poplar timber contained potentially toxic polynuclear aromatic hydrocarbon (PAH) derivatives (Kamdem et al., 2000).

Heat treatment affects all the wood components, i.e. cellulose, hemicelluloses, lignin, and extractives. Emissions and degradation products of wood differ according to wood species. Differences can be especially detected between hardwood and softwood, which have different cell types (Sjöström, 1993).

Thermally modified wood is less hygroscopic and more dimensionally stable.

This has been attributed to degradation of hemicelluloses and to condensation reactions that hinder the uptake of moisture by forming new bonds between wood polymers such as lignin (Alén et al., 2002; Sivonen et al., 2002; Windeisen et al., 2007; Tjeerdsma and Militz, 2005). Degradation of hemicelluloses may take place via formation of soluble carbohydrates, and formation of volatile products (Alén et al., 2002; Windeisen and Wegener, 2009). Furans are well known thermal degradation products of polysaccharides; for example furfural (F) and 5-(hydroxymethyl) furfural (HMF) are abundant (Alén et al., 2002; Peters et al., 2008).

Long and Wang (2007) investigated the emissions from four common woods (spruce, poplar, masson pine, and Eucalyptus urophylla) at room temperature using high-performance liquid chromatography and gas chromatography, and the results revealed the principles of release for aldehydes and terpenes. Similarly, Hyttinen et al. (2010) compared the VOCs emitted from air-dried and heat-treated Norway spruce, Scots pine, and European poplar woods in an enclosed metal chamber and discovered the effect of different treatment conditions on volatile compounds.

Furfurals have a nutty smell and contribute a lot to the odour of heat-treated wood together with other substances such as maltol or acetic acid (Miller, 1998). Furfural is very volatile and an essential part of VOCs. Furfural can also evaporate from finished products.

The aim of the research was to find differences in the amount of Volatile Organic Compounds emitted by heat-treated samples at different temperatures (180 °C and 200 °C) and untreated wood without finished surface compared to those with finished surface with the waterborne lacquer. The investigation of VOC emissions emitted by heat-treated wood has to be focused on the influence of the finished surfaces of tested samples on the amount of VOC emissions.

It is very important to find correlation between the type of waterborne lacquer used for the surface finishing and VOC emissions and also to identify individual volatile organic compounds from the thermally modified wood without finishing.

2 MATERIALS AND METHODS

2.1 MATERIJALI I METODE

The tested woods (spruce (Picea abies L. Karst.) with the density of 0.41 g/cm³ and poplar (Populus alba L.) with the density of 0.39 g/cm³) obtained from KATRES company Ltd., Czech supplier of heat-treated wood, were investigated. The pre-dried wood samples were modified at 180 °C and 200 °C in a heat treatment process.

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2.1 Density determination of test samples

Prior to heat treatment, samples were dried in a heating oven at 103 ± 2 °C. The oven-dry weight of the samples was determined. After the heat treatment, the oven-dry weight of the same samples was re-measured. The weight loss (\(W_L\)) of the samples, caused by heat treatment, was calculated according to the following formula,

\[
W_L (\%) = 100 \left( \frac{W_{AH} - W_{WAH}}{W_{WAH}} \right)
\]

where \(W_{AH}\) is the initial oven-dry weight of the sample prior to heat treatment (g) and \(W_{WAH}\) is the oven-dry weight of the samples after heat treatment (g). The equilibrium moisture content (EMC) of the test samples was determined before the tests.

The air-dried density of the samples was determined according to the following formula (ISO 3131 1975),

\[
D_{12} = \frac{M_{12}}{V_{12}} (g/cm^3)
\]

where \(M\) is the sample weight (g) and \(V\) is the sample volume (cm³).

Untreated and heat-treated wood samples were prepared from the same tree. Air-dried wood samples were taken from the normal manufacturing process, wrapped in aluminium foils and delivered to the test laboratory.

The samples were cut into pieces with dimensions 740 mm x 40 mm x 2 mm (longitudinal, tangential, axial) and then divided into two halves.

The first half of these samples was put into the test chamber. The samples of heat-treated material were obtained directly from the production of heat-treated wood. These wood samples were also divided into two halves.

One half of these heat-treated samples were put into the chamber (ISO 16000-9, 2007) immediately after the delivery from the plant, where they were treated.

The second halves of untreated as well as heat treated samples were finished by waterborne lacquer (with non-volatile share of 35 %). Acryl-polyurethane water dispersion is achieved with the addition of special binders and water repellents. This coating system contains about 10 % of 2-buthoxyethanol (CAS: 111-76-2); 0.05 % of Benzisothiazolinon (CAS: 2634-33-5); 0.1 % of Methylisothiazolinon (CAS: 2682-20-4); 0.015 % of reaction mixture 5-chlor-2-methyisothiazol-3(2H)- on and 2-methylisothiazol-3(2H)-on (CAS:55965-84-9). The finished samples were placed into the chamber three hours after finishing.

2.2 Methodology of research

2.2. Metodologija istraživanja

In step 1, the samples of the air-dried wood (spruce and poplar) with an area of 1 m² were prepared for testing. Then, VOC emission emitted by different wood samples was collected into the desorption tubes on the sorbent Tenax TA (ISO 16000 part 1 and 5, 2007).

2.3 Thermal modification process

2.3. Proces toplinske obrade

Thermal modification was carried out using a small-scale laboratory heat treatment chamber (Katres company Ltd., Czech Republic) at 180 or 200 °C. The schedule of the five-stage thermal modification process throughout 50 hours was achieved with a temperature control system. Data of the heat-treatment process was monitored by (wet and dry bulb) thermometer, consisting of two thermometers, one dry and the other kept moist with water on a sock. Values give an indication of atmospheric humidity i.e. psychrometer difference.

The maximum temperatures (180 or 200 °C) were maintained for 3h.

2.4 Air samples

2.4. Uzorci zraka

In the present study, air samples from tested samples were collected onto Tenax TA adsorbent (sampling rate 200 mL·min⁻¹, time 180 min) from small space
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VOC emissions from test samples were measured as a function of time (time from insertion of test sample into the test chamber).

3 RESULTS

This research deals with VOC emissions emitted by solid Spruce (Picea abies) and Poplar (Populus alba) wood treated at 200 °C and 180 °C. The emissions of Volatile Organic Compounds from heat treated wood and air-dried (natural) wood were compared with GC-MS analysis.

VOC emissions from test samples were measured as a function of time (time from insertion of test sample into the test chamber). VOC emissions from natural wood, heat treated wood and finished surface of

Table 1. Emission of VOCs from untreated wood – spruce

| Compounds | Natural wood - untreated | Spruce wood - Drvo smreke |
|-----------|--------------------------|---------------------------|
| No. Unit / Jedinica | After 3 hours<sup>a</sup> | After 24 hours<sup>b</sup> | After 72 hours<sup>c</sup> | After 672 hours<sup>d</sup> |
| 1 Ethyl Acetate | <0.1 | <0.1 | 0.2±0.1 | <0.1 |
| 2 Benzene | <0.1 | 0.2±0.1 | 0.2±0.1 | 0.2±0.1 |
| 3 1-Methoxy-2-Propanol | (0.3±0.1<sup>e</sup>) | (0.1±0.03) | <0.1 | (0.8±0.2) |
| 4 Pentanal | (2±0.6) | (1.3±0.4) | (1.1±0.3) | (0.6±0.2) |
| 5 Trichlorethylene | <0.1 | <0.1 | <0.1 | <0.1 |
| 6 Toluene | (1±0.3) | (1±0.3) | (1.2±0.4) | (2±0.6) |
| 7 Hexanal | (5.4±1.6) | (4.4±1.3) | (3.8±1.1) | (2.1±0.6) |
| 8 Tetrachlorethylene | <0.1 | 0.2±0.1 | 0.2±0.1 | 0.2±0.1 |
| 9 n-Butyl acetate | (1.3±0.4) | (0.4±0.1) | (0.9±0.3) | (0.9±0.3) |
| 10 Furfural | (7.8±2.3) | (2.5±0.8) | (1.8±0.5) | (1±0.3) |
| 11 Ethylbenzene | (0.7±0.2) | (0.2±0.1) | (0.5±0.2) | (0.7±0.2) |
| 12 m,p-Xylene | (1.8±0.5) | (0.8±0.2) | (1.8±0.5) | (2±0.6) |
| 13 Styrene | <0.1 | (0.1±0.03) | <0.1 | <0.1 |
| 14 o-Xylene | (0.4±0.1) | (0.1±0.03) | (0.4±0.1) | (0.4±0.1) |
| 15 Butoxy-Ethanol | (0.3±0.1) | (0.1±0.03) | <0.1 | <0.1 |
| 16 o-Pinene | (0.1±0.03) | (0.1±0.03) | (0.1±0.03) | (0.3±0.1) |
| 17 Camphene | <0.1 | <0.1 | <0.1 | <0.1 |
| 18 3-Ethyl-Toluene | (0.3±0.1) | (0.3±0.1) | (0.3±0.1) | (0.3±0.1) |
| 19 4-Ethyl-Toluene | (0.3±0.1) | (0.3±0.1) | (0.4±0.1) | (0.3±0.1) |
| 20 1,3,5-Trimethyl-Benzene | <0.1 | <0.1 | <0.1 | <0.1 |
| 21 Phenol | (0.7±0.2) | (0.5±0.2) | (0.5±0.2) | (0.3±0.1) |
| 22 n-Pinene | (0.4±0.1) | (0.4±0.1) | (0.2±0.1) | (0.2±0.1) |
| 23 2-Ethyl Toluene | (0.1±0.03) | (0.1±0.03) | (0.1±0.03) | (0.1±0.03) |
| 24 Myrcene | <0.1 | <0.1 | <0.1 | <0.1 |
| 25 1,2,4-Trimethyl-Benzene | <0.1 | (0.2±0.1) | (0.2±0.1) | (0.2±0.1) |
| 26 α-Phellandrene | <0.1 | <0.1 | <0.1 | <0.1 |
| 27 3-ð-Carene | (0.6±0.2) | (0.4±0.1) | (0.4±0.1) | (0.4±0.1) |
| 28 1,2,3-Trimethyl-Benzene | (0.1±0.03) | (0.1±0.03) | (0.1±0.03) | (0.1±0.03) |
| 29 Limonene | (1.1±0.3) | (0.4±0.1) | (0.4±0.1) | (0.1±0.03) |
| 30 y-Terpine | <0.1 | <0.1 | <0.1 | <0.1 |
| 31 Bornyl Acetate | <0.1 | <0.1 | <0.1 | <0.1 |
| 32 TVOC<sub>MS</sub> | (44±13) | (22±7) | (19±6) | (17±5) |

<sup>a</sup> Time of measurement (time from insertion of test sample into the test chamber) / Vrijeme mjerenja (vrijeme od stavljanja uzoraka u komoru do vremena proveđene mjerenja); <sup>b</sup> results are shown as average result expanded measurement uncertainty / rezultati su prikazani kao prosječna vrijednost rezultata ± proširena mjerna nesigurnost; <sup>c</sup> TVOC<sub>MS</sub> – Total Volatile Organic Compounds determined by Mass Spectrometry / ukupna emisija hlapljivih organskih spojeva određena masnom spektrometrijom.
heat treated wood were monitored during one month (i.e. 28 days) according the standard ČSN EN ISO 16000-9.

The results of measurements of emissions emitted by native spruce and poplar in dependence of time after the sample preparation are shown in Tables 1 and 2.

The surface of natural wood samples was treated by grinding before insertion of the test sample into the test chamber. Therefore, the wood structure was disturbed. This fact caused gradual release of chemicals, especially aldehydes (Pentanal, Hexanal). The values of TVOC is decreasing in time.

Based on the obtained results (Tables 1 to 4), it is concluded that heat-treatment of wood increases the quantity of VOC emissions emitted by tested samples. The main difference was found in the amount of emitted furfural and phenol in the gaseous blend evaporated by heat-treated spruce and poplar in normal conditions. The temperature of heat-treatment has a great influence on the treated wood.

The higher the temperature during spruce heat-treatment, the higher are the furfural emissions. Furfural and phenol are typical chemicals produced as a result of thermal degradation of wood components. The surface finished by waterborne lacquer does not decrease the amount of emissions escaping from heat-treated spruce and poplar wood. Surprisingly, waterborne lacquers even elevated the amount of VOCs.

Figures 2 and 4 show the influence of wood modification temperature and of the time between the VOC measurement and wood modification. The amount of emitted VOC declines with the increasing time between wood modification and measurement of VOC emissions emitted by tested samples. Heat-treated spruce wood

### Table 2: VOCs emitted by tested sample of untreated wood – poplar

| Compounds | After 3 hours<sup>a</sup> | After 24 hours<sup>a</sup> | After 72 hours<sup>a</sup> | After 672 hours<sup>a</sup> |
|-----------|--------------------------|---------------------------|---------------------------|---------------------------|
|           | Natural wood – untreated | Poplar wood               |                           |                           |
| No.       | Unit / Jedinica           | µg/m³                     | µg/m³                     | µg/m³                     | µg/m³                     |
| 1         | Ethyl Acetate             | (0.2 ± 0.1)<sup>b</sup>   | (0.4 ± 0.1)               | < 0.1                     | < 0.1                     |
| 2         | Benzene                  | < 0.1                     | < 0.1                     | < 0.1                     | < 0.1                     |
| 3         | 1-Methoxy-2-Propanol     | (0.1 ± 0.03)              | < 0.1                     | < 0.1                     | (0.8 ± 0.2)               |
| 4         | Pentanal                 | (1.6 ± 0.5)               | (0.8 ± 0.2)               | (0.3 ± 0.1)               | (0.3 ± 0.1)               |
| 5         | Trichlorethylene          | < 0.1                     | < 0.1                     | < 0.1                     | < 0.1                     |
| 6         | Toluene                  | (0.8 ± 0.2)               | (0.7 ± 0.2)               | (0.5 ± 0.2)               | (0.7 ± 0.2)               |
| 7         | Hexanal                  | (10.1 ± 3)                | (5.1 ± 1.5)               | (0.9 ± 0.3)               | (0.8 ± 0.2)               |
| 8         | Tetrachloretylene         | < 0.1                     | < 0.1                     | < 0.1                     | < 0.1                     |
| 9         | n-Butyl acetate          | (1.4 ± 0.4)               | (0.4 ± 0.1)               | (0.8 ± 0.2)               | (0.8 ± 0.2)               |
| 10        | Furfural                 | (1.3 ± 0.4)               | (1 ± 0.3)                 | (0.3 ± 0.1)               | (0.3 ± 0.1)               |
| 11        | Ethylbenzene             | (0.7 ± 0.2)               | (0.2 ± 0.1)               | (0.2 ± 0.1)               | (0.4 ± 0.1)               |
| 12        | m,p-Xylene               | (2.2 ± 0.7)               | (0.7 ± 0.2)               | (0.8 ± 0.2)               | (1.2 ± 0.4)               |
| 13        | Styrene                  | < 0.1                     | < 0.1                     | < 0.1                     | < 0.1                     |
| 14        | α-Xylene                 | (0.4 ± 0.1)               | (0.1 ± 0.03)              | < 0.1                     | (0.1 ± 0.03)              |
| 15        | Butoxy-Ethanol           | (0.1 ± 0.03)              | < 0.1                     | < 0.1                     | < 0.1                     |
| 16        | α-Pinene                 | < 0.1                     | < 0.1                     | < 0.1                     | < 0.1                     |
| 17        | Camphene                 | < 0.1                     | < 0.1                     | < 0.1                     | < 0.1                     |
| 18        | 3-Ethyl-Toluene          | (0.1 ± 0.03)              | (0.1 ± 0.03)              | < 0.1                     | (0.1 ± 0.03)              |
| 19        | 4-Ethyl-Toluene          | (0.3 ± 0.1)               | (0.3 ± 0.1)               | (0.1 ± 0.03)              | (0.1 ± 0.03)              |
| 20        | 1,3,5-Trimethyl-Benzene  | < 0.1                     | < 0.1                     | < 0.1                     | < 0.1                     |
| 21        | Phenol                   | (0.7 ± 0.2)               | (0.8 ± 0.2)               | (0.3 ± 0.1)               | (0.5 ± 0.2)               |
| 22        | β-Pinene                 | (0.1 ± 0.03)              | (0.1 ± 0.03)              | (0.1 ± 0.03)              | (0.1 ± 0.03)              |
| 23        | 2-Ethyl Toluene          | (0.1 ± 0.03)              | (0.1 ± 0.03)              | (0.1 ± 0.03)              | (0.1 ± 0.03)              |
| 24        | Myrcene                  | < 0.1                     | < 0.1                     | < 0.1                     | < 0.1                     |
| 25        | 1,2,4-Trimethyl-Benzene  | < 0.1                     | < 0.1                     | < 0.1                     | < 0.1                     |
| 26        | α-Phellandrene           | < 0.1                     | < 0.1                     | < 0.1                     | < 0.1                     |
| 27        | 3-δ-Carene               | (0.1 ± 0.03)              | (0.1 ± 0.03)              | (0.1 ± 0.03)              | (0.2 ± 0.1)               |
| 28        | 1,2,3-Trimethyl-Benzene  | (0.1 ± 0.03)              | (0.1 ± 0.03)              | (0.1 ± 0.03)              | (0.1 ± 0.03)              |
| 29        | Limonene                 | (0.1 ± 0.03)              | (0.1 ± 0.03)              | (0.1 ± 0.03)              | (0.1 ± 0.03)              |
| 30        | γ-Terpine                | < 0.1                     | < 0.1                     | < 0.1                     | < 0.1                     |
| 31        | Bornyl Acetate           | < 0.1                     | < 0.1                     | < 0.1                     | < 0.1                     |
| 32        | TVOC<sub>MS</sub>        | (24 ± 7)                  | (13 ± 4)                  | (10 ± 3)                  | (8 ± 2)                   |

<sup>a</sup>Time of measurement (time from insertion of test sample into the test chamber) / vrijeme mjerenja (vrijeme od stavljanja uzoraka u komoru do vremena provedbe mjerenja); <sup>b</sup>results are shown as average result ± expanded measurement uncertainty / rezultati su prikazani kao prosječna vrijednost rezultata ± proširena mjerna nesigurnost; <sup>c</sup>TVOC<sub>MS</sub> – Total Volatile Organic Compounds determined by Mass Spectrometry / ukupna emisija hlapljivih organskih spojeva određena masnom spektrometrijom.
### Table 3

| Compounds                  | Wood treatment process | 180 °C | 200 °C |
|----------------------------|------------------------|--------|--------|
|                            | After 3 hours          | After 24 hours | After 48 hours | After 72 hours |
|                            | After 672 hours        | After 72 hours | After 72 hours | After 72 hours |
|                            | After 3 hours          | After 24 hours | After 48 hours | After 72 hours |
|                            | After 672 hours        | After 72 hours | After 72 hours | After 72 hours |
| Ethyl Acetate              | < 0.1                  | < 0.1      | < 0.1      | < 0.1         | < 0.1         |< 0.1         |< 0.1         |< 0.1         |
| Benzene                    | < 0.1                  | < 0.1      | < 0.1      | < 0.1         | < 0.1         |< 0.1         |< 0.1         |< 0.1         |
| 1-Methoxy-2-Propanol       | (0.1 ± 0.03)           | < 0.1      | < 0.1      | < 0.1         | < 0.1         |< 0.1         |< 0.1         |< 0.1         |
| 1-Bromo-3-Methyl-2-Butene  | (7.6 ± 1.9)            | (5.8 ± 1.5)| (4.4 ± 1.2)| (5.4 ± 1.8)   | (4.1 ± 1.5)   |< 0.1         |< 0.1         |< 0.1         |
| 4-Pentanal                 | (0.5 ± 0.2)            | (0.3 ± 0.1)| (0.2 ± 0.1)| (0.3 ± 0.1)   | (0.2 ± 0.1)   |< 0.1         |< 0.1         |< 0.1         |
| 3 Toluene                  | < 0.1                  | < 0.1      | < 0.1      | < 0.1         | < 0.1         |< 0.1         |< 0.1         |< 0.1         |
| 6 Hexanal                  | (1.3 ± 0.4)            | (0.3 ± 0.1)| (0.3 ± 0.1)| (0.3 ± 0.1)   | (0.3 ± 0.1)   |< 0.1         |< 0.1         |< 0.1         |
| 7 Tetrachlorethylene       | < 0.1                  | < 0.1      | < 0.1      | < 0.1         | < 0.1         |< 0.1         |< 0.1         |< 0.1         |
| 8 Benzaldehyde             | (2.3 ± 0.6)            | (0.4 ± 0.1)| (0.4 ± 0.1)| (0.4 ± 0.1)   | (0.4 ± 0.1)   |< 0.1         |< 0.1         |< 0.1         |
| 9 n-Butyl acetate          | (2.1 ± 0.6)            | (0.4 ± 0.1)| (0.4 ± 0.1)| (0.4 ± 0.1)   | (0.4 ± 0.1)   |< 0.1         |< 0.1         |< 0.1         |
| 10 1,3,5-Trimethyl-Benzene | < 0.1                  | < 0.1      | < 0.1      | < 0.1         | < 0.1         |< 0.1         |< 0.1         |< 0.1         |
| 11 Phenol                  | (4.7 ± 1.4)            | (3.5 ± 1.1)| (3.5 ± 1.1)| (3.5 ± 1.1)   | (3.5 ± 1.1)   |< 0.1         |< 0.1         |< 0.1         |
| 12 1,3,5-Trimethyl-Benzene | < 0.1                  | < 0.1      | < 0.1      | < 0.1         | < 0.1         |< 0.1         |< 0.1         |< 0.1         |
| 13 Styrene                 | (0.3 ± 0.1)            | < 0.1      | < 0.1      | < 0.1         | < 0.1         |< 0.1         |< 0.1         |< 0.1         |
| 14 o-Xylene                | (0.2 ± 0.1)            | < 0.1      | < 0.1      | < 0.1         | < 0.1         |< 0.1         |< 0.1         |< 0.1         |
| 15 Behenyl Alcohol         | (0.1 ± 0.03)           | < 0.1      | < 0.1      | < 0.1         | < 0.1         |< 0.1         |< 0.1         |< 0.1         |
| 16 α-Pinene                | < 0.1                  | < 0.1      | < 0.1      | < 0.1         | < 0.1         |< 0.1         |< 0.1         |< 0.1         |
| 17 Myrcene                 | < 0.1                  | < 0.1      | < 0.1      | < 0.1         | < 0.1         |< 0.1         |< 0.1         |< 0.1         |
| 18 1,2,3-Trimethyl-Benzene | < 0.1                  | < 0.1      | < 0.1      | < 0.1         | < 0.1         |< 0.1         |< 0.1         |< 0.1         |
| 19 Limonene                | (0.6 ± 0.2)            | (0.2 ± 0.1)| (0.2 ± 0.1)| (0.2 ± 0.1)   | (0.2 ± 0.1)   |< 0.1         |< 0.1         |< 0.1         |
| 20 γ-Terpinene             | < 0.1                  | < 0.1      | < 0.1      | < 0.1         | < 0.1         |< 0.1         |< 0.1         |< 0.1         |
| 21 Bornyl acetate          | < 0.1                  | < 0.1      | < 0.1      | < 0.1         | < 0.1         |< 0.1         |< 0.1         |< 0.1         |
| TVOC                      | (98 ± 29)              | (51 ± 15)  | (46 ± 14)  | (22 ± 7)      | (80 ± 24)     | (54 ± 16)    | (27 ± 8)     |< 0.1         |
### Table 4: VOC Emissions from Test Sample of Heat Treated Poplar Wood at Temperature 180 and 200 °C

| Compounds | After 3 hours | After 72 hours | After 672 hours |
|-----------|---------------|----------------|-----------------|
| No. Unit | °C | μg/m³ | °C | μg/m³ | °C | μg/m³ | °C | μg/m³ |
| Ethyl Acetate | 3.1 ± 0.2 | 0.2 ± 0.1 | < 0.1 | < 0.1 | 0.1 ± 0.03 | < 0.1 | < 0.1 | < 0.1 | 0.7 ± 0.2 | < 0.1 | < 0.1 | < 0.1 | 0.2 ± 0.1 | < 0.1 | < 0.1 | < 0.1 |
| Benzene | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | (0.2 ± 0.1) | (0.2 ± 0.1) | (0.2 ± 0.1) |
| 1-Methoxyl-2-Propanol | 0.1 ± 0.03 | < 0.1 | < 0.1 | < 0.1 | (0.1 ± 0.03) | < 0.1 | < 0.1 | < 0.1 | (0.1 ± 0.03) | (0.1 ± 0.03) | < 0.1 | < 0.1 | < 0.1 | (0.1 ± 0.03) | < 0.1 | < 0.1 | < 0.1 |
| Pentanal | (3.1 ± 0.2) | (0.3 ± 0.1) | (0.3 ± 0.1) | (0.3 ± 0.1) | (0.3 ± 0.1) | (0.3 ± 0.1) | (0.3 ± 0.1) | (0.3 ± 0.1) |
| Trichloroethylene | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| Toluene | (18.5 ± 5.3) | (4.2 ± 1.1) | (4.2 ± 1.1) | (4.2 ± 1.1) | (4.2 ± 1.1) | (4.2 ± 1.1) | (4.2 ± 1.1) | (4.2 ± 1.1) |
| Hexanal | 1.1 ± 0.3 | 0.3 ± 0.1 | 0.3 ± 0.1 | 0.3 ± 0.1 | 0.3 ± 0.1 | 0.3 ± 0.1 | 0.3 ± 0.1 | 0.3 ± 0.1 |
| Tetrachloroethylene | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| n-Butyl Acetate | (3.6 ± 1.1) | (0.3 ± 0.1) | (0.9 ± 0.3) | (0.4 ± 0.1) | (0.8 ± 0.2) | (0.4 ± 0.1) | (0.1 ± 0.03) | (0.1 ± 0.03) |
| Furfural | (47.7 ± 14.3) | (32.3 ± 9.7) | (26.7 ± 8) | (13.8 ± 4.1) | (76.5 ± 23) | (48.2 ± 14.3) | (34.2 ± 10.3) | (18.7 ± 5.6) |
| Ethylbenzene | (1.7 ± 0.5) | (0.2 ± 0.1) | (0.2 ± 0.1) | (0.2 ± 0.1) | (0.4 ± 0.1) | (0.2 ± 0.1) | (0.2 ± 0.1) | (0.2 ± 0.1) |
| m,p-Xylene | (5 ± 1.5) | (0.3 ± 0.1) | (0.8 ± 0.2) | (0.7 ± 0.2) | (1.2 ± 0.4) | (0.7 ± 0.2) | (0.3 ± 0.1) | (0.5 ± 0.2) |
| Styrene | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | (0.1 ± 0.03) |
| o-Xylene | (1.1 ± 0.3) | (0.1 ± 0.03) | (0.1 ± 0.03) | (0.1 ± 0.03) | (0.3 ± 0.1) | (0.3 ± 0.1) | (0.1 ± 0.03) | (0.1 ± 0.03) |
| Butoxyl Ethanol | (0.1 ± 0.03) | < 0.1 | < 0.1 | < 0.1 | (0.1 ± 0.03) | < 0.1 | < 0.1 | < 0.1 |
| α-Pinene | (0.1 ± 0.03) | (0.1 ± 0.03) | (0.1 ± 0.03) | (0.1 ± 0.03) | (0.1 ± 0.03) | (0.1 ± 0.03) | (0.1 ± 0.03) | (0.1 ± 0.03) |
| Camphene | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| 3-Ethyl Toluene | (0.4 ± 0.1) | (0.1 ± 0.03) | < 0.1 | (0.1 ± 0.03) | (0.4 ± 0.1) | < 0.1 | (0.3 ± 0.1) | (0.3 ± 0.1) |
| 4-Ethyl Toluene | < 0.1 | (0.1 ± 0.03) | < 0.1 | (0.1 ± 0.03) | (0.4 ± 0.1) | < 0.1 | (0.3 ± 0.1) | (0.3 ± 0.1) |
| 1,3,5-Trimethyl Benzene | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| Phenol | (41.6 ± 12.5) | (33.4 ± 10.0) | (25.5 ± 7.7) | (16.3 ± 4.9) | (185.3 ± 55.6) | (93.7 ± 28.1) | (63.5 ± 19.1) | (41.7 ± 12.5) |
| β-Pinene | (0.1 ± 0.03) | (0.1 ± 0.03) | (0.1 ± 0.03) | (0.1 ± 0.03) | (0.1 ± 0.03) | (0.1 ± 0.03) | (0.1 ± 0.03) | (0.1 ± 0.03) |
| 2-Ethyl Toluene | (0.1 ± 0.03) | (0.1 ± 0.03) | < 0.1 | (0.1 ± 0.03) | (0.1 ± 0.03) | (0.1 ± 0.03) | (0.1 ± 0.03) | (0.1 ± 0.03) |
| Myrcene | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| 1,2,4-Trimethyl Benzene | (0.2 ± 0.1) | < 0.1 | < 0.1 | < 0.1 | (0.2 ± 0.1) | (0.2 ± 0.1) | (0.2 ± 0.1) | (0.2 ± 0.1) |
| α-Phellandrene | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| 3-δ-Carene | (0.4 ± 0.1) | (0.1 ± 0.03) | (0.1 ± 0.03) | (0.2 ± 0.1) | (0.1 ± 0.03) | (0.2 ± 0.1) | (0.1 ± 0.03) | (0.1 ± 0.03) |
| 1,2,3-Trimethyl Benzene | (0.1 ± 0.03) | (0.1 ± 0.03) | (0.1 ± 0.03) | (0.1 ± 0.03) | (0.1 ± 0.03) | (0.1 ± 0.03) | (0.1 ± 0.03) | (0.1 ± 0.03) |
| Limonene | (0.1 ± 0.03) | (0.1 ± 0.03) | (0.1 ± 0.03) | (0.1 ± 0.03) | (0.2 ± 0.1) | (0.1 ± 0.03) | (0.1 ± 0.03) | (0.1 ± 0.03) |
| γ-Terpinene | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| Bornyl Acetate | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| TVOC | (59 ± 18) | (52 ± 17) | (42 ± 12) | (42 ± 12) | (59 ± 18) | (52 ± 17) | (42 ± 12) | (20 ± 6) | (137 ± 41) | (68 ± 14) | (27 ± 8) |

**Note:** All values are in μg/m³, and concentrations are given for temperatures of 180 and 200 °C.
Figure 2 Amount of Furfural and Phenol emitted by heat-treated spruce wood after 3, 24, 72 and 672 h
Slika 2: Količina furfurala i fenola koju emitira toplinski obrađena smrekovina nakon 3, 24, 72 i 672 sata

Figure 3 Comparison of TVOC from Norway Spruce – heat treated wood at 180 °C and 200 °C and untreated wood
Slika 3: Usporedba TVOC-a koju emitira smrekovina – toplinski obrađena pri 180 i 200 °C i neobrađeno (prirodno) drvo

Figure 4 Amount of Furfural and Phenol emitted by heat-treated poplar wood after 3, 24, 72 and 672 h
Slika 4: Količina furfurala i fenola koju emitira toplinski obrađena topolovina nakon 3, 24, 72 i 672 sata
Čech: Comparison of VOC Emissions from Natural Wood and Heat Treated Wood

emitted more Furfural than Phenol, while the opposite was observed with heat-treated poplar wood.

Figures 3 and 5 show a comparison of TVOC from heat treated wood - spruce (*Picea abies*) and poplar (*Populus alba* L.) at 180 °C and 200 °C and untreated wood in dependence on time. The highest concentration of TVOC was emitted by thermowood at 200 °C. The measured values of TVOC decrease in time.

Figures 6 and 8 show the influence of wood modification temperature and of time between VOC measurement and surface finishing. The amount of VOC emission decreases with the decreasing temperature of wood modification. Heat treated spruce wood emitted a higher amount of furfural 3 hours after finishing (299 \( \mu g \cdot m^{-3} \)), while heat treated poplar wood emitted higher concentration of phenol (129 \( \mu g \cdot m^{-3} \)) after finishing.

Figures 7 and 9 present data of TVOC emitted by heat treated spruce and poplar wood before and after finishing. TVOC emitted by heat treated spruce and poplar wood significantly increased after finishing. This phenomenon can be explained by the increase of Buthoxy-ethanol, the amount of which is shown in Figures 10 and 11.

Figures 10 and 11 show the influence of wood modification temperature and of time between VOC measurement and surface finishing. The amount of Buthoxy-ethanol can be measured 3 hours after finishing. This phenomenon can be explained by the use of waterborne lacquer for finishing of heat treated wood. Waterborne lacquer used for finishing of heat treated wood contains about ten percent of this chemical (product safety data sheet).

4 DISCUSSION
4. RASPRAVA

Based on the results of this paper, VOC emissions from natural and heat treated wood can be assessed.
Figure 7 Comparison of TVOC from Norway Spruce – heat treated wood at 180 °C and 200 °C, before and after finishing

Slika 7. Usporedba TVOC-a koji emitira smrekovina – toplinski obradena pri 180 i 200 °C, prije i nakon završne obrade vodenim lakom

Figure 8 Amount of Furfural and Phenol emitted by heat-treated Poplar wood after finishing

Slika 8. Količina furfurala i fenola koji emitira toplinski obradena topolovina nakon završne obrade vodenim lakom

Figure 9 Comparison of TVOC from White Poplar – heat treated wood at 180 °C and 200 °C, before and after finishing

Slika 9. Usporedba TVOC-a koji emitira topolovina – toplinski obradena pri 180 i 200 °C, prije i nakon završne obrade vodenim lakom
Natural wood

Tables 1 and 2 show the concentrations of VOCs emitted by natural, untreated, spruce and poplar wood. One of the major compounds found in our VOC collection from air-dried wood, hexanal, is known to be formed by oxidation of unsaturated fatty acids (Risholm-Sundman et al., 1998). Hexanal has also been a frequently analysed compound in the emissions of parquets and other wood products (Saarela, 1999).

Concentrations of other individual volatile organic compounds (VOCs) are very low and their values are comparable to background values (from 0.1 µg m⁻³ for terpenes to almost 8 µg m⁻³ for furfural).

Values of TVOC (Total Volatile Organic compounds) are very low; however, values decrease depending on measurement time (Hyttinen et al., 2010).

Heat treated wood before finishing

The temperature of heat-treatment has a great influence on the amount of furfural emitted by tested heat-treated wood. The higher the temperature during spruce heat-treatment, the higher is the furfural emission. However, during poplar heat treatment, the phenol emission is higher compared to furfural. Furfural and phenol are typical chemicals produced as a result of thermal degradation of wood components.

Furfural and 5-hydroxymethylfurfural (HMF) are common degradation products from monosugars, where HMF is formed from hexoses, whereas furfural mainly originates from pentoses (Fengel and Wegener, 1983, Alén et al., 2002; Peters et al., 2008). Heat treated process used for thermally modified wood emitted more VOC emissions at the temperature of 200 °C than at 180 °C (Manninen et al., 2002). The highest amount of Furfural emitted by heat treated spruce wood at 200 °C amounted to 227 µg m⁻³ after 3 hours, while the highest amount of Phenol emitted by heat treated poplar wood amounted to 185 µg m⁻³, measured at the same time. Heat treated wood (spruce and poplar) emitted a very small amount of terpenes (from 0.1 to 0.7 µg m⁻³).

Heat treated wood after finishing

The surface finished by waterborne lacquer does not decrease the amount of emissions escaping from

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Čech: Comparison of VOC Emissions from Natural Wood and Heat Treated Wood

Figure 10 Amount of ButoxyEthanol emitted by heat-treated Spruce wood after finishing

Slika 10. Količina butoksiethanola koji emitira toplinski obrađena smrekovina nakon završne obrade vodenim lakom

Figure 11 Amount of Buthoxy-Ethanol emitted by heat-treated Poplar wood after finishing

Slika 11. Količina butoksiethanola koji emitira toplinski obrađena topolovina nakon završne obrade vodenim lakom
heat-treated spruce and poplar wood. Finished heat treated wood emitted high amounts of Butoxy-ethanol, especially by heat treated process at 180 °C (spruce emitted more than 8 000 µg m⁻³, poplar more than 6 000 µg m⁻³). This effect has a significant impact on the value of TVOC.

TVOC emissions were significantly higher from heat-treated than from normal, air-dried wood samples. Terpenes were the main compounds emitted from softwood (spruce) and heat-treatment decreased their emissions. Terpenes partly evaporate and partly degrade during the heat-treatment process (McGraw et al., 1999). 4-Methyl-1-(1-methylethyl)-benzene (p-cymene) and 1-methyl-2-(1-methylethyl)-benzene (o-cymene) were detected to a higher degree in air-dried than in heat-treated softwood samples. These compounds are degradation products of camphene, delta-carene, and limonene (McGraw et al., 1999).

Terpenes were the main compounds emitted from softwood samples. In agreement with (Peters et al., 2008), emissions of furfural increased and those of hexanal decreased in heat-treated wood samples when compared to the air-dried ones. This phenomenon was observed in all wood species. This was to be expected, because hexanal belong to the prevailing aldehydes in natural wood, whereas furfural is a major degradation product of hemicelluloses.

VOC emission profile changed dramatically during the heat treatment process. Although VOC emissions from the heat-treated samples were lower than from air-dried wood, oxidised organic compounds were also formed during the treatment. These have more unpleasant odour and are typically more irritating than terpenes, which dominate in the emissions of native softwoods. However, air-dried wood samples also emitted oxidised organic compounds, and terpenes might be oxidised to aldehydes and acids during the usage of the wood product (especially when ozone is present in the air). In the present study, emissions of wood species were tested for a month. Actually, VOC emissions from wood (as any other materials) under constant conditions keep decreasing at least for one year. However, TVOC emissions from heat-treated wood products were relatively low already in the first days of testing.

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Česk: Comparison of VOC Emissions from Natural Wood and Heat Treated Wood

The surface finished by waterborne lacquer does not decrease the amount of emissions escaping from heat-treated spruce and poplar wood. Surprisingly, waterborne lacquers even elevated the amount of VOCs.

In the next step of this research, focus should be placed on the study of the influence of heat treatment on VOC emissions emitted by different kinds of wood and influence of finished surfaces of heat treated wood. It would also be important to find the correlation between the type of surface finishing and VOC emissions, i.e. to study the effect of the quality and quantity of VOC emissions emitted by heat treated wood on the way of finishing the heat-treated wood.
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