

# Emission profile of thermal treatment Sitka spruce chips and fibres by HS-SPME/GC-MS technique

## *Abstract*

The aim of the work undertaken was to assess the emission profile, with special attention to the volatile organic compounds (VOCs), of Sitka spruce by headspace solid phase microextraction (HS-SPME) method combined with gas-chromatography-mass spectrometry (GC-MS). The emission profile from wood chips and fibres under different thermal treatments was assessed.

Emission profile of untreated wood chips consists only of terpene emission, presenting some aldehyde emission after heat treatments. Emission profile from fibres consists mainly in butylated hydroxytoluene (BHT) and acetone. Under thermal treatments, aldehyde emission can be identified as well as hydrocarbons release.

## **1. Introduction**

Sitka spruce (*Picea sitchensis*) is one of the most softwood common in Great Britain (Moore, 2011) used in the manufacture of three main types of wood-based panels (WBPs): particleboard (PB), oriented strand board (OSB) and medium density fibreboard (MDF).

Current regulations require wood panels industry to meet air emission standard, namely on volatile organic compounds (VOCs). Until now, no limit values for the upper VOC concentration emitted from wood and wood based panels have been taken under official regulation in Europe. However, some national regulations from EU countries, such as Germany and France have been published.

In the last years, the biggest efforts to reduce emission from wood-based panels were focused on formaldehyde emissions, driven by the reclassification of formaldehyde as “carcinogenic to humans (Group 1)” by International Agency of Research on Cancer (IARC 2006). Several formaldehyde scavengers can be found in the literature, from natural sources such as tannins, charcoal, pozzolan, wool, among others (Eom *et al.* 2006, Kim *et al.* 2006, Kim 2009, Curling *et al.* 2012). Other inorganic scavengers, such as sodium metabisulphite, were added and have shown excellent ability to reduce formaldehyde, allowing the production of “zero emission” boards (Costa *et al.* 2013a, Costa *et al.* 2013b).

Concerning other VOCs, scarce studies have been published. Costa *et al.* (2013c) have showed that sodium metabisulphite is also effective against other aldehydes, but has no effect on terpenes, or other VOCs.

VOC analysis can be performed through several techniques, which cannot be directly correlated. ISO 16000 defines equipment, sampling, as well as analytical procedures and is the method generally accepted for VOC emission from WBP; however it is very time

consuming and less versatile. Headspace Solid Phase Microextraction (HS-SPME) method in VOC analysis is a suitable and rapid sampling method, presenting also the advantages of a solvent free, non-destructive, allowing a direct analysis and comparable fast detection (Espert *et al.* 2005). SPME is very versatile, easy to use, flexible and portable technique, being applied with success in a large range of applications for VOC analysis (Zhu *et al.* 2013).

In this work was assessed the emission profile from Sitka spruce chips and fibres thermally treated using HS-SPME/GC-MS technique. Colour analysis was used to assess the effects of the thermal treatments on the fibres.

## **2. Materials and methods**

### **Materials**

Sitka spruce chips and urea-formaldehyde (UF) resin were collected from the Kronospan industrial plant (Chirk, Wrexham, UK).

### **Methods**

#### *Fibre preparation and boards production*

Fibres were produced from wood chips collected at the BC Technology Transfer centre at Mona Industrial Park, Anglesey, Wales. A standard protocol for fibre production in a pilot plant was followed (pressure: 8 bar, 2500 rpm).

Fibres were blended in a laboratory scale blender with a standard UF resin. Resin load was 12 % and pressing time was 240 seconds at 180 °C (platen temperature) for a panel with 12 mm of final thickness. Density target was 640 kg·m<sup>3</sup>. Two boards were produced for each fibre treatment (on a total of 6 boards).

#### *Thermal treatments*

Wood chips and fibres were placed in an oven coupled with a vacuum system. Pressure during the heat treatment was 100 ± 20 mbar.

#### *Colour analysis*

Colour analysis of boards were performed using Datacolour Check II plus. For each board, two measurements in two different places of the same board, in a total of four measurements per board. Two board replicates were considered for each test condition.

### *HS-SPME analysis*

Wood particles with  $0.15 \pm 5$  g and fibres with  $0.10 \pm 0.2$  g were placed in a 20 mL headspace vials (Figure 1). Vials with samples were then placed in a hot plate platform with controlled temperature at  $70$  °C (Figure 2). A Divinylbenzene / Carboxen / Polydimethylsiloxane (DVB/CAR/PDMS)  $50/30$   $\mu\text{m}$  fibre was used for sampling. First sampling starts after 10 minutes and was performed during 10 minutes (run 1); second sampling starts at minute 60 and was performed during 10 minutes too (run 2). Once sampling was complete, the fibre was immediately inserted in the GC injector for desorption.



Figure 1: Wood and fibre samples in headspace vials.



Figure 2: Sampling apparatus (left). Detail of the vial in the temperature controlled platform with DVB/CAR/PDMS fibre during sampling (right).

### *GC-MS analysis*

A PerkinElmer Clarus 680 GC coupled to a PerkinElmer Clarus 600C Mass Spectrometer detector was used. Chromatographic separation was performed with a capillary column

Agilent J&W VF-5ms with 30 m x 0.25 mm (0.25  $\mu\text{m}$ ); injector temperature 250 °C, 1 mL·min<sup>-1</sup> of helium as carrier gas and a split ratio of 2:1. The oven was programmed as following rates: initial temperature of 40 °C (2.5 minutes hold) followed by a ramp of 5 °C·min<sup>-1</sup> to 200 °C and a second ramp at 10 °C·min<sup>-1</sup> to 240 °C with a post-run for 5 minutes. The mass scan range was 40-600 with no solvent delay. Desorption time was 1 minute.

VOCs were identified by matching sample mass spectrum with those of the National Institute of Standards and Technology (NIST) MS spectral library for peaks presented in the chromatograms.

### **3. Results and discussion**

#### *MDF Colour analysis*

Colour analysis was carried out according to CIELAB method. Few differences are found between different boards. However, it is clearly seen that samples thermally treated at 215 °C are darker than controls and samples treated at 135 °C. These colour differences are not so clear than in fibres treated for GC-MS analysis (see Figure 2). These small differences are related to the amount of fibres treated at the same time in the oven. When a small amount are placed in the oven, uniform temperatures are easily achieved in all fibres; while when higher amount of fibres are placed in the oven, due to the low fibre thermal conductivity, the core mat does not attain the same temperature than in mattress surface. Despite temperature was not checked during treatment, it was visible colour differences between surface and mattress core.

#### *Emission profile from wood chips*

The first experiments concerning the optimization of the HS-SPME procedure was focused on sampling time and samples weight. No significant differences on GC-MS chromatograms were found when sampling were performed during 30 and 10 minutes. It was adopted a sampling of 10 minutes in order to avoid possible overload peaks on samples with higher concentration of VOCs. No differences were also found in samples with weight between 0.10 and 0.40 g. Nevertheless, wood chips were chosen in order to present similar weight and surface area.

When wood chips were analysed directly after collected from the industrial plant (moisture content  $\approx$  60 %), the VOCs emitted were terpenes (both in run 1 and run 2).

When wood chips were dried in an oven during 60 h at 100 °C the emission profile changes significantly. Terpenes are no longer the main source of VOCs, being overcome by aldehydes. Commonly, aldehydes are secondary emissions formed by oxidation of fatty acids in the wood (Steckel et al. 2011), which could be the cause of the increase of aldehydes

emission. Around one tenth of the total emission was acetone and between 20 to 25 % carbon dioxide. Despite carbon dioxide not being considered as a VOC, its presence is useful to understand the phenomena that can be involved during drying. Carbon dioxide is from the decomposition of wood cells structure (Anonymous, 2010). When these samples previously dried were submitted to a second thermal treatment at 135 °C, their emission profile changed again, increasing terpenes emissions.

When wood chips were placed in an oven at temperatures until 135 °C, no significant changes in their emission profile can be found when compared with wood chips. Only terpenes are emitted after thermal treatment. After 24 hours, the emission profile of these samples changed slightly, releasing also aldehydes. When samples were treated at 215 °C, no compounds are released (both in run 1 and run 2). However, after 24 hours, VOC emissions can be identified, namely terpene and aldehyde emission. Other VOCs in lower concentration can also be found as well as carbon dioxide.

#### *Emission profile from wood fibres*

No terpenes were found in fibre emission. Baumann *et al.* (1999) compared VOC emission from particleboards and MDF and stated that terpenes were almost completely absent in MDF samples. Temperature in the pressurized refiner, in this process, is generally held between 160 °C and 185 °C, resulting that this high temperatures may drive terpenes from the furnish resulting in lower emissions by the fibres. On the other hand, fibres emit a higher concentration of butylated hydroxytoluene (BHT) and acetone. BHT, as well as acetone, are usually related to the wood decomposition. Acetone may be formed promptly by oxidation of several terpenes (Wisthaler *et al.* 2001). Bhaskar *et al.* (2008) identified a higher concentration of BHT from softwood after hydrothermal treatment at 280 °C. In the same study, the presence of acetic acid was also reported. 24 hours after fibre production, a high amount of hydrocarbons (alkanes) are also released from fibres, being hexane and heptane the compounds in higher concentration, followed by other alkanes with longer carbon chains. Acetone emission is less relevant; however a significant amount of carbon dioxide can be detected.

Fibres exposed to thermal treatments at 135 °C do not release BHT; however a significant emission of aldehydes and acetone is detected. 24 hours after the treatment, aldehydes concentration increases substantially, becoming the main emitted group. Carbon dioxide emission contribution to the total emission also increased slightly, and no significant differences were found between run 1 and 2. Treatments at 215 °C, when compared with treatments at 135 °C, increased the contribution of aldehydes as well as for the hydrocarbons for the total emission profile. In the run 2, only BHT emission is found. Neither terpenes nor acetic acid emission was detected in fibres thermally treated.

#### **4. Conclusions**

Emission profile from Sitka spruce is strongly dependent on the heat treatment. HS-SPME/GC-MS demonstrate to be an interesting technique for emission profile characterization in wood chips and fibres.

Emission from wood chips before thermal treatment was only terpenes, however, after oven dry, main emission was composed by aldehydes, carbon dioxide and acetone. Wood chips exposed only at thermal treatment at 135°C or 215 °C emits terpenes, but also aldehydes, being the proportion of aldehydes to the total emission higher when higher temperatures are applied.

Fibres produced from these wood chips emit mainly acetone and butylated hydroxytoluene (BHT), however, after 24 hours, hydrocarbons and carbon dioxide emission are detected, while no acetone is released. When thermally treated, emissions are mainly constituted by aldehydes and acetone, and no BHT emission is found, except in the run 2 of samples exposed at 215 °C, where BHT is the unique compound detected.

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