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PROCESSING PELLETS TOWARDS LOW EMISSIONS

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ABSTRACT

Fuel pellets are usually produced from raw materials with high lignocellulosic content like bio-mass from wood, straw etc. with a huge variety of the raw material quality grades. While high calorific value is the most desired end-product property, other product characteristics are also of interest. Gas emissions could be crucial for the subjective acceptance of pellets as "green product" and could lead to higher indoor concentrations of unwanted volatile substances if the pellets are stored inside the premises.

VOC (volatile organic compounds) emissions from pellets produced from pine and spruce were evaluated at the early stages of the product lifecycle - from wood shredding through transport and storage of the freshly produced pellets. It was found out that the VOC emission profile depends on wood type and lifecycle stage. The emitted VOC belonged exclusively to the substance classes of terpenes and aldehydes. The observations showed that spruce- and pinewood based pellets differentiated mainly in their aldehyde emissions whereby pinewood based pellets emitted substantially more aldehydes. The treatment of pinewood chips with the blue stain fungus Ceratocystis coerulescens for four weeks led to a reduction in aldehyde emissions of the produced pellets with more than 80%.Thus the profile of the VOC emissions of treated pinewood based pellets was much more similar to that of spruce based pellets.

1 NTRODUCTION AND PROJECT BACKGROUND

Conversion of energy systems towards sustainable concepts is a mayor task nowadays. Reduced production of greenhouse gases is ecologically and legally desired. Expansion of the bio based energy sector supports this strategy and further helps to assure availability of energy as well as to increase local use of resources. However, there is a constant conflict concerning utilisation of such resources for solid applications such as for paper products or wood based products on the one hand, and energy carriers such as pellets on the other. At the same time there is a global conflict about the utilisation of agricultural and other spaces for breeding of food plants, and plants for solid or energetic use.

Three members from Austrian Cooperative Research (ACR), i.e. Holzforschung Austria (HFA), OFI Technologie & Innovation GmbH and Österreichischer Kachelofenverband (KOV), joined for a closer cooperation (www.BioUp.at), in order to gain further insight in processing and optimization of production steps and product utilities of pellets. One of the major tasks within this consortium is the procession of nowadays unutilized bio-based resources as well as the further engineering of existing production processes. Fresh wood as a typical industrial processed material is often understood as a typical reference material. This further helps to better understand functional principles such as impact of processing parameter on material friction or product properties. However, the BioUp is in general open for any kind of research task related to raw materials processing, process- and product engineering.

The present study is dedicated to the problem of emissions from the end product (fuel pellets). Off-gassing is nowadays widely discussed. Carbon monoxide (CO)-emissions from bio-based pellets are of major interest due to human health risk. The process of CO-emissions is widely unclear. Currently no distinct answer can be given which factors influence CO formation from stored pellets. However, it is hypothesized, that a reduction of VOC (volatile organic compounds)-emissions from the product might be associated with a reduced risk of CO-emissions (Rossner et al. 2013).

Processes influencing the VOC emission rate might occur undetected, such as due to production process stages, material aging while storage or generation of new surfaces due to manipulation. Especially process settings such as temperature or moisture content can be assumed to show significant influence on VOC emissions. On the other hand, the VOC emission spectrum might be influenced on purpose, if such processes are better understood. Furthermore, the VOC emission rate might also be reduced by additional processes, such as material modification. One promising wood modification process could be the application of blue-stain fungi.

The blue-stain fungus Ceratocystis coerulescens is known as an effective decomposer of unsaturated fatty acids in wood. Since unsaturated fatty acids are known to be precursors of volatile aldehydes (Svedberg et al. 2004) their reduction in the raw material can be expected to cause a reduction in the VOC emissions from the end product since aldehydes are known to be major constituents of the total volatile organic compounds (TVOC) emitted from pinewood based products. Blue stain fungi are particularly suited for selective decomposition of only the extractives content in softwood without degrading its lignocellulosic backbone (Stratev et al. 2011). Albino strains of blue staining fungi are commercially used as resin and fatty acids decomposers in the pulp production (Farrell et al. 1993). Similar applications are also known for solid wood products as well as for wood based panel products.

2 OBJECTIVES

Fuel pellets are usually produced from raw materials with high lignocellulosic content like bio-mass from wood, straw etc. with a huge variety of the raw material quality grades. While high calorific value is the most desired end-product property, other product characteristics are also of interest. Gas emissions could be crucial for the subjective acceptance of pellets as “green product” and could lead to higher indoor concentrations of unwanted volatile substances if the pellets are stored inside the premises.

The objectives of this research were 1) to characterize the VOC emissions from two different softwood based pellet types, 2) to demonstrate the impact of several production processes on VOC emissions from the processed material, 3) to evaluate the potential of fungal pretreatment of raw material (wood chips) in order to reduce the VOC emissions from pellets, and 4) to evaluate the changes in VOC emissions after pellets transportation and during their storage.

3 MATERIAL AND METHODS

Pellet production was performed within the BioUp pilot plant (see poster contribution within this symposium from Pichler et al. 2014).

3.1 Pellets production through processing of native wood species

Bark-free chips from Scotts pine (Pinus sylvestris) and Norway spruce (Picea abies) were selected as raw materials. TMP-woodchips (i.e. thermo-mechanical pulping chips) were obtained from two industrial saw-mills. Both chip species contained sapwood as well as heartwood or mature wood respectively. Figure 1 illustrates the processing and analytical pathways.

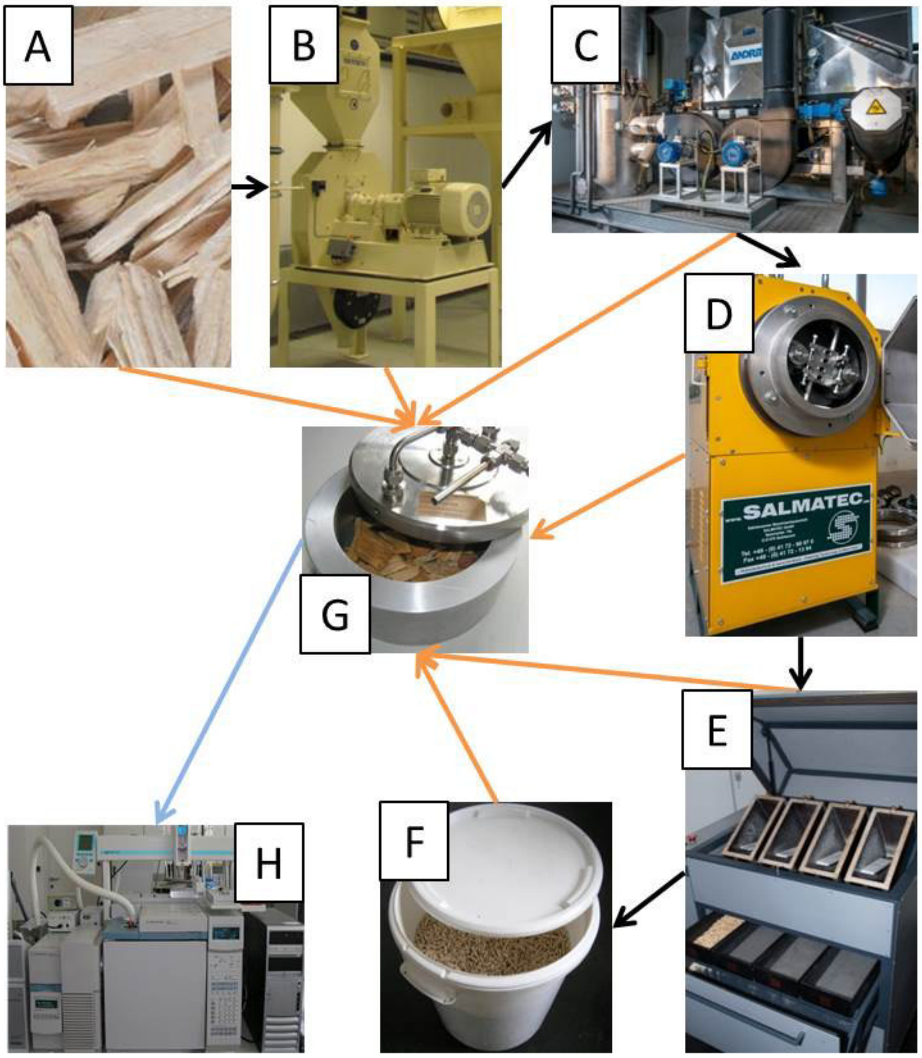

Figure 1. Pathways for material processing (dark arrows) and sampling (bright arrows): A) wood chips, B) hammer mill, C) belt dryer, D) ring die pellet press, E) tumbler, F) storage in closed buckets; F) modified FLEC including Tenax® sampling tube, G) TD-GC/MS

Wood chips (stage A) from pine and spruce were separately milled within a hammer mill (to stage B) and technically dried (to stage C) by using a belt dryer in order to gain optimum particle size and water content for further pelletizing. Pelletizing was conducted within a ring die pellet press (stage D). Freshly produced pellets were further processed (to stage E) within a tumbler loading pellets with mechanical forces thus simulating transportation processes (see below). The pellets were then stored in closed buckets (stage F) for up to six weeks in order to simulate aging. VOC (volatile organic compounds) emissions from all stages were evaluated through exposition of material sample aliquots in a modified FLEC cell (Field and Laboratory Emission Cell; by defined temperature and air flow rate) for a certain time interval and by trapping the volatiles in Tenax® sampling tube (stage G).

3.2 Pellets production through processing of fungal modified wood

Blue stain fungus-treated (*Ceratocystis coerulescens*) pine chips were also used as feedstock (stage A*) for the production of treated pellets (stage D*) in order to investigate the potential of the selected fungi for reducing VOC emissions. The fungal incubation period was chosen to be four weeks in order to ensure enough time for the fungus to metabolize the unsaturated fatty acids in the wood. The exact incubation conditions as well the inoculation scheme will be presented in a following extended article.

3.3 Examination of the influence of mechanical transport on VOC emissions

Mechanical as well as pneumatic transportation of pellets could also have impact on VOC emissions throughout product life time. Manipulation of pellets always yields formation of new product surfaces due to cross-sectional breaking and axial abrasion. Furthermore, while movement in the transportation sleeve the surface of the pellets is subjected to friction and as a result the material temperature rises. Primary VOC (*i.e.* volatile substances that evaporate directly from the material without any alteration) will tend to evacuate the pellets material faster than at neutral conditions. The pneumatic air ventilation at higher temperatures increases the oxidative potential of the pellets environment. Thus the autoxidative process which normally takes place in the fresh wood material (Roffael, 2006) and the corresponding secondary VOC Emissions (*i.e.* volatile substances that are formed from nonvolatile precursors as a result of oxidative processes) will be intensified.

For the examination of the impact of pneumatic transportation on VOC emissions a part of the freshly produced pellets (stage D) were not put into the tumbler thus forming the stage of the non-transported pellets (E*). These pellets were separately stored (to stages F*) and characterized regarding their VOC emissions and the results were compared against the “transported” pellets.

3.4 Time schedule of the experiments and labeling of the different stages

In virtue of limitations in the capacities of the production- and measurement- systems it was not possible that all pellet variances (spruce, untreated pine, treated pine, transported spruce etc.) were produced and examined simultaneously. This is usually the biggest drawback by conducting VOC related experiments, because during processing of one material fraction there are changes which occur in the VOC potential of the unprocessed material fractions. Therefore it is of importance to know the time schedule of the experiments in order to interpret the observed differences accordingly.

In the present study, the major time gap occurred due to fungal treatment of pine wood chips. This process took four weeks. Reference material was stored throughout this time under comparable conditions without any fungal treatment. However, this reference material was subjected to natural processes. Hence, the VOC emission spectrum changed within that time. In order to evaluate the impact of fungal treatment, a reference value for non-treated pine wood chips after four weeks storage was determined additionally.

3.5 VOC emissions determination

Aliquots of 25 g material were used for the VOC emission determinations. The material samples were added without any further processing (like drying) into a cylindrical aluminum chamber with an internal diameter of 150 mm and a volume of 1,68 l. A FLEC® cell (www.chematec.com) was used as lid of the chamber as its inlet was connected to the air supply of the test chamber. VOC sampling was conducted by connecting Tenax® sorption tubes (www.markes.com) at the FLEC® cell outlet. The air flow and the sampling volume were chosen to be 100 ml/min and 1,5 l.

Loaded Tenax®-tubes were subjected to VOC-measurement following the thermal desorption measurement principle described in DIN ISO 16000-6 (2004) by means of TD-GC/MS (thermal desorption gas chromatography coupled with mass spectrometry: Markes Ultra TD - Agilent 6890N/5973 GC/MS). Qualitative and quantitative interpretation of derived chromatograms was based on a calibration covering more than 70 single VOCs. If possible, detected substances were evaluated based on the calibration for the identified substance or for a similar substance if missing from the calibration. The portion of substances that had to be evaluated based on toluene d8 equivalents was lower than 5 % compared to the TVOC throughout the whole research. Due to reasons of simplicity, results presented here will represent the sum of single substances belonging to two different substance classes, i.e. terpenes and aldehydes.

4 RESULTS

Native pine wood showed the highest total amount of VOC emissions (TVOC) throughout the whole experiment. Figure 2 illustrates the alteration of VOC composition among terpenes (green) and aldehydes (red) throughout the experiment. While terpenes dominated the emissions (>95%) of chips and fresh powder, aldehydes from autoxidation of fatty acids appeared after technical drying. Throughout further processing, aldehydes dominated the emission spectrum.

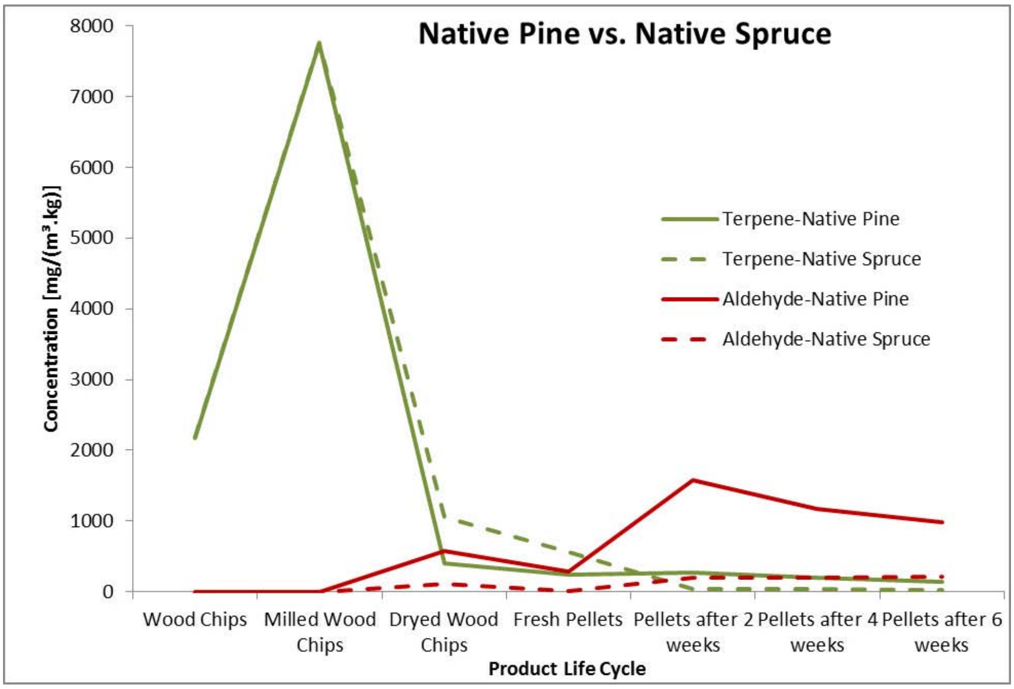

Figure 2. Comparison of native pine vs. native spruce: VOC measurement results at several product life cycle stages for fresh wood chips (stage A), after milling (stage B), after drying (stage C), directly after pelletizing (stage D) as well as after storage (stage F). (terpenes = green, aldehydes = red, native pine = full line, native spruce = dashed line)

Comparison of native pine wood and blue-stain treated pine wood is given in Figure 3. By means of fungal treatment (dashed and dotted line), this characteristic VOC profile of pinewood based products was significantly altered. Due to natural alterations within the sored material, a reference value was taken for non-treated pine chips. This reverence value is about 2000 mg/(m³.kg) lower compared to native pine wood chips without storage. Hence, strong alterations actually occur in this stage with respect to primary VOCs. This fact must be seen as a potential overlaying factor concerning VOC emissions for fungal treated wood. However, formation of secondary VOCs occurs in later stages of the product life cycle.

After technical drying, TVOC of fungal treated material decreased substantially due to the reduction of aldehyde emissions. Even for aged pellets, a considerable reduction of aldehyde emissions was observed due to fungal treatment.

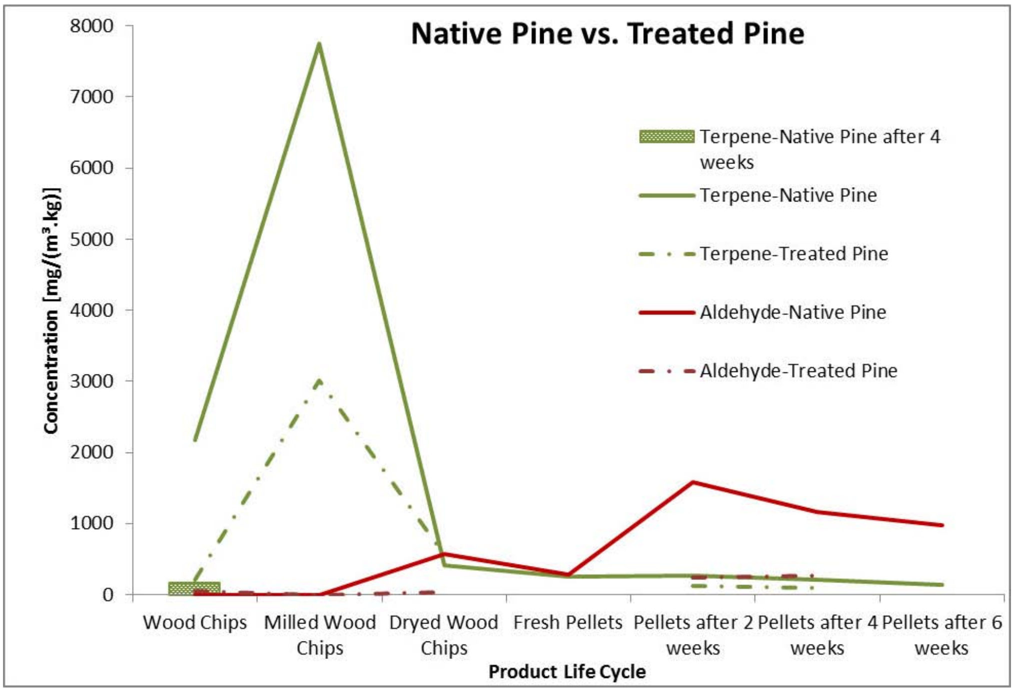

Figure 3. Comparison of native vs. treated pine: VOC measurement results at several product life cycle stages for fresh wood chips (stage A, A*), after milling (stage B, B*), after drying (stage C, C*), directly after pelletizing (stage D) as well as after storage (stage F, F*). (terpenes = green, aldehydes = red, native pine = full line, treated pine = dashed and dotted line, native pine chips after storage = box)

Comparison of fungal treated pine with native spruce demonstrated, that fungal treatment is suitable for the production of low emitting pine pellets, reaching emission levels such as spruce pellets (Fig. 4). Once again, the offset for terpene emissions due to storage must be considered here.

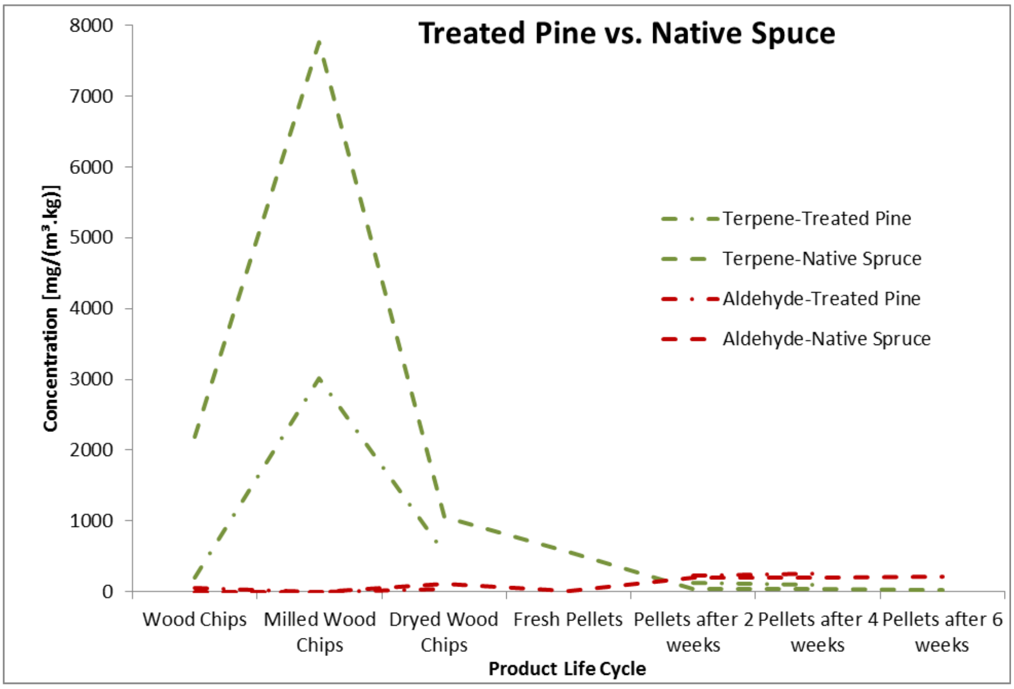

Figure 4. Comparison of treated pine vs. native spruce: VOC measurement results at several product life cycle stages for fresh wood chips (stage A), after milling (stage B, B*), after drying (stage C, C*), directly after pelletizing (stage D) as well as after storage (stage F, F*). (terpenes = green, aldehydes = red, native spruce = dashed line, treated pine = dashed and dotted line)

Transportation simulations (stage E) also showed a VOC-reduction, whereas this effect was most pronounced for native pine pellets of low age (Fig. 5). Due to abrasive forces while transportation, new surfaces were generated leading to increased emissions during transport, and hence led to lower primary VOC emissions thereafter. However, VOC reduction by means of abrasion is not worthwhile and less effective than fungal treatment.

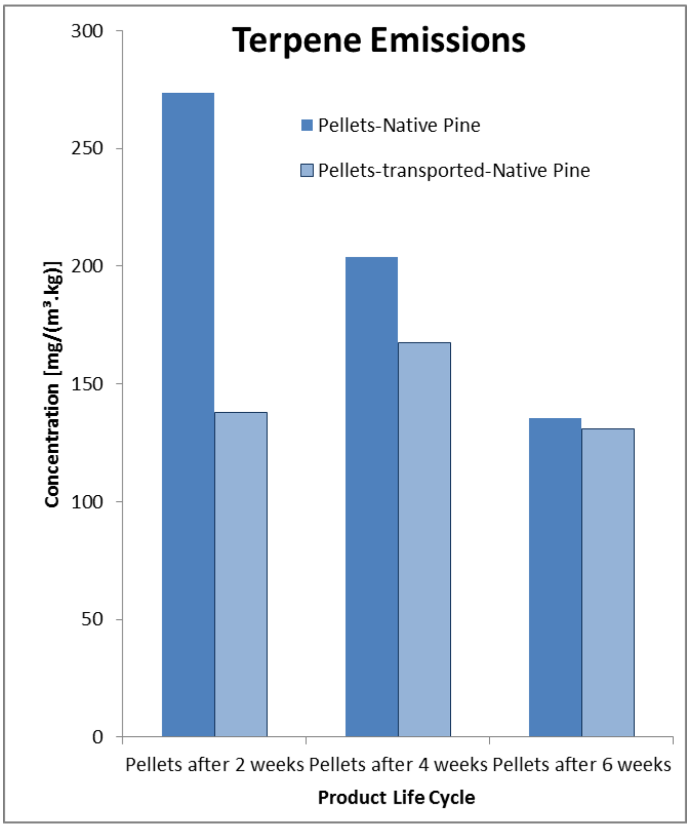

Figure 5. Impact of transportation simulation on terpene emissions from pellets produced from native pine wood.

5 DICUSSION AND CONCLUSION

During the pellets production the highest emission rates were found for milled wood chips, as particle surface was increased leading to easier evaporation of volatiles from the material matrix. At this stage the emitted VOC belonged almost exclusively to the group of monoterpenes. Terpene emissions showed a distinct decline during the following stages. Such trend is known for terpenes from other applications, representing a typical behavior of primary VOC. On the other hand, emissions of secondary VOC such as aldehydes arose as their formation was catalyzed by processing conditions.

The highest VOC emissions from pellets were found for native pine wood. Pellets from native spruce wood showed much lower aldehyde emissions compared to native pine wood and comparable terpene emissions.

Treating native pine wood with blue-stain fungi for four weeks led to reduction in the VOC emissions of the raw material and in the end product. The emission profile for treated pine wood turned out to be similar to the profile of native spruce wood.

Pellet transportation turned out to reduce terpene emissions most probably as a result of the temperature increase due to friction.

The formation of secondary VOCs should be decreased. The most pronounced increase was found for pellets produced from native pine while storage. Application of spruce wood as well as blue-stain fungi treated pine wood can reduce such undesired effects.

It is concluded that the formation of undesired emissions from wood pellets can be reduced by means of controlled processing and raw material selection, including wood modification. Treatment of fresh wood chips by means of blue-stain fungi seems to be very promising in this context. Further research trials were actually started within BioUp aiming to better understand interactions between processed materials and applied processes, in order to reduce VOC emissions on the one hand, and to eliminate the risk of CO formation on the other.

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