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Research paper

Self-heating properties of softwood samples investigated by using isothermal calorimetry

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ABSTRACT

The investigation focused on obtaining experimental results from the self-heating properties of different softwood samples during lab-scale storage. The samples investigated were a mixture of dried soft wood sawdust, softwood pellets 8 mm in diameter, and aged softwood sawdust stored outdoors for three months. Isothermal calorimetry was used to measure the heat released from the biomass samples and assess the contribution to self-heating during storage. Softwood samples were stored at 20 °C, 50 °C, 55 °C and 60 °C, and the metals manganese, copper and iron were added as a water solution to investigate if the presence of metals would increase the risk of self-heating. For most sample series, the highest levels of heat release were found after approximately 10 days of storage; sample series stored at 50 °C displayed the highest levels. The addition of copper resulted in levels of heat release 135% higher than samples without metal added.

1. Introduction

The self-ignition of organic materials is known within various areas, such as coal piles, woodchips piles, dried sewage sludge and insulation contaminated with fatty acids [1–4]. Self-ignition in stored biological materials will probably increase in the future due to the increased use of biomass for bioenergy. There are some concerns that gaseous emissions from biofuel storage will add to greenhouse gas emissions [5] and that storage will affect the quality of wood pellets [6,7]. During large-scale storage of woody biomasses, physical, biological and chemical processes lead to deterioration of the fuel and to self-heating [7–12]. Despite the low moisture content, fungal growth and self-heating have been observed during the storage of wood pellets [7,13], and investigations of the self-heating properties of wood pellets have been performed [14–16].

In some cases, self-heating combined with the low thermal conductivity of the material can lead to self-ignition. The raw material used for pellet production is usually stored in large piles outdoors, exposed to the weather. During transportation, handling and storage, wood pellets easily take up moisture [17]; rewetting occurs due to insufficient cooling in the pellet production, accidental wetting by weather or handling routines. The material is also susceptible to contamination during handling from rocks, pieces of metal or microbiological active material, e.g. soil. When this occurs, an increased microbial growth with subsequent heating of the material can take place. Microorganisms that perform degradation processes in wood or biomass material utilize energy from the stored energy in the organic molecules constituting the biomass. Fats, proteins and carbohydrates can be easily digested in metabolic reactions and are easily accessible to both bacteria and fungi. However, the structural compounds of cellulose lignin and hemicellulose, which form the wood structures, are more resistant to degradation, since their large complexes cannot be transported into a cell and the major degradation of lignocellulosic material is therefore degraded by fungal extracellular enzymes [18]. Fungi can produce a wide range of enzymes, viz. cellulases, hemicellulases and ligninases, that degrade the wood structure [19,20]. Several of these wood degrading enzymes have important components in the form of metallic ions of copper, iron or manganese [20]. The lignolytic extracellular enzymes of basidiomycetes are mainly divided into Laccase, Lignin peroxidase, Mn-peroxidase and Versatile peroxidases. Laccase is a copper oxidase generating hydrogen peroxide that degrade extra cellular compounds [21], while Lignin peroxidase, Mn peroxidase and Versatile peroxidases use heme groups [22]. Furthermore, Brown rot fungi have non-enzymatic

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mechanisms for degradation, where they produce hydrogen peroxide that together with a Fenton reaction releases hydroxide radicals [19,23,24]. Additionally, both fungi and bacteria have electron shuttle system to enhance the extracellular degradation of cellulose and lignin [25–27]. In the early stages of wood decomposition, soft rot and white rot fungi dominate the communities, while brown rot and different forms of mycorrhiza are more involved late in the decay [28]. The fungal enzymatic activity releases metabolites that can be utilized further by the fungal and bacterial community [29]. The microbial metabolic activity degrades the organic structures of the biomass and releases their excess heat to their environment; heat that risks becoming trapped in the pile, resulting in an increased temperature. As well, thermophilic fungi can be active in the degradation of biomass material in composts with temperatures above 45 °C [30], while their thermostable enzymes can be active up to 61 °C. The metabolic activity produces heat proportional to the rate of the metabolic processes, which can be measured by isothermal calorimetry [16,31–33]. An increased heat release would add to the self-heating of the material; by measuring the heat released from different biomass samples, the biomass suitability for storage can be assessed. The objective of this study was to measure the heat released from woody biofuels, stored under different temperatures. Measurements were performed with an isothermal calorimeter to investigate if the addition of microbial active material, trace metals and wetting of the material would contribute to a temperature rise and self-heating of the material, as demonstrated [16]. The metals chosen for the investigation are naturally present in soft wood as trace elements, ranging from 4 mg kg^{-1} to 296 mg kg^{-1} for the whole tree [34].

2. Materials and methods

The materials and method used in the investigation were selected to simulate as much as possible conditions that could occur during accidental wetting and contamination of large scale storages of woody biomass.

2.1. Softwood samples

The biomass samples used in the investigation were a selection of the biofuels collected from a commercial wood pellets manufacturer located in southern Sweden (Småland region, lat. ~57° N). At the pellet plant, 8 mm pellets were produced from a mixture of 20% softwood shavings (sawmill dried to about 10% moisture content) and 80% aged softwood sawdust (sawdust stored outdoors in large piles for more than three months, increasing the durability of the produced pellets). The shavings and aged sawdust were mixed together and dried to a moisture of 13% before pressed into pellets. The softwood material used for pellet production was mainly Norway spruce (*Picea abies*), according to the manufacturer. The softwood biomass samples used in the investigation were a selection of the biomass samples available at the pellet plant, (see also Fig. 1):

- aged soft wood sawdust (softwood sawdust stored outdoors for more than three months)
- dried mixture of aged sawdust and shavings (the softwood material mixed together in the proportion used to produce pellets; dried to a moisture content of 13% but before actually pressed into pellets)
- pellets 8 mm in diameter (produced at the pellet plant as described above)

2.2. Preparation of samples

The three types of investigated soft wood samples were sterilized to ensure minimal random microbial activity. This was followed by inoculation of the samples with partially degraded forest residues to simulate accidental contamination leading to microbial growth. Water was added to ensure sufficient moisture contents for microbial growth, and to simulate accidental wetting of samples. The samples were stored at different temperatures to simulate the varying storage temperatures for materials in different parts of a pile during large-scale storage. Additionally, metals were added to the samples to investigate the possible catalytic effects from the presence of metals in large-scale storages, or even elevated levels of trace elements naturally present in wood, might have on self-ignition.

The 2g soft wood samples were placed in 20 cm^3 glass ampoules and sterilized in a Harvey SterileMax Sterilizer at 135 °C for 180 min to minimize the microbial activity in the samples. The first few sample series were sterilized at 135 °C for 90 min, but some samples still showed increased thermal output (an indication of microbial activity) compared to the baseline when measured in the isothermal calorimeter TAM Air. The samples that still indicated microbial activity were sterilized once more, after which the thermal output was the same as the baseline. For the following sample series, the sterilization time was extended to 180 min.

Following sterilization, 7% partially degraded forest residues (forest residues from soft wood containing bark, needles, branches, stored outdoors for a longer period of time and no longer suitable for use as biofuel) were added to the samples to introduce a microbial culture to the sterilized samples, simulating accidental contamination.

According to the pellet manufacturer, the moisture content was above 50% in the aged sawdust, 13% in the dried mixture of sawdust and 7% in the pellet samples. To ensure sufficient moisture contents for microbial growth, and to simulate accidental wetting of the samples, an additional 20% moisture (tap water) was added to the samples. Fungal growth will occur above wood moisture contents of 16–20% and significant decomposition by wood-rotting fungi will take place above the fiber saturation point for wood at approximately 30% moisture content. At 100% relative humidity, wood is in equilibrium with a moisture content of 30%, the fiber saturation point. The prepared samples in the 20 cm^3 glass ampoules were put into closed glass cans containing water to ensure 100% relative humidity and prevent loss of moisture content in the samples during storage. The closed glass cans containing water and sample ampoules were stored for up to 78 days at atmospheric levels of oxygen in ovens with temperatures between 20 and 60 °C. The ovens used were Termaks TS 8056 with a temperature range up to 250 °C ± 1 °C and temperatures used for sample storage were: 20 °C, 50 °C, 55 °C and 60 °C. The temperatures used for the sample series were approximately between room temperature (no cooling needed; 20 °C) and the highest temperature possible for calorimetric measurements in the isothermal calorimeter used (60 °C). Sample series stored at 40 °C and 45 °C were also prepared and stored, but showed slower and lower results and were not prioritized, no results given. Sample series stored at 20 °C also showed slower and lower results, but some results are given. Samples were temporarily removed from the ovens to perform calorimetric measurements. During storage and when beginning the measurements, the samples were aerated by opening the glass cans and adding air into the ampoules using a pipette.

Manganese, iron and copper were added to samples to investigate the possible catalytic effects to self-heating of the material from the presence of metals. Manganese was added as an oxide (MnO_2), copper was added as a nitrate ($Cu(NO_3)^*3H_2O$) and iron

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