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Research article

Antioxidants as additives in wood pellets as a mean to reduce off-gassing and risk for self-heating during storage

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ABSTRACT

Spontaneous self-heating and off-gassing of wood pellets during storage is well-recognized problem. The reason for the phenomena is be autoxidation of fatty/resin acids in the pellets material. Two antioxidants, TBHQ (tert-Butylhydroquinone) and PG (propyl gallate), have been used as additives during pellets production in order to investigate how effective these antioxidants are in blocking autoxidation. Off-gassing of volatile aldehydes, CO and CO_2 from wood-pellets and depletion of O_2 during storage at room temperature in two different scales of closed storage systems were investigated and antioxidant fortified pellet batches and a reference batch without additive were compared. The results show that TBHQ is an efficient antioxidant at a low concentration (0.5%) in blocking autoxidation of fatty/resin acids in wood pellets. The CO emissions are reduced between 72 and 90% depending on the pellets temperature. Some of the fatty acids are almost intact in the samples with TBHQ compared to reference sample; showing that TBHQ blocking degradation by autoxidation of those fatty acids. For PG, autoxidation has not been blocked. The total amount of emitted aldehydes are 77% less than in pellets made with antioxidants as compared to the reference pellets, showing that TBHQ is acting as inhibitor in the autoxidation processes.

1. Introduction

Emissions of greenhouse gases, particularly carbon dioxide from fossil fuel sources, causes great concern due to the long term effect on climate [1]. Biomass is one of the most important alternative energy options available to meet increasingly strict emissions targets [2,3]. Both solid and liquid biofuels are forms of biomass that have become widely used and a major source being wood pellets. Wood fuel pellets are produced by compressing waste (sawdust, wood shavings) from the wood production industry at high temperature and pressure. The annual production and consumption of wood pellets in the EU-28 in 2015 was about 14.1 and 20.3 million tons, respectively [4].

However, during storage and transport of wood pellets spontaneous emissions of CO, CO_2 and CH_4, often combined with a pungent smell, have been reported [5,6]. These emissions, known as “off-gassing”, imply a severe safety hazard for the exposed personnel [7,8]. Several incidents are reported where off-gassing in combination with poor ventilation have caused carbon monoxide poisoning or death due to severe lack of oxygen in the storage, in both industrial and household settings [5,9,10]. Off-gassing has also been associated with self-heating and fire incidents in the pellet industry [11–13]. Occupational exposure off VOC during production of wood pellets is investigated before [14].

Fatty and resin acids are part of constituents of the extractives fraction in wood, and unsaturated fatty acids and certain resin acids are well known to undergo autoxidation [15]. This autoxidation is an exothermic reaction and are known to play a key role in the formation of VOC's (such as aldehydes and ketones [13] contributing to health effects by being irritants in eyes and upper respiratory tract [16, 17] and suggested end products being CO, CO_2, and CH_4 [13, 18].

Antioxidants are well known to reduce the autoxidation of unsaturated fatty acids, e.g. in food applications and for prolonging shelf life of pharmaceuticals [19, 20].

The autoxidation of unsaturated fatty acids has been discussed in some detail [21, 22] although the full mechanism is not described in detail. From linoleic acid (C18:1) main unsaturated fatty acid in pinewood, hexanal is reported to be the main aldehyde formed [23]. Because of the complexity and largely unknown end composition from the autoxidation, the total energy release from this exothermic reaction is hard to estimate.

However, studies so far indicate that the autoxidation is one of the main causing reactions in the self-heating in pellets storage [24]. Another factor, which under certain meteorological conditions can give

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rise to considerably heating, is the heat of condensation formed when air humidity condensates on the pellets [18,25].

Thus, removal or stabilizing of these compounds in the sawdust prior to pelletizing will provide means to decrease or stop the autoxidation and thereby reducing the risk for off-gassing and self-heating. Previous work demonstrated that supercritical CO_2 ($scCO_2$) extraction of the sawdust prior to pelletizing, reducing the content of fatty and resin acids considerably, was effective in reducing the serious off-gassing problems associated with storage of wood fuel pellets [18].

The purpose of the study was to select and apply an effective antioxidant for blocking (preventing) autoxidation of fatty/resin acids (lipids) in wood pellets and to demonstrate if adding a relevant antioxidant to the pellets raw material (pine sawdust) will reduce/eliminate off-gassing of volatile aldehydes, CO, CO_2 and CH_4 from wood-pellets during storage.

2. Experimental

The experiments were conducted using pine sawdust to make pellets fortified with two antioxidants and using reference batches from the same material. The investigation was made in two steps

Laboratory scale setup for registering off-gassing of carbon monoxide, carbon dioxide, and oxygen depletion from the batches of pellets during storage at 22 °C and 45 °C in airtight 19-L cylinders. The measurements performed during several days for each sample. Off-gassing of aldehydes/ketones were measured during 48 h for each sample

Pilot plant study. Then, a verification study was made in a 60 days pilot plant study (scale 1 m^3 containers) using the antioxidant giving the best result in the laboratory experiments. The produced pellets were stored at room temperature during 60 days in two airtight (each) and the off-gassing measurements were made (as in the laboratory experiments). In parallel, using the same batches of pellets the progress of fatty acid oxidation was determined during the experiment

2.1. Antioxidants

Two phenolic antioxidants tert-Butylhydroquinone, TBHQ (E319) and propyl gallate, PG (E310) were used as additive, in laboratory and/or pilot plant scale production of pellets. Physical and chemical properties of the antioxidants are shown in Table 1. The antioxidant capacity was determined according to the DPPH method [26–28].

2.2. Samples

Pellets Batches used are summarized in Table 2. Pellet raw materials, dried fresh Scots pine (*Pinus sylvestris* L.) delivered by Agroenergi Neova pellets AB:

a) from the Malmbäck plant
b) from the Ulricehamn plant.

Pellets produced for laboratory and pilot scale experiments are summarized in Table 2. All pellets were manufactured at the SLU pilot plant facility (BTC, Biomass Technology Centre, SLU [30]) using a Bühler pellet press (DPCB pelletizer, Bühler Ag, Uzwil, Switzerland). Antioxidants were added to the pellet raw material prior to pelletizing using a Euromilling HM 2000 screw mixer (Denmark).

The pellet Batches produced for laboratory tests (1–3) were cooled to 22 °C and bagged (polyethylene), stored at 4 °C prior to use. Batches produced for pilot scale storage test (Batches 4, 5) were used directly after cooling to 22 °C.

The added level for each antioxidant was based on antioxidative capacity information found in the literature [31] and the European pellets standard (EN 14961-1) in which the level of additives allowed is maximum 2% [32].

2.3. Off-gassing measurements and oxygen depletion measurements

2.3.1. Measuring off-gassing under laboratory conditions experiment

Off-gassing measurements were made according to Attard et al. [18]. Briefly; two sealed 19-L Plexiglas cylinders (H = 420 mm, ϕ = 240 mm, internal volume = 19 dm^3) were used. The cylinders were filled with the pellet samples (8 kg aliquots of the produced Batches) to 70% of their volume capacity. Experiments was done at 22 °C and, at 45 °C achieved using an external heating element (Flexible IBC2 heating jacket 0–90 °C, LKM Thermosafe Ltd., UK; applied around the container and maintained at 65 °C giving an average internal temperature of 45 °C). Gas emissions (CO, CO_2, and CH_4) and oxygen levels were measured (ppm) during a one-week period using a multi-instrument based on electrochemical and infrared (IR) sensors (ECOM J2KN Pro-IN gas analyser, Palgo AB, Sweden).

2.3.2. Measuring off-gassing under pilot plant conditions experiment

For pilot plant off-gassing measurements, two sealed polyethylene containers were used (IBC, Reconditioned Intermediate bulk container (Container Standard), 1200 × 1000 × 1168 mm, gastight with a 225 mm lid for filling on top and 80 mm outlet for emptying). The containers were filled with 500 kg of pellet Batches 4 and 5 respectively to c:a 70% of their volume capacity directly after production including 30 min of cooling. The experiment was done at 22 °C with measures of gas emissions (CO, CO_2) and oxygen levels 1–2 times/day on day 1–8 and once a day thereafter until a total of 60 days using the same instrument as for the laboratory measurements. Temperature logging was done using five loggers (Tinytag Plus 2, Intab, Sweden) in each container and two in the room. Temperatures were registered once every hour during the experiment.

In addition, 8 kg samples of the same Batches (4 and 5) were run in parallel to the 500 kg pilot storage experiment as control experiment. That was done in order to verify the observations in the laboratory experiments, done under the same conditions and with the same equipment (19-L cylinders). This experiment was made as the laboratory experiments. The total experiment time was however extended to 30 days, as compared to the laboratory scale experiments 7 days.

2.4. Determination of fatty and resin acids content in pellets

Determination of fatty acids (lipid content) and resin acids were made according to Attard et al. [18]. In short; Three gram pellets were

Table 1
Antioxidants used. DPPH antioxidant capacity values (EC50) obtained for the different samples. The data are presented as the mean of six measurements from two separate solutions (mean and standard deviation (SD %)). EC50 (μg/mL) represents the concentration of an antioxidant necessary to decrease the initial DPPH radical concentration in the test by 50% [26–28].

Antioxidant	Source	Anti-oxidative capacity EC50 (μg of sample/mL)	Literature data EC50 (μg of sample/mL)[28, 29]	Melting point (°C)	Water solubility (g/L)	Used for test
Tert-butylhydro-quinone (TBHQ)	Sigma-Aldrich, 97%	2.00 ± 0.04	1.90 ± 0.07	126.5–128.5	2.0	Lab and pilot scale
Propyl gallate (PG)	Sigma-Aldrich, ≥98%	1.01 ± 0.01	0.9 ± 3.9	146–150	3.5	Lab scale