energies

MDPI

Article

Off-Gassing and Oxygen Depletion in Headspaces of Solid Biofuels Produced from Forest Residue Biomass

Kazimierz Warmiński [1,2,*], Klaudia Anna Jankowska [1], Agnieszka Bęś [1] and Mariusz Jerzy Stolarski [2,3]

[1] Department of Chemistry, Faculty of Agriculture and Forestry, University of Warmia and Mazury in Olsztyn, Prawocheńskiego 17, 10-720 Olsztyn, Poland; agnieszka.bes@uwm.edu.pl (A.B.)
[2] Centre for Bioeconomy and Renewable Energies, University of Warmia and Mazury in Olsztyn, Plac Łódzki 3, 10-724 Olsztyn, Poland; mariusz.stolarski@uwm.edu.pl
[3] Department of Genetics, Plant Breeding and Bioresource Engineering, Faculty of Agriculture and Forestry, University of Warmia and Mazury in Olsztyn, Plac Łódzki 3, 10-724 Olsztyn, Poland
* Correspondence: kazimierz.warminski@uwm.edu.pl; Tel.: +48-89-5233560

Abstract: As living standards improve worldwide, the demand for energy increases. However, climate changes and decreasing fossil fuel deposits have increased interest in renewable energy sources, including pellets produced from forest residues. This study aimed to compare changes in concentration of gases (CO, CO_2, O_2, volatile organic compounds—VOCs) in enclosed headspaces above pellets produced from deciduous (oak OA, birch BI) and coniferous (pine PI, spruce SP) dendromass and selected types of commercial pellets during their storage. The experiment measured the concentration of gas released from the pellets in storage daily for 14 days. The highest mean CO concentration was found for PI pellets (1194 ppm), and the lowest was for OA (63.3 ppm). Likewise, the highest CO_2 concentration was noted for PI pellets (4650 ppm), and the lowest was for BI (1279 ppm). The largest VOC amount was released in the headspace above PI (88.8 ppm), and the smallest was above BI (4.6 ppm). The oxygen concentration was the lowest as measured for PI (minimum 16.1% *v*/*v*) and for SP (19.3% *v*/*v*). The threshold limit value (8 h) for CO was exceeded for all the pellets under analysis and, in the case of CO_2, only for PI after day 10 of incubation. The study findings are extremely important from a scientific (but mainly from a practical) perspective because of the safety of storing and transporting wood pellets. The knowledge of autooxidation processes in those biofuels can help organize their logistics and storage and result in proper warehouse ventilation and monitoring of noxious gases.

Keywords: bioenergy; wood pellet; storage; off-gassing; carbon monoxide; autooxidation; toxic gas

Citation: Warmiński, K.; Jankowska, K.A.; Bęś, A.; Stolarski, M.J. Off-Gassing and Oxygen Depletion in Headspaces of Solid Biofuels Produced from Forest Residue Biomass. *Energies* **2024**, *17*, 216. https://doi.org/10.3390/en17010216

Academic Editors: Fernando Rubiera González and Prasad Kaparaju

Received: 28 November 2023
Revised: 24 December 2023
Accepted: 29 December 2023
Published: 30 December 2023

1. Introduction

Interest in energy generation from renewable sources is growing due to increasing energy demand, concerns about climate change and dwindling fossil fuel resources. Biomass, which can be used for obtaining heat and electricity and producing fuels, is an alternative to fossil fuels [1]. Poland heavily relies on solid biofuels as its main renewable energy source (RES), constituting almost 70% of its renewable energy production [2]. This value is about 40% in the European Union (EU). Solid biomass is classified into firewood from forests, agricultural residues (e.g., cereal and rape straw, grass), lignocellulosic biomass of energy crops and production waste from wood processing and the food industry [1,3]. However, forest biomass is still the major feedstock in the production of solid biofuels. Scots pine (*Pinus sylvestris* L.) is the dominant species in forests in Poland. It accounts for 58.6% of the whole forest area. Other species occupy a small percentage of the Polish forest area (oak 8.0%, birch 6.8%, spruce 5.3% and others). Coniferous trees account for 68.6% of the forest area, and deciduous trees for 31.4% [4]. Coniferous species also dominate in the EU, with consequences for the wood acquisition structure. About 350 million cubic

meters of coniferous and 150 million cubic meters of non-coniferous roundwood is obtained annually [5].

Wood chips from forests and the wood processing industry are the major solid fuel used to power medium-sized and large heating plants and combined heat and power plants [6,7]. However, making pellets from solid biomass is an increasingly popular trend. This is visible worldwide and in the EU, including Poland. It is a consequence of the fact that pellets are a standardized solid biofuel, which makes logistics and supply to medium-sized and large bioenergy-generating plants easier [8,9]. This biofuel is also convenient and cost-effective in powering small boiler rooms by individual users [10–12]. Wood pellets are usually produced from sawmill production residues, e.g., sawdust [3]. Pellet production is growing steadily, and it was higher in 2021 by approximately 6.8% compared with 2020. The production output in the EU grew by 9%. Pellet production in Poland increased rapidly, by 38%, and by 32% in Lithuania. The largest amount of pellets in the EU in 2021 was produced by Germany (3,355,000 tons). The production output in Poland amounted to 1,800,000 tons [13].

The growing interest in pellets worldwide creates logistical issues, such as those associated with storage and transport. Pellets should be stored in closed warehouses as they absorb moisture readily. Large firms or heating plants usually store them in bulk in large silos, and individual users store them in home storage rooms or bags in their cellars [14,15]. Safe storage and transportation of wood pellets is an important aspect of using solid biofuels as an RES [16]. Various gases, such as carbon dioxide (CO_2), toxic carbon monoxide (CO), methane (CH_4) and volatile organic compounds (VOC), including low-molecular-weight aldehydes (mainly hexanal), are found to be released during pellet storage [16–19]. Combined with poor ventilation, the off-gassing lowers the air quality inside and seriously threatens human health (and even life), especially with high concentrations of CO. Numerous cases of fatal poisonings of people in warehouses and ships carrying wood pellets have been documented, which makes the presence of efficient ventilation crucial [20,21]. Pellet off-gassing in storage is caused by autooxidation of lipophilic compounds in biomass, especially unsaturated fats and free fatty acids (e.g., linoleic acid) and resin acids. This results in oxygen depletion in the room, which poses an additional threat to human health and life. The amount of emitted gas depends on the temperature, relative humidity, headspace volume, oxygen level, storage method, accessible pellet surface, type of material from which the pellets are made and extractive content [22–29]. The autooxidation process is exothermic, so gas is emitted with heat release, resulting in pellet self-heating and increasing the danger of self-ignition and fire.

Apart from fatty acid autooxidation, VOCs can be produced from endogenous natural monoterpenes in biomass, especially coniferous trees. Monoterpenes are the most volatile compounds in wood, responsible for its characteristic forest smell. The most common ones include α-pinene, β-pinene and Δ^3-carene. Monoterpenes are present in resin and essential oils. Spruce wood contains monoterpenes at 0.1–0.15% d.m., and the concentration in pine is higher—0.2–0.6% [3]. Pellet self-heating causes their temperature to rise, accelerating the endogenous monoterpene evaporation.

Off-gassing and self-heating studies focus mainly on pellets produced from coniferous biomass because of their widespread presence on the market and the potentially high content of lipophilic substances susceptible to autooxidation. Pellets made from pine and spruce have been the most widely studied to date [18,26,30–36]; less frequently studied are other species, such as loblolly pine, European larch, *Larix gmelini*, Douglas fir, cedarwood and eucalyptus [21,27,37–39], and very rarely, typical deciduous trees such as common ash and cork [21,37]. Therefore, there is a knowledge gap regarding off-gassing from pellets made from deciduous species compared with coniferous species. Therefore, this study aimed to compare the changes in concentration of gases (CO, CO_2, O_2, VOCs) in enclosed headspaces above pellets produced from deciduous (oak, birch) and coniferous (pine, spruce) dendromass and selected commercial pellets during their storage under controlled

conditions. Understanding this phenomenon occurring in wood pellets of various origins is essential for developing a strategy and systems for their safe storage and transport.

2. Materials and Methods

2.1. Materials

Wood pellets made from forest wood sawdust, with a diameter of 6.2 mm, particle density of 1.23 g cm^{-3} and moisture content of 4.2–8.8%, were used in the experiment (Table 1). Four experimental pellet batches were produced from spruce (SP), pine (PI), oak (OA) and birch (BI) sawdust. Moreover, two batches of commercial pellets were used for the experiment, which were produced, according to the manufacturer's instructions (Tartak Olecko, Olecko, Poland), from coniferous (pine–spruce; MP1) and mixed (deciduous–coniferous, MP2) sawdust.

Table 1. Physical characteristics of wood pellets used in the experiment. Mean ± standard deviation.

Pellet	Material	Diameter (mm)	Particle Density (g cm^{-3})	Moisture (%)
PI	Pine sawdust	6.28 ± 0.03	1.223 ± 0.025	7.81 ± 0.04
SP	Spruce sawdust	6.12 ± 0.08	1.309 ± 0.069	4.23 ± 0.11
OA	Oak sawdust	6.12 ± 0.10	1.204 ± 0.085	8.79 ± 0.08
BI	Birch sawdust	6.17 ± 0.06	1.261 ± 0.052	6.40 ± 0.18
MP1	Sawdust from coniferous species	6.35 ± 0.08	1.208 ± 0.036	8.22 ± 0.02
MP2	Sawdust from coniferous and deciduous species	6.20 ± 0.07	1.182 ± 0.043	6.25 ± 0.05
Mean		6.21 ± 0.11	1.231 ± 0.343	6.95 ± 159

2.2. Gas Concentration Measurement

The experimental system shown in Figure 1 was used in the study. It consisted of a borosilicate glass bottle with a nominal capacity of 2000 cm^3 and a measured total capacity of 2286 cm^3 (Simax Kavalierglass a.s., Prague, Czech Republic) as well as a sampling port glass pipe (diameter of 5 mm), copper inlet pipe (diameter of 4.6 mm) and silicon pipes.

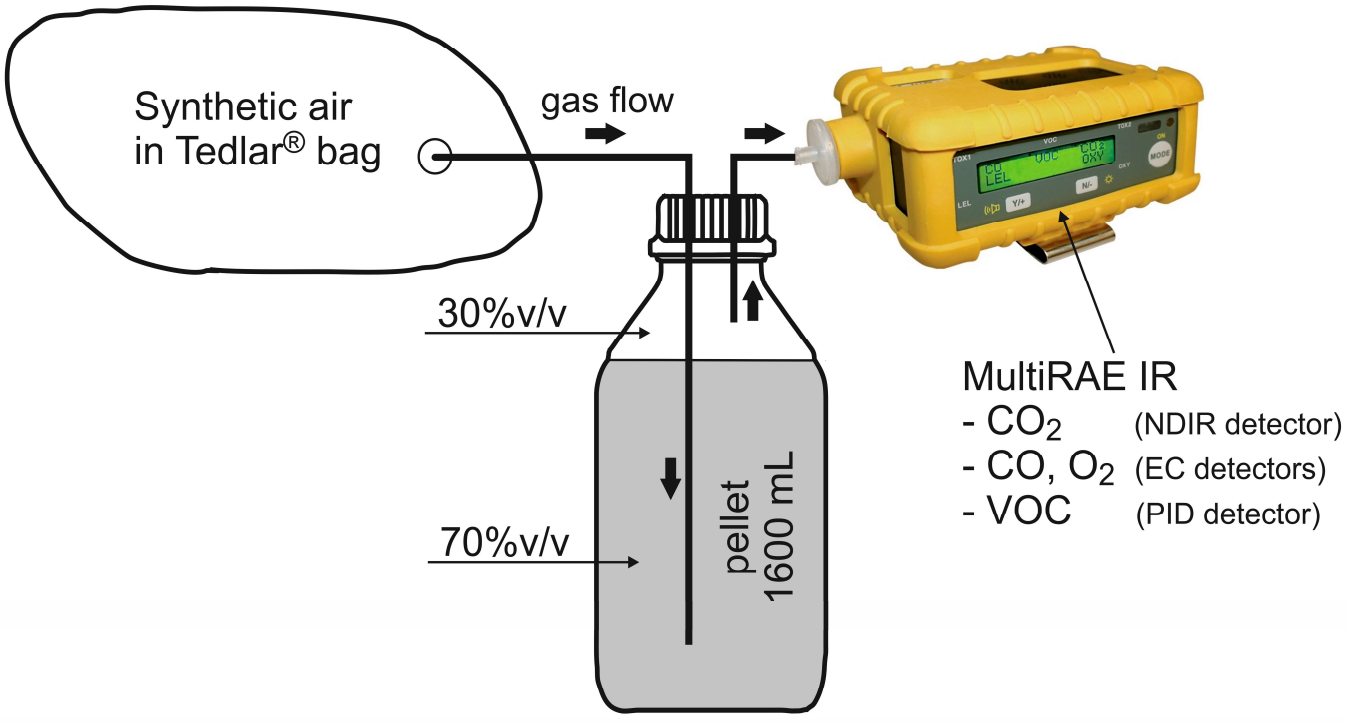

Figure 1. Measurement system diagram.

The experiment measured the concentration of gas released from the pellets in storage every day for 14 days (except Sundays). Bottles with the materials for the analysis (two samples of each pellet type) were prepared on the first day of the laboratory analyses. A sample of 1600 cm^3 of each pellet type was measured in a glass measuring cylinder and weighed on the laboratory balance (WPS2100/C/2, Radwag, Radom, Poland) with an accuracy of 0.01 g. The pellet bulk volume was equivalent to 70 percent of the total capacity of the bottle in the experimental system, following the recommendations of other authors [32,40].

The weighed pellets were transferred to bottles, which were closed with a screw cap, connected to the steel bottle with compressed synthetic air of chromatographic quality (Euro-Gaz, Olsztyn, Poland, 5.0, 99.999%, concentrations of CO_2, CO and VOC under 1 ppm). Blowing-through at 4 $dm^3 \cdot min^{-1}$ was conducted for two minutes. Subsequently, the pipes were connected (inlet–outlet), so they closed the bottle's circulation, cutting out the external air.

The filled bottles were put in a dark room at room temperature (20 ± 1 °C). After a predefined time, concentrations of the released gases (CO, CO_2, O_2 and VOCs) in the headspace above the pellets were measured with a MultiRAE IR gas analyzer (RAE Systems, Hong-Kong, China). The gas collection and analysis time was two minutes for each time. The gas flow rate forced by the analyzer's internal pump was 0.15 L min^{-1}. The analyzer and the measurement methods are characterized in Table 2.

Table 2. Characteristics of the MultiRAE IR gas analyzer.

Gas	Measurement Method	Unit	Measurement Range	Resolution	Response Time (s)
CO_2	Non-dispersive infrared (NDIR)	ppm	0–20,000	10	60
CO	Electrochemical (EC)	ppm	0–500	1	20
O_2	Electrochemical (EC)	% *v*/*v*	0–30	0.1	15
VOC	Photoionization (PID)	ppm *	0–200	0.1	10
			200–2000	1	10

* Converted to isobutylene.

Before the measurement started, the analyzer's zero point was controlled every day, i.e., it was connected to the Tedlar® bag (Restek, Bellefonte, PA, USA) with synthetic air for 5 min. Subsequently, the analyzer was connected to the sampling port in the bottle with pellets. The inlet pipe was connected to the Tedlar® bag with synthetic air during the measurement so that the volume of air collected from the headspace was made up of pure air. The concentrations of the gases under analysis in consecutive everyday measurements were adjusted, considering the dilution with synthetic air [32]. After each measurement, the analyzer measurement objectives were blown through with nitrogen with a purity of 5.0 (Euro-Gaz, Olsztyn, Poland, 99.999%).

2.3. Statistical Analysis

The statistical analyses of all the data concerning the gas concentration changes were based on a two-way ANOVA analysis. The six types of solid biofuels were the first factor in the analysis (wood pellets), and the measurement dates were the second factor. The mean concentration of all the measurement dates and the mean values were assessed with Tukey's Honest Significant Difference (HSD) test, with the homogeneous groups determined at the significance level of $\alpha < 0.05$. Moreover, the correlation and regression analysis between CO, CO_2 and VOC concentrations was performed separately for each pellet type. All statistical analyses were performed with STATISTICA 13 (TIBCO Software Inc., Palo Alto, CA, USA).

3. Results and Discussion

3.1. Gas Concentration Changes

The everyday measurements of CO, CO_2, VOC and O_2 concentrations in the headspace enabled assessment of the changes in autooxidation of substances contained in wood, from which the pellets were produced. The results of the statistical analysis of the concentration of gases in the headspace above the wood pellets are shown in Table 3. It shows significant differences between the CO concentrations above the materials under study (pellet types). A significant increase in concentration in time and an interaction between the measurement time and the material were also noted. As in the case of CO concentration, a significant impact of the material, time and inter-factorial interaction was also observed for other gases.

Table 3. Analysis of variance (ANOVA) for gas concentrations.

Source of Variation	CO		CO_2		VOC		O_2	
	F	***p***	***F***	***p***	***F***	***p***	***F***	***p***
Intercept	246.80	<0.0001	13,413	<0.0001	1874.26	<0.0001	255,206	<0.0001
Material (M)	43.84	0.00012	519.79	<0.0001	287.17	<0.0001	127.63	<0.0001
Time (T)	63.22	<0.0001	579.75	<0.0001	1581.84	<0.0001	38.08	<0.0001
M x T	14.20	<0.0001	37.80	<0.0001	246.64	<0.0001	12.70	<0.0001

F—*F*-statistic; *p*—probability level (*p*-value).

All of the curves shown in Figure 2 exhibit a growing tendency, i.e., the CO concentration in the headspace under study increased with the incubation time. The study results show that the highest CO concentrations were noted for PI pellets. The peak CO concentration (2044 ppm) was noted on day 12. Apart from PI pellets, those from SP emitted high levels of CO compared with the other pellet types (796 ppm on the 12th day of incubation). Carbon monoxide emission from both commercial pellets (MP1 and MP2) was similar, as in the case of pellets produced from deciduous trees (BI and OA). The CO concentration for the two latter types during the 14 days of the study increased slightly—the highest level for BI pellets was 176 ppm, and 105 ppm for OA. The CO concentration as determined in the study conducted by Tumuluru et al. [33] for wood pellets (with a moisture content of 5%) after 11 days of storage (at 20 °C) was ca. 1600 ppm, which was close to the results of the current study. Svedberg et al. [19] suggested that the generation of CO during storage of wood pellets was caused by autooxidation of residual lipophilic extraction substances in the pellets, mainly fats and unsaturated fatty acids. However, they did not rule out the possibility of the formation of CO from other organic substances contained in pellets, such as cellulose, hemicellulose and lignin. Similarly, Rahman and Hopke [23] pointed out that the VOC concentration was significantly lower than that of CO, which suggested that VOCs might not be the only source of CO.

Changes in CO_2 concentration during wood pellet storage exhibited a similar tendency of CO (Figure 3). The highest gas concentration was noted for pellets from PI (over 7800 ppm). This level was nearly twice as high as the CO_2 concentration for SP pellets (4246 ppm). This parameter for OA pellets and commercial pellets (MP1, MP2) was similar. The highest CO_2 concentration was over 3000 ppm. The lowest CO_2 emission was measured above pellets produced from birch sawdust (2000 ppm). The same order of magnitude of CO_2 concentration for commercial wood pellets produced in Canada was determined in a different study. Tumuluru et al. [33] found CO_2 at approx. 3000 ppm, whereas Yazdanpanah et al. [41] noted approx. 4000 ppm in the headspace above pellets after several days of storage. A much higher CO_2 concentration was found in a British study above pellets produced from fresh pine sawdust. The CO_2 concentration was approx. 15,000 ppm after 14 days [32].

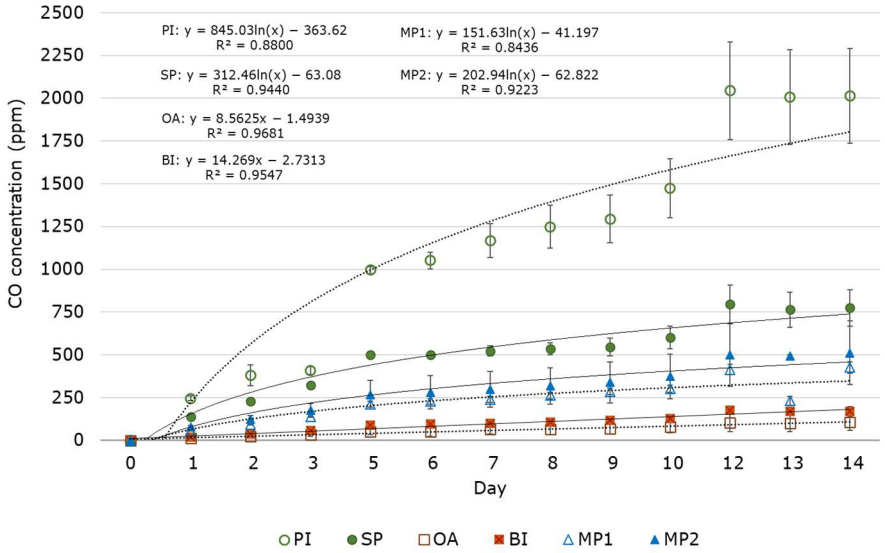

Figure 2. Changes in CO concentration in the headspace above pellets during their storage. PI, SP, OA, BI, MP1 and MP2—see explanations in Table 1. Whiskers represent standard error.

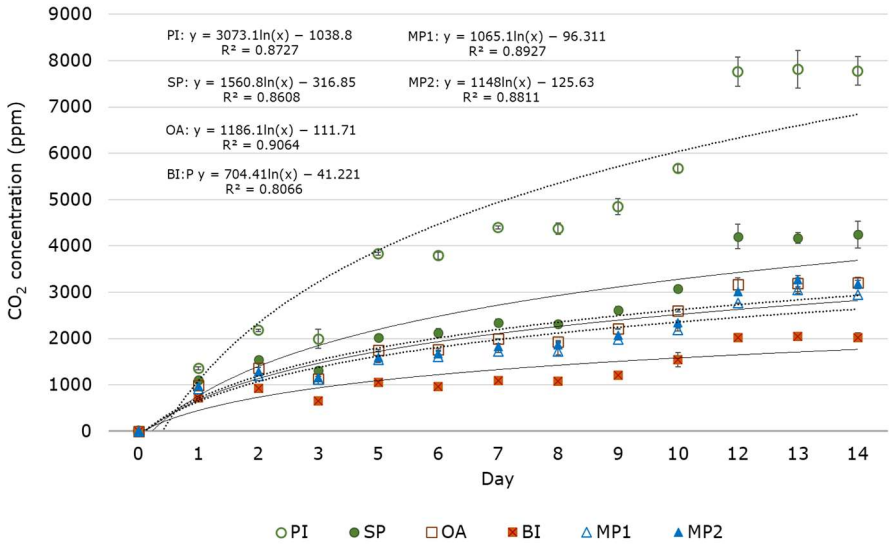

Figure 3. Changes in CO_2 concentration in the headspace above pellets during their storage.

PI pellets also emitted the largest amounts of VOC. The maximum VOC concentration in the headspace was 156 ppm (Figure 4). Compared with the other pellets, a high VOC concentration was found in MP2 made from coniferous–deciduous sawdust, which may suggest that they were produced mainly from pine sawdust. Pellets produced from deciduous (OA and BI) sawdust emitted the lowest amounts of VOCs. The following VOC concentrations were found on the last day of incubation: 12 and 10 ppm. Rahman and Hopke [23] examined (coniferous and mixed) wood pellets and showed the headspace contained such volatile compounds as formaldehyde, ethanal, propanal, butanal, pentanal, hexanal, nonanal, decanal, octadecanoic and hexadecanoic acid, with ethanal, formaldehyde and hexanal dominating above both pellet types under examination. According to Pohleven et al. [42], VOC emission from deciduous wood was much lower than from coniferous wood (e.g., PI or SP). This was caused by a high content of volatile terpenes of coniferous wood and higher lipid content. Most contemporary studies indicate an abiotic nature of the oxidative processes that take place mainly on the surface of wood pellets. The substrates in these reactions were unsaturated fatty acids and their esters, including linoleic, linolenic and oleic acids, which occur in abundance in coniferous wood [23,27,32,36]. The

oxidation reaction produced carbon oxides and VOCs, including aldehydes, carboxylic acids and other low-molecular-weight organic compounds. Hexanal is the main product of linoleic acid oxidation, but there could also be other products, such as pentanal and hexanoic acid.

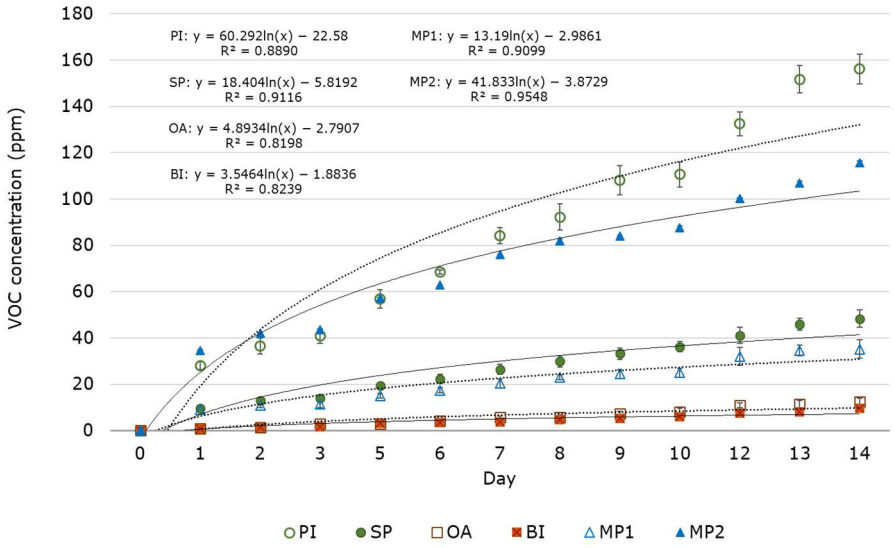

Figure 4. Changes in VOC concentration in the headspace above pellets during their storage.

Oxygen was seen to deplete gradually in the headspace during the pellet storage (Figure 5). The fastest O_2 depletion was observed above PI pellets. This is where the lowest value was found among the pellets under study throughout the measurements (16.1% v/v). A slight decrease in O_2 concentration was observed in SP pellets (from 20.9 to 19.3% v/v). Depletion of O_2 was not significant in the remaining pellets—the concentration remained at a similar level to the initial one (approx. 20.7% v/v). The differences resulted from the various chemical compositions of coniferous and deciduous wood. The lowest O_2 concentration for PI and SP pellets corresponded to a higher capability of generating CO. It was found in studies conducted by other authors that the O_2 concentration decreased with the emission of harmful gases during the storage and transport of wood pellets in enclosed spaces. Since oxygen is consumed in the autooxidation processes, its concentration decreases with the incubation time [25]. Along with the presence of CO, this is another factor that poses a threat to the lives of people staying in poorly ventilated rooms and cargo bays where wood pellets are stored [20,43]. The atmosphere is regarded as poor in oxygen when the O_2 concentration is below 19.5% v/v, but a person's ability to judge the situation and to breathe does not worsen until it drops below 16% v/v. Sudden fatigue and misjudgment of the situation appear at 14% v/v, and breathing difficulties at 11% v/v. Death may occur within several minutes [44].

It should be noted that coniferous wood is much richer in unsaturated fatty acids than deciduous wood [21]. Therefore, in PI pellets, autooxidation processes occur with greater efficiency, and consequently, the flux of released gases and their concentrations in the headspace are higher. Attard et al. [32] showed that the partial removal of lipids and resins from pine sawdust during the extraction process with supercritical CO_2 contributed to a significant reduction in the concentrations of CO and CO_2 (by about 85%) and aldehydes (by 26–87%) in the headspace air of pellets made from this sawdust, compared to reference pellets. These results confirm the importance of lipids in the off-gassing of wood pellets. On the other hand, Siwale et al. [26] studied the influence of extractive contents on off-gassing during the storage of pine wood pellets. They obtained different extractive contents in these experiments by extracting sawdust with acetone and adding oils with different unsaturated fatty acid contents (linseed oil and tall oil) and unequivocally showed that unsaturated fatty acids in pine pellets are one of the main causes of gas emissions and oxygen loss in

the headspace of stored wood pellets. This finding is also confirmed by the results of other studies [21,25,27,31].

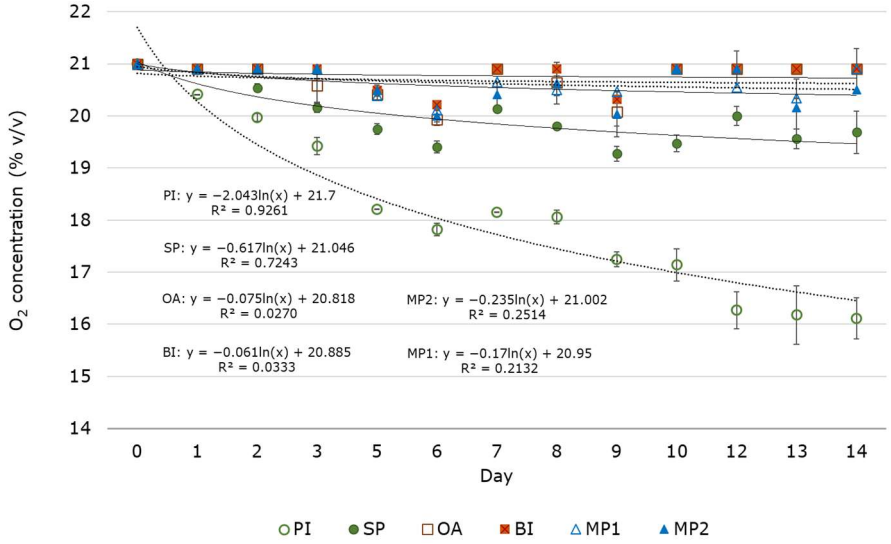

Figure 5. Oxygen depletion in the headspace above pellets during their storage.

Rahman and Hopke [23], on the other hand, suggest that the source of CO is not only lipid autooxidation reactions. They hypothesized that it is a multiple-step process. As a result of oxidation of unsaturated compounds (unsaturated fatty acids and terpenes), hydroxyl radicals are formed. This is followed by reactions of hemicellulose and hydroxyl radicals, resulting in the release of the largest amounts of CO. The hypothesis posed by Rahman and Hopke [23] was confirmed in an experiment with pellets with the addition of a radical scavenger. A positive effect of the addition of antioxidants on slowing down autooxidation processes in pellets was also found by Sedlmayer et al. [30] and Arshadi et al. [40]. Such additives may have practical applications for reducing the off-gassing of wood pellets, especially those made from pine sawdust. However, it should be emphasized that this requires further research into, among other things, the effect of antioxidants on emissions from pellet combustion and economic viability.

3.2. Mean Gas Concentration Compared with the Limit Values

The mean concentrations of the emitted gases and oxygen from all the measurement days are shown in Table 4. The CO concentrations above OA and BI pellets were the lowest (63.3 and 105.2 ppm, respectively), and they were not statistically different (homogeneous group "c"). The highest mean CO concentration of all the study days was noted above the PI pellets, at 1194 ppm (homogeneous group "a"), followed by SP pellets (519 ppm, homogeneous group "b"). The smallest amounts of CO_2 were emitted by BI pellets (mean concentration 1279 ppm), and the largest were from PI (4650 ppm) and SP (2590 ppm). Another statistically homogeneous group ("c") included OA, MP1 and MP2 pellets, for which the CO_2 concentrations were 1897, 2021 and 2108 ppm, respectively. The statistical analysis isolated four homogeneous groups for VOC concentrations. The lowest VOC concentration was found above the pellets from birch and oak sawdust (4.6 and 6.2 ppm, homogeneous group "d"), and the highest was for pellets from PI (88.8 ppm, homogeneous group "a"). Unlike for CO and CO_2 concentrations, the second-highest VOC concentration was observed for MP2 pellets, for which the mean VOC concentration was 74 ppm (homogeneous group "b"). The value of this attribute for SP pellets was 2.5 times lower than for MP2.

The largest oxygen depletion in the headspace was observed in the bottle with the PI pellets. The mean O_2 concentration from the whole study period was 17.9% v/v. Another outstanding result was the O_2 concentration above SP pellets (19.9% v/v). The mean O_2 concentration did not differ statistically and ranged from 20.6% to 20.8% for both

commercial pellets and BI, respectively. These values did not deviate much from the oxygen concentration in the atmospheric air.

The CO concentrations above all pellets were high. The results cannot be transposed to the actual conditions of pellet storage in warehouses or cargo bays on ships. However, in order to illustrate the problem, one can assume that if pellets are stored in a non-ventilated room of a limited space (a warehouse or a silo), harmful gases (especially CO) can accumulate at a similar level. A worker will not stay in such a room throughout a shift (8 h) but will occasionally enter for a short time. Therefore, a short-term exposure limit (STEL) at a workplace was taken for comparison, which refers to a time not longer than 15 min and not more frequently than twice within a shift, at a minimum interval of 1 h, according to the occupational health and safety (OSH) regulations valid in Poland and the European Union [45,46]. The STEL for CO and CO_2 is 100 and 15,000 ppm (117 and 27,000 mg m^{-3}, respectively, at 20 °C and a pressure of 1 atm). Considering these norms, one may claim that the CO concentration in the headspace over the pellets will exceed the STEL in nearly all cases except OA pellets. Further, the STEL for CO_2 will not be exceeded in any case (Table 4). However, this analysis is a certain simplification, because the concentrations presented in Table 4 are mean values from the entire period. A repeated analysis of Figure 2 shows that CO concentration in the headspace above OA exceeded the STEL beginning with day 12 of the incubation. Moreover, the threshold limit value, the time-weighted average (TWA), in the air at a workplace, determined for an 8 h shift, is lower than the STEL, and for CO and CO_2, it is 20 and 5000 ppm (23 and 9000 mg m^{-3}), respectively. The TWA levels for CO were exceeded beginning with the first day of incubation for all the pellet types (Figure 2). The TWA for CO_2 was exceeded only for PI pellets beginning with day 10 of incubation (Figure 3). A low oxygen concentration (mean 17.9, minimum 16.1% v/v, Figure 5) was another adverse factor present in the PI pellet headspace. This atmosphere could be regarded as poor in oxygen but with no immediate threat to human life [44].

Table 4. Gas concentrations in the pellet headspace and the limit values (mean of all the measurement days).

Pellet	CO (ppm)	CO_2 (ppm)	VOC (ppm)	O_2 (% *v*/*v*)
PI	1194.2 a	4650 a	88.8 a	17.9 c
SP	518.9 b	2590 b	28.3 c	19.9 b
OA	63.3 c	2108 c	6.2 d	20.7 a
BI	105.2 c	1279 d	4.6 d	20.8 a
MP1	240.3 bc	1897 c	21.6 c	20.6 a
MP2	313.3 bc	2021 c	74.4 b	20.6 a
Mean	405.9	2424	37.3	20.1
Limit value *				
STEL (15 min)	100	15,000		
TWA (8 h)	20	5000		

a, b, c, d—the values in columns with the same letters do not differ statistically (homogeneous groups); Tukey's HSD test ($\alpha < 0.05$). TWA—measured or calculated in relation to a reference period of 8 h time-weighted average; STEL—short-term exposure limit. A limit value above which exposure should not occur and that is related to a 15 min period; * limit values (TWA, STEL) according to the Polish Ministry Regulation [46] and Commission Directive [45].

3.3. Correlations between Gas Concentrations

Correlations between gas concentrations in the pellet headspace are shown in Figures 6 and 7. There was a highly significant correlation between the measured concentration of CO_2 and CO for pellets PI, SP, MP2 and OA (determination coefficient R^2 within the range of 0.9021–0.9869) (Figure 6). The correlation was significant for BI pellets ($R^2 = 0.8599$). These correlations were positive, i.e., the CO_2 concentration grew with the CO concentration. This was similar to the correlation between the CO and VOC concentrations. The R^2 coefficient was under 0.9 only for MP1 pellets, which means that the concentrations

of the compounds under study were closely correlated with the other pellets (Figure 7a). The CO_2 and VOC concentrations in all the pellet headspaces were highly correlated (Figure 7b). The highest determination coefficient R^2 was for MP1 pellets (0.9701), and the lowest (although still high) was for BI pellets (0.9050).

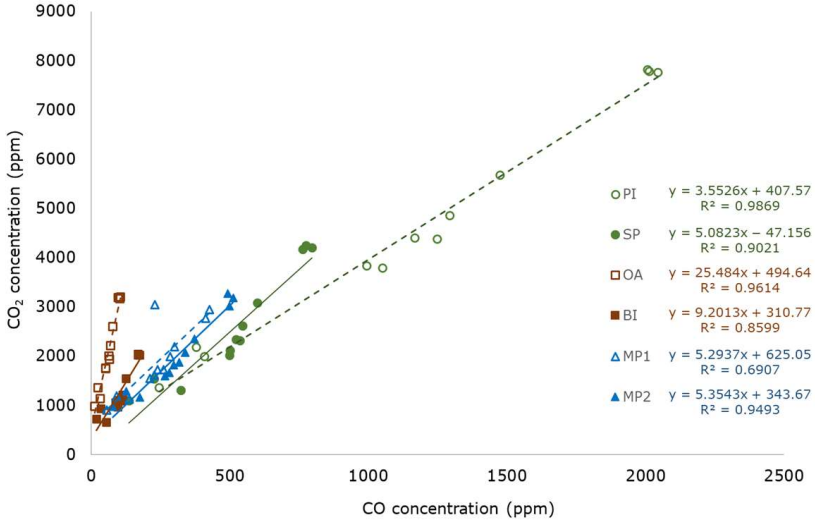

Figure 6. Correlation and regression analysis for CO and CO_2 concentrations for the pellets under study.

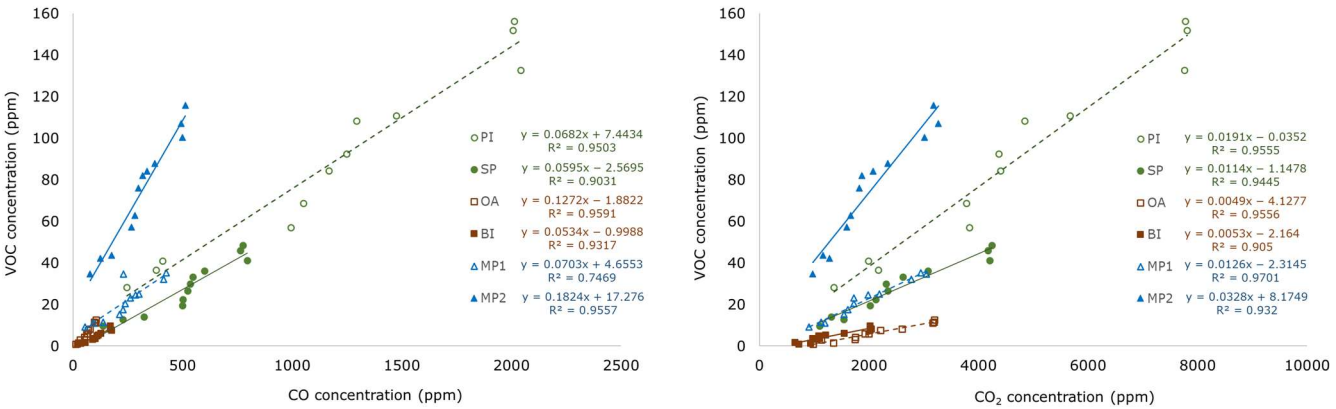

Figure 7. Correlation and regression analysis for (**a**) VOC and CO concentrations; (**b**) VOC and CO_2 concentrations for the pellets under study.

Similar relationships were also determined by Attard et al. [32]. A close correlation between CO, CO_2 and VOC results from the specific nature of autooxidation reactions occurring in plant material containing resin acids and lipids, especially unsaturated fatty acids. Their source in VOC could also be other volatile secondary metabolites present in biomass [3,47].

4. Conclusions

This study examined O_2 depletion and CO, CO_2 and VOC emissions in an enclosed space with wood pellets produced from forest residues from both coniferous and deciduous wood. The findings indicate a high gaseous carbon compound concentration and rapid oxygen depletion. The concentrations of the gases under analysis were found to change over time, which indicates the progressing autooxidation processes. The PI pellets exhibited the highest emission potential, and the SP pellets exhibited slightly lower levels. In general, concentrations of carbon oxides were much higher for pellets produced from coniferous

than deciduous sawdust. Additionally, significant oxygen depletion in the headspace (by nearly 5% v/v) was observed in the case of PI pellets after 14 days of incubation. It is noteworthy that the mean CO concentrations were higher than the STEL (15 min), as defined in the EU OSH regulations, for nearly all the pellets under study. The mean concentration of CO above the PI pellets was 12 times higher than the STEL, and the maximum (after 14 days of incubation) was even over 20 times higher. The pellets produced from deciduous wood were much safer in this regard, as even the maximum CO concentration after 14 days of incubation was approx. 100–170% of the STEL.

The current findings are extremely important from a scientific and practical perspective concerning the safety of storage and transport of solid biofuels in the form of pellets. Carbon monoxide is a highly toxic gas, and additionally, oxygen depletion in the warehouse air poses a serious threat to the health and life of workers on cargo ships transporting pellets as well as biofuel end users. Changes in the gas concentrations are associated with the processes of autooxidation, particularly the unsaturated fatty acids present in woody biomass. These are exothermic processes, resulting in self-heating, with potential fires possible in large warehouses or cargo bays on ships. The knowledge of the autooxidation processes in solid biofuels of forest origin may be helpful in organizing their logistics and storage. Considering the safety of people and property, it should be pointed out that proper ventilation of the rooms, the CO and O_2 concentration and the pellet temperature should be monitored during the storage and sea freight of wood pellets, especially those produced from coniferous wood. Moreover, pellets can be produced with additives containing antioxidants (synthetic or natural) that slow down autooxidation processes and, thus, off-gassing during storage. Therefore, future research should focus in a more comprehensive manner on factors that reduce the off-gassing of stored pellets as well as on the impact of these factors on the economic viability and emissions of burning pellets enriched with antioxidants. Wood pellets can be considered safe and sustainable fuel when these conditions are met.

Author Contributions: Conceptualization, K.W. and M.J.S.; methodology, K.W.; validation, K.W., A.B. and M.J.S.; formal analysis, K.W. and K.A.J.; investigation, K.W. and K.A.J.; resources, K.W. and M.J.S.; data curation, K.W. and K.A.J.; writing—original draft preparation, K.W. and M.J.S.; writing—review and editing, K.W., K.A.J., A.B. and M.J.S.; visualization, K.W. and A.B.; supervision, K.W.; project administration, K.W.; funding acquisition, K.W. and M.J.S. All authors have read and agreed to the published version of the manuscript.

Funding: The results presented in this paper were obtained as part of a comprehensive study financed by the University of Warmia and Mazury in Olsztyn, Faculty of Agriculture and Forestry, Department of Chemistry (grant No. 30.610.002-110) and Department of Genetics, Plant Breeding and Bioresource Engineering (grant No. 30.610.007-110). The project was financially supported by the Minister of Science and Higher Education in the range of the program entitled "Regional Initiative of Excellence" for the years 2019–2022, Project No. 010/RID/2018/19; amount of funding 12.000.000 PLN.

Data Availability Statement: Data are contained within the article.

Acknowledgments: We would like to thank the staff of the Department of Chemistry for their technical support during the experiment.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Stolarski, M.J.; Warmiński, K.; Krzyżaniak, M.; Olba-Zięty, E.; Akincza, M. Bioenergy technologies and biomass potential vary in Northern European countries. *Renew. Sustain. Energy Rev.* **2020**, *133*, 110238. [CrossRef]
2. Statistics Poland. *Energy from Renewable Sources in 2021*; Statistics Poland: Warsaw, Poland, 2022.
3. Malik, B.; Pirzadah, T.; Islam, S.; Tahir, I.; Kumar, M.; Rehman, R. Biomass Pellet Technology: A Green Approach for Sustainable Development. In *Agricultural Biomass Based Potential Materials*; Hakeem, K.R., Jawaid, M.Y., Alothman, O., Eds.; Springer International Publishing: Cham, Switzerland, 2015; pp. 403–433.
4. Statistics Poland. *Statistical Yearbook of Forestry 2022*; Statistics Poland: Warsaw, Poland, 2022.
5. Eurostat. Roundwood Removals by Type of Wood and Assortment. Agriculture, Forestry and Fisheries. Available online: https://ec.europa.eu/eurostat/databrowser/view/for_remov/default/table?lang=en (accessed on 13 October 2023).

6. Nunes, L.J.R.; Godina, R.; Matias, J.C.O.; Catalão, J.P.S. Evaluation of the utilization of woodchips as fuel for industrial boilers. *J. Clean. Prod.* **2019**, *223*, 270–277. [CrossRef]
7. Moskalik, T.; Gendek, A. Production of chips from logging residues and their quality for energy: A review of european literature. *Forests* **2019**, *10*, 262. [CrossRef]
8. Cardozo, E.; Malmquist, A. Performance comparison between the use of wood and sugarcane bagasse pellets in a Stirling engine micro-CHP system. *Appl. Therm. Eng.* **2019**, *159*, 113945. [CrossRef]
9. Hamzah, N.; Zandi, M.; Tokimatsu, K.; Yoshikawa, K. Wood biomass pellet characterization for solid fuel production in power generation. *Int. J. Renew. Energy Sources* **2018**, *3*, 32–40.
10. Stolarski, M.J.; Warmiński, K.; Krzyżaniak, M.; Olba-Zięty, E.; Stachowicz, P. Energy consumption and heating costs for a detached house over a 12-year period—Renewable fuels versus fossil fuels. *Energy* **2020**, *204*, 117952. [CrossRef]
11. Sandro, N.; Agis, P.; Gojmir, R.; Vlasta, Z.; Müslüm, A. Using pellet fuels for residential heating: A field study on its efficiency and the users' satisfaction. *Energy Build.* **2019**, *184*, 193–204. [CrossRef]
12. Thomson, H.; Liddell, C. The suitability of wood pellet heating for domestic households: A review of literature. *Renew. Sustain. Energy Rev.* **2015**, *42*, 1362–1369. [CrossRef]
13. Bioenergy Europe. *Statistical Report*; Pellets: Brussels, Belgium, 2022.
14. Rahman, M.A.; Rossner, A.; Hopke, P.K. Carbon monoxide off-gassing from bags of wood pellets. *Ann. Work Expo. Health* **2018**, *62*, 248–252. [CrossRef]
15. Alakoski, E.; Jämsén, M.; Agar, D.; Tampio, E.; Wihersaari, M. From wood pellets to wood chips, risks of degradation and emissions from the storage of woody biomass—A short review. *Renew. Sustain. Energy Rev.* **2016**, *54*, 376–383. [CrossRef]
16. Soto-Garcia, L.; Ashley, W.J.; Bregg, S.; Walier, D.; LeBouf, R.; Hopke, P.K.; Rossner, A. VOCs emissions from multiple wood pellet types and concentrations in indoor air. *Energy Fuels* **2015**, *29*, 6485–6493. [CrossRef] [PubMed]
17. Rahman, M.A.; Rossner, A.; Hopke, P.K. Occupational exposure of aldehydes resulting from the storage of wood pellets. *J. Occup. Environ. Hyg.* **2017**, *14*, 417–426. [CrossRef] [PubMed]
18. Pöllinger-Zierler, B.; Sedlmayer, I.; Reinisch, C.; Hofbauer, H.; Schmidl, C.; Kolb, L.; Wopienka, E.; Leitner, E.; Siegmund, B. Interrelation of volatile organic compounds and sensory properties of alternative and torrefied wood pellets. *Energy Fuels* **2019**, *33*, 5270–5281. [CrossRef]
19. Svedberg, U.R.A.; Högberg, H.-E.; Högberg, J.; Galle, B. Emission of hexanal and carbon monoxide from storage of wood pellets, a potential occupational and domestic health hazard. *Ann. Occup. Hyg.* **2004**, *48*, 339–349.
20. Hedlund, F.H.; Hilduberg, Ø.J. Fatal Accidents During Marine Transport of Wood Pellets Due to Off-Gassing: Experiences from Denmark. In *Biomass Volume Estimation and Valorization for Energy*; Tumuluru, J.S., Ed.; IntechOpen Limited: London, UK, 2017; pp. 73–97.
21. Emhofer, W. Emissions from Wood Pellets during Storage. Ph.D. Thesis, Faculty of Mechanical and Industrial Engineering, Vienna University of Technology, Vienna, Austria, 2015.
22. Meier, F.; Sedlmayer, I.; Emhofer, W.; Wopienka, E.; Schmidl, C.; Haslinger, W.; Hofbauer, H. Influence of oxygen availability on off-gassing rates of emissions from stored wood pellets. *Energy Fuels* **2016**, *55*, 132. [CrossRef]
23. Rahman, M.A.; Hopke, P.K. Mechanistic pathway of carbon monoxide off-gassing from wood pellets. *Energy Fuels* **2016**, *30*, 5809–5815. [CrossRef]
24. Soto-Garcia, L.; Huang, X.; Thimmaiah, D.; Denton, Z.; Rossner, A.; Hopke, P. Measurement and modeling of carbon monoxide emission rates from multiple wood pellet types. *Energy Fuels* **2015**, *29*, 3715–3724. [CrossRef]
25. Siwale, W.; Frodeson, S.; Finell, M.; Arshadi, M.; Jonsson, C.; Henriksson, G.; Berghel, J. Understanding off-gassing of biofuel wood pellets using pellets produced from pure microcrystalline cellulose with different additive oils. *Energies* **2022**, *15*, 2281. [CrossRef]
26. Siwale, W.; Frodeson, S.; Berghel, J.; Henriksson, G.; Finell, M.; Arshadi, M.; Jonsson, C. Influence on off-gassing during storage of Scots pine wood pellets produced from sawdust with different extractive contents. *Biomass Bioenergy* **2022**, *156*, 106325. [CrossRef]
27. Wang, S.; Yuan, X.; Li, C.; Huang, Z.; Leng, L.; Zeng, G.; Li, H. Variation in the physical properties of wood pellets and emission of aldehyde/ketone under different storage conditions. *Fuel* **2016**, *183*, 314–321. [CrossRef]
28. Kuang, X.; Shankar, T.J.; Bi, X.T.; Lim, C.J.; Sokhansanj, S.; Melin, S. Rate and peak concentrations of off-gas emissions in stored wood pellets—Sensitivities to temperature, relative humidity, and headspace volume. *Ann. Occup. Hyg.* **2009**, *53*, 789–796. [PubMed]
29. Kuang, X.; Shankar, T.J.; Sokhansanj, S.; Lim, C.J.; Bi, X.T.; Melin, S. Effects of headspace and oxygen level on off-gas emissions from wood pellets in storage. *Ann. Occup. Hyg.* **2009**, *53*, 807–813. [PubMed]
30. Sedlmayer, I.; Bauer-Emhofer, W.; Haslinger, W.; Hofbauer, H.; Schmidl, C.; Wopienka, E. Off-gassing reduction of stored wood pellets by adding acetylsalicylic acid. *Fuel Process. Technol.* **2020**, *198*, 106218. [CrossRef]
31. Sedlmayer, I.; Arshadi, M.; Haslinger, W.; Hofbauer, H.; Larsson, I.; Lönnermark, A.; Nilsson, C.; Pollex, A.; Schmidl, C.; Stelte, W.; et al. Determination of off-gassing and self-heating potential of wood pellets—Method comparison and correlation analysis. *Fuel* **2018**, *234*, 894–903. [CrossRef]
32. Attard, T.M.; Arshadi, M.; Nilsson, C.; Budarin, V.L.; Valencia-Reyes, E.; Clark, J.H.; Hunt, A.J. Impact of supercritical extraction on solid fuel wood pellet properties and off-gassing during storage. *Green Chem.* **2016**, *18*, 2682–2690. [CrossRef]

33. Tumuluru, J.; Lim, C.; Bi, X.; Kuang, X.; Melin, S.; Yazdanpanah, F.; Sokhansanj, S. Analysis on storage off-gas emissions from woody, herbaceous, and torrefied biomass. *Energies* **2015**, *8*, 1745–1759. [CrossRef]
34. Emhofer, W.; Lichtenegger, K.; Haslinger, W.; Hofbauer, H.; Schmutzer-Roseneder, I.; Aigenbauer, S.; Lienhard, M. Ventilation of carbon monoxide from a biomass pellet storage tank—A study of the effects of variation of temperature and cross-ventilation on the efficiency of natural ventilation. *Ann. Occup. Hyg.* **2015**, *59*, 79–90. [PubMed]
35. Granström, K.M. Sawdust age affect aldehyde emissions in wood pellets. *Fuel* **2014**, *126*, 219–223. [CrossRef]
36. Arshadi, M.; Gref, R. Emission of volatile organic compounds from softwood pellets during storage. *For. Prod. J.* **2005**, *55*, 132–135.
37. Arranz, J.I.; Miranda, M.T.; Montero, I.; Nogales, S.; Sepúlveda, F.J. Influence factors on carbon monoxide accumulation in biomass pellet storage. *Energies* **2019**, *12*, 2323. [CrossRef]
38. Li, H.; Wang, S.; Huang, Z.; Yuan, X.; Wang, Z.; He, R.; Xi, Y.; Zhang, X.; Tan, M.; Huang, J.; et al. Effect of hydrothermal carbonization on storage process of woody pellets: Pellets' properties and aldehydes/ketones emission. *Bioresour. Technol.* **2018**, *260*, 115–123. [CrossRef] [PubMed]
39. Liu, Y.; Shen, J.; Zhu, X.D. Headspace solid-phase microextraction for the determination of volatile organic compounds in *Larix gmelini* particles. *Phys. Procedia* **2012**, *32*, 605–613. [CrossRef]
40. Arshadi, M.; Tengel, T.; Nilsson, C. Antioxidants as additives in wood pellets as a mean to reduce off-gassing and risk for self-heating during storage. *Fuel Process. Technol.* **2018**, *179*, 351–358. [CrossRef]
41. Yazdanpanah, F.; Sokhansanj, S.; Rezaei, H.; Jim Lim, C.; Lau, A.; Tony, X.; Melin, S.; Shankar, J.; Soo, C. Measurement of off-gases in wood pellet storage. In *Advances in Gas Chromatography*; Guo, X., Ed.; InTech: London, UK, 2014.
42. Pohleven, J.; Burnard, M.; Kutnar, A. Volatile organic compounds emitted from untreated and thermally modified wood—A review. *Wood Fiber Sci.* **2019**, *51*, 231–254. [CrossRef]
43. Koppejan, J.; Loennermark, A.; Persson, H.; Larsson, I.; Blomqvist, P.; Arshadi, M.; Valencia-Reyes, E.; Melin, S.; Howes, P.; Wheeler, P.; et al. *Health and Safety Aspects of Solid Biomass Storage, Transportation and Feeding*; IEA Bioenergy: Utrecht, The Netherlands, 2013.
44. International Association of Classification Societies (IACS). *Confined Space Safe Practice, Recommendation No. 72, Rev.3 Dec 2018*; IACS: London, UK, 2018.
45. European Commission (EC). Commission Directive (EU) 2017/164 of 31 January 2017 establishing a fourth list of indicative occupational exposure limit values pursuant to Council Directive 98/24/EC, and amending Commission Directives 91/322/EEC, 2000/39/EC and 2009/161/EU. *Off. J. Eur. Union* **2017**, *27*, 115–120.
46. Government of the Republic of Poland. Regulation of the Ministry of Family, Labour and Social Policy of 12 June 2018 on the highest permissible concentrations and intensities of agents harmful to human health at a workplace. *J. Law Republ. Pol. (Dz. U.)* **2018**, *1286*, 1–40.
47. Svedberg, U.; Petrini, C.; Johanson, G. Oxygen depletion and formation of toxic gases following sea transportation of logs and wood chips. *Ann. Occup. Hyg.* **2009**, *53*, 779–787.