Article

Analysis on Storage Off-Gas Emissions from Woody, Herbaceous, and Torrefied Biomass

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Abstract: Wood chips, torrefied wood chips, ground switchgrass, and wood pellets were tested for off-gas emissions during storage. Storage canisters with gas-collection ports were used to conduct experiments at room temperature of 20 °C and in a laboratory oven set at 40 °C. Commercially-produced wood pellets yielded the highest carbon monoxide (CO) emissions at both 20 and 40 °C (1600 and 13,000 ppmv), whereas torrefied wood chips emitted the lowest of about <200 and <2000 ppmv. Carbon dioxide (CO_2) emissions from wood pellets were 3000 ppmv and 42,000 ppmv, whereas torrefied wood chips registered at about 2000 and 25,000 ppmv, at 20 and 40 °C at the end of 11 days of storage. CO emission factors (milligrams per kilogram of biomass) calculated were lowest for ground switchgrass and torrefied wood chips (2.68 and 4.86 mg/kg) whereas wood pellets had the highest CO of

about 10.60 mg/kg, respectively, at 40 °C after 11 days of storage. In the case of CO_2, wood pellets recorded the lowest value of 55.46 mg/kg, whereas switchgrass recorded the highest value of 318.72 mg/kg. This study concludes that CO emission factor is highest for wood pellets, CO_2 is highest for switchgrass and CH_4 is negligible for all feedstocks except for wood pellets, which is about 0.374 mg/kg at the end of 11-day storage at 40 °C.

1. Introduction

Woody and herbaceous biomasses, stored in humid environments for long periods, will absorb moisture and decompose, bringing about changes in physical properties, chemical composition and energy value [1]. The same authors found that after one year of storage, wood chips lost about 25%–55% of their energy value, which is mainly due to moisture adsorption. These changes in the physical, chemical and energy properties can decrease the market value of the fuels. Wood chips with high moisture are sensitive to biochemical reactions during storage [2,3]. Zoch *et al.* [4] indicated that chips from whole-tree aspen release much more heat and lose dry weight six times faster than clean, debarked chips. Moran [5] reported that the decay rate for mixed hardwood whole-tree chips (mainly oak) stored in an outside pile was roughly three times that for clean, debarked chips. Their research indicated that temperature profile of the wood chips stored for 7–14 days rose to 60–70 °C due to chemical and biological reactions that release oxygen-depleting off gases, such as CO, CO_2, and CH_4, during storage. Quantification of these off-gases has been considered important because fatal accidents have been reported at wood-chip and pellet warehouses during material unloading [6]. The risks associated with the transportation of seemingly harmless cargo (wood pellets and wood chips) are now well known and recorded. Several researchers have indicated that at storage temperatures >30 °C wood chips and wood pellets emit high amounts of CO (>10,000 ppmv), CO_2 (>30,000 ppmv), and CH_4 emission (>2000 ppmv) [7–13]. These reported CO and CO_2 emissions for wood chips and wood pellets are well above the threshold concentration levels established by U.S. Department of Labor Occupational Safety and Health Administration. According to Back and Allen [14], Höll and Pieczonka [15], and Piispanen and Saranpää [16], dry woods like Scots pine and Norway spruce contain about 3%–5% triglycerides, which can undergo oxidation and yield hexanal and other off-gases (such as CO). Svedberg *et al.* [11] indicated that in addition to CO, wood pellets also emitted hexanal during storage.

The threshold level established by U.S. Department of Labor Occupational Safety and Health Administration for carbon monoxide concentration is 35 ppm for a time-weighted 8-h period. Concentration levels ≥800 ppm for 45 min can result in dizziness, nausea, and convulsions resulting in death after a 2–3 h period. The threshold level of CO_2 is 5000 ppm as an 8-h time-weighted average. At very high levels (30,000 ppm (short-term exposure level) and above), CO_2 can cause asphyxiation as it replaces oxygen in the blood resulting in loss of judgment, dizziness, drowsiness, and rapid breathing. The CH_4 threshold level is 500,000 ppm over 8-h time-weighted average. Higher concentrations can result in asphyxiation by displacing oxygen. CH_4 is also one of the main constituents of natural gas, which can

result in explosions [7]. In addition to the safety issues, the emissions from biomass can have a significant effect on the greenhouse gas emissions. Emery and Mosier [17] indicated that during storage of biomass, the dry matter losses can increase net greenhouse gas emissions. The same authors suggested a greater understanding of the biomass storage losses and greenhouse gas fluxes is necessary to accurately assess biomass storage options to ensure the design of the biomass supply logistics system meets the greenhouse gas reduction mandates required for biofuel production.

Increasing the storage stability or reducing reactivity of the biomass to the storage environment can help reduce the storage off-gas emissions. In general, both woody and herbaceous biomass is dried to 10% (w.b.) moisture content in a rotary drier to increase their storage stability. This dried biomass is further used for pelletization [18]. Pellets are considered as stable products as they have moisture in the range of 5%–7% (w.b.). Currently, torrefaction (a thermal pretreatment process) helps reduce the biomass moisture content to a very low value about <2% (w.b.) making it hydrophobic and suitable for thermochemical applications like pyrolysis, gasification, and co-firing [19–23]. Torrefaction of biomass is a thermochemical process that can be described as a mild form of pyrolysis at temperatures typically ranging between 200 and 300 °C in an inert and reduced environment, resulting in a solid, uniform product with lower moisture and higher energy content [24–27]. Tumuluru *et al.* [19] described the physiochemical and structural changes in biomass at different temperature regimes. Torrefaction temperatures >200 °C result in breakage of inter- and intra-molecular, hydrogen, C–O, and C–C bonds. Breaking chemical bonds leads to the emission of hydrophilic and oxygenated compounds [19]. Also, the destruction of OH groups during torrefaction makes biomass hydrophobic and increases storage stability [28].

Objective

There is a great deal of interest in understanding the off-gas emissions during storage of different biomass forms used for energy applications. Most of the data reported on storage off-gas emissions were for wood pellets and wood chips. Our earlier work on profiling and quantifying the off-gases [7–10,13] from wood pellets has helped the Wood Pellets Association of Canada to develop material safety data sheets for storage and transportation. Off-gas emissions data for other feedstocks—like switchgrass, and thermally pretreated (torrefied) biomass—that are gaining popularity for bioenergy applications, are not available. The off-gas emission data for herbaceous and torrefied biomass will be very useful in understanding the health-hazard risks and proposing mitigation methods and also will help to develop material safety data sheets for their safe storage and transportation. Our earlier studies on wood pellets indicated that increasing the storage temperature to >30 °C increases the off-gas emissions exponentially during the first 10 days of storage, whereas storage temperatures ≤20 °C resulted in a linear increase in off-gas emission with respect to storage time [7,13]. The specific objective of this study is to examine off-gas-emission concentration from torrefied wood chips, ground switchgrass, raw wood chips, and wood pellets at a 20 °C room temperature and an elevated storage temperature of 40 °C for an 11-day storage period. Further emission-concentration data for all the feedstock was used to calculate an emission factor (milligrams of off-gas emitted per kilogram of biomass).

2. Material and Methods

2.1. Raw Material and Properties

Clean pine-wood chips and wood pellets were collected from a shipping location in Vancouver, BC, Canada (Fibreco, Inc., North Vancouver) and tested for moisture content. The procured wood chips were further torrefied at 250 °C for 30 min in a fixed-bed reactor and then cooled and stored in airtight containers. Wood chips were dried to about 10% moisture content (w.b.) in a convective oven at 40–50 °C. Switchgrass (*Panicum virgatum*) was procured from a farm in Manitoba and ground to a 2-mm particle size using a hammer mill. The ground samples were stored in air-sealed bags in a commercial refrigerator set at 4 °C. Off-gassing experiments were conducted in the same year (2007–2008) the feedstocks were procured. The moisture content of the wood chips, ground switchgrass, torrefied wood chips, and wood pellets at the beginning of these experiments was determined using the AOAC method (*i.e.*, the oven method, where the biomass was kept at 105 °C for 24 h and was expressed in wet basis) [29]. The reported values are an average of three measurements. All raw materials were further tested for bulk and particle density following the ASABE S267 standard procedure [30,31].

2.2. Particle Density and Porosity

A gas multi-pycnometer (QuantaChrome, Boynton Beach, FL, USA) was used to determine the particle density of the feedstocks by calculating the displaced volume of nitrogen gas by a known mass of sample material [31]. The pressure was set at around 40 kPa (near maximum as specified by the instrument specifications). Equation (1) is used to calculate the sample volume (Vp):

$$V_P = V_C - V_R \left(\frac{P_1}{P_2} - 1 \right)$$

(1)

where:
  P_1 = pressure reading after pressurizing the reference cell (kPa)
  P_2 = pressure after connecting the reference cell to the sample cell
  V_c = sample volume
  V_R = reference volume.

The particle density (ρ_s) of the sample is calculated by dividing mass (m_p) by the pycnometer particle volume (V_{pvc}). The experiments were conducted in triplicates. The porosity values were calculated using the bulk and particle-density values using Equations (2) and (3):

$$\rho_s = \frac{m_p}{V_{pvc}}$$

(2)

$$\text{Porosity} = \left(1 - \frac{\rho_b}{\rho_s}\right)$$

(3)

where:
  ρ_b = bulk density
  ρ_s = particle density.

2.3. Off-Gas Measurement

Canisters were used to conduct the storage studies (Figure 1). Canisters were filled to about 95% of their volume with different feedstocks. A 3.125-mm-diameter port with a control valve installed on the canister lid was used to collect the off-gas samples. The different biomass materials (*i.e.*, wood chips, wood pellets, torrefied wood chips, and ground switchgrass) were placed in the canister, leaving a headspace of about 5%. In the present study, a minimum head space of 5% was selected based on our earlier study on storage of wood pellets at both low and high storage temperatures [13]. Studies at 20 °C were carried out in a laboratory set at 20 °C and the higher temperature of 40 °C using a laboratory oven. A gas chromatography (GC)-14A fuel-cell analyzer (Shimadzu, Kyoto, Japan) was used to analyze the off-gas samples. A standard gas composition of CO: 1000 ppmv; CO_2: 5000 ppmv; and CH_4: 1000 ppmv was used to calibrate the GC. Approximately 10-mL off-gas sample was collected using an airtight syringe (A-85137-20 mL SGE Gas-Tight Syringe, Luer-Lock, Mandel Scientific, Guelph, ON, Canada) and injected into the GC-14A [7,13]. In the present study off-gas measurements reported are from single measurements by other researchers [7–13,32].
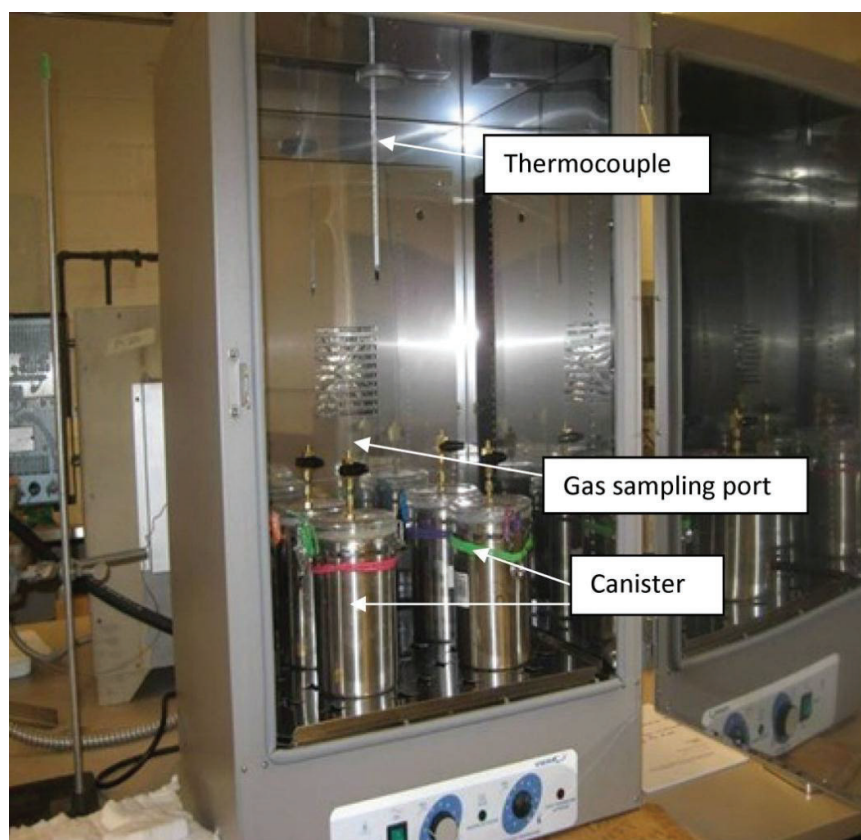

Figure 1. Storage canisters filled with different feedstocks.

2.4. Emission Factor Calculation

Yazdanpanah *et al.* [32] used concentration data to calculate the emission factor (milligrams of off-gas per kilogram of material). Table 1 indicates the equations constants used in the emission factor calculation. At constant temperature T (K) and pressure P (Pa), the emission factor (f_i) (milligrams of

off-gas per kilogram of materials, mg/kg) is related to volumetric gas concentration (C_i), as expressed in Equation (4):

$$f_i = \frac{PC_iVgM_{wt}}{RTM} \times 1000 \tag{4}$$

where:

R = gas constant (8.31 J/mol·K)

T = temperature (K)

M_{wt} = gas molecular weight (g/mole)

M = mass of material in the container (kg)

V_g = gas volume in the container (m^3)

P_a = absolute pressure of the container (generally, there is minimal change in P_a at relatively low temperatures associated with the observed tests [7]). In their study, pressure in the storage container was measured using a pressure transducer (PX143-01BD5V, 91 Pa, Omega, Laval, QC, Canada) and the data was logged into a computer using LabVIEW software

C_i = volumetric concentration of a particular off-gassing measure by GC (expressed as fraction volume/volume).

Table 1. Constants used for emission factor (g/kg) calculation based on off-gas concentration data.

S. No.	Equation Parameters	Value
1	Molecular weight of CO, CO$_2$, and CH$_4$ (M$_{wt}$)	28, 44, and 16
2	Volumetric concentration of particular off gas (m^3)	Gas concentrations measured using GC (ppmv/1,000,000)
3	Temperature (K)	293 and 313
4	Pressure (Pa)	101,300
5	Gas constant (R) (J/mol·K)	8.31
6	Mass of the biomass stored in the container (m$_w$) (kg)	Ground switchgrass: 0.36 Wood pellets: 1.60 Wood chips: 0.64 Torrefied wood chips: 0.54
7	Volume of the gas in the container, including headspace of 5% (m^3)	Ground switchgrass: 0.0021 Wood pellets: 0.00119 Wood chips: 0.00152 Torrefied wood chips: 0.00154

Note: Volume of gas in the container calculation was based on the bulk porosity of the materials. The porosity calculation was based on the bulk and particle-density values.

Equation (5) presents the sample calculation for emission factor (mg/kg) for off-gas CO at the end of 11-day storage at 40 °C storage temperature. The various constants used for calculation of emission factor are given below:

$$\frac{101300 \times 13294.7 \times 0.00118 \times 28 \times 1000}{8.31 \times 313 \times 1.6 \times 1000000} = 10.69 \, mg/kg \tag{5}$$

where CO concentration at 40 °C for wood pellets at the end of 11-day storage: 13,294 ppmv (0.013294 m^3); storage temperature: 40 °C (313 K); porosity: 0.41 (calculated using bulk density: 710 kg/m^3; and particle density: 1210 kg/m^3); total porosity (including headspace of 5% of the container): 0.41 + 0.05 = 0.46; volume of the container (m^3): 0.00256; gas volume in the container: total porosity (including 5% of headspace) × volume of the container: 0.00118 m^3; mass of wood pellets in the container: 1.60 kg; molecular weight of CO: 28 (g/mole); absolute pressure in the container: 101,300 (Pa) and gas constant (R): 8.31 (J/mol·K).

3. Results and Discussion

3.1. Physical Properties

The moisture content and bulk- and particle-density of wood chips, ground switchgrass, torrefied wood chips, and wood pellets are given in Table 2. Leaving a headspace of 5%, ground switchgrass of about 0.36 kg, wood pellets of about 1.60 kg, wood chips of about 0.64 kg, and torrefied wood chips of about of 0.54 kg were used to fill the storage canister.

Table 2. Physical properties of herbaceous, woody and torrefied biomass ($n = 3$).

S. No.	Biomass Feedstock	Moisture Content (%, w.b.)	Bulk Density (kg/m^3)	Particle Density (kg/m^3)	Porosity
1	Ground switchgrass	10.21 ± 0.21	151 ± 9	650 ± 21	0.76
2	Wood pellets	5.02 ± 0.16	710 ± 19	1210 ± 8	0.41
3	Wood chips	12.12 ± 0.12	265 ± 12	580 ± 17	0.54
4	Torrefied wood chips	1.8 ± 0.19	225 ± 23	505 ± 11	0.55

3.2. Off-Gas Concentrations

Figures 2 through 7 indicate the emission levels of CO, CO_2, and CH_4 from ground switchgrass, wood chips, torrefied wood chips, and wood pellets at both 20 and 40 °C for a storage period of 11 days. Figure 2 indicates that the maximum CO emissions were recorded by wood pellets (about 1600 ppmv), followed by wood chips (about 600 ppmv); torrefied wood chips and switchgrass emitted significantly less CO (less than 200 ppmv). Figure 3 shows that a maximum concentration of about 13,000 ppmv was recorded for wood pellets at 40 °C; however, torrefied wood chips show the lowest recorded amount of about 2000 ppmv. Wood chips and ground switchgrass recorded about 3000 ppmv. CO_2 emissions from the four biomass feedstocks at 20 °C indicated that wood pellets emitted a maximum of about 3000 ppmv; switchgrass and torrefied wood chips recorded the lowest amounts (2000 ppmv) (see Figure 4). At 40 °C, wood pellets emitted about 42,000 ppmv, which corroborates results reported in the literature [7–13], whereas torrefied wood chips emitted the lowest CO_2 amounts at about 25,000 ppmv. Wood chips and switchgrass registered at about 30,000 ppmv (see Figure 5). Figures 6 and 7 show the CH_4 emissions at 20 °C and at 40 °C. The torrefied wood chips recorded the lowest CH_4 amounts (about 5 ppmv) at 20 °C, while the wood pellets registered about 45 ppmv. These concentrations can be considered marginal when compared to CO and CO_2 emissions. At 40 °C, the wood pellet samples registered at about 1300 ppmv, which was by far the highest compared with other feedstocks. The torrefied wood chips recorded the lowest amounts, less than 100 ppmv.
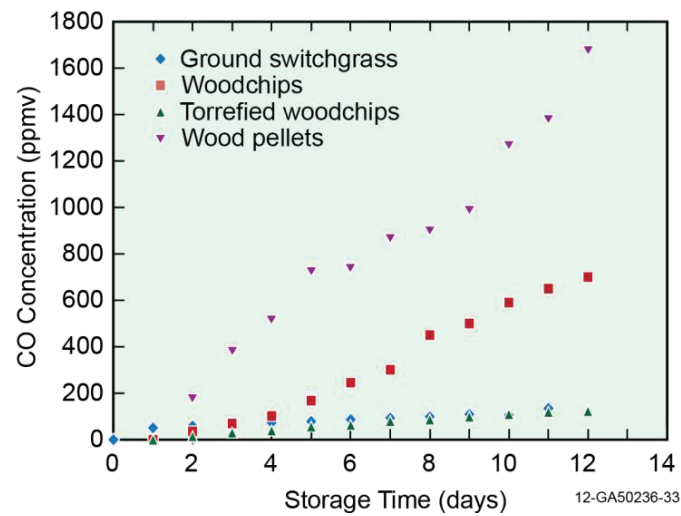
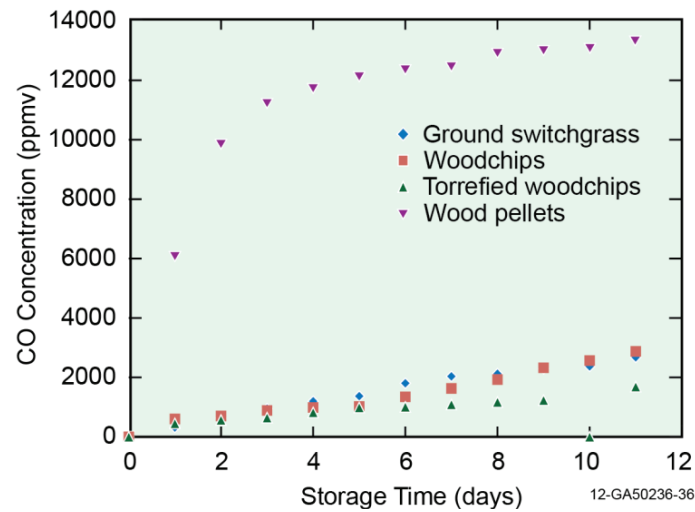**Figure 2.** CO concentration at 20 °C storage temperature.

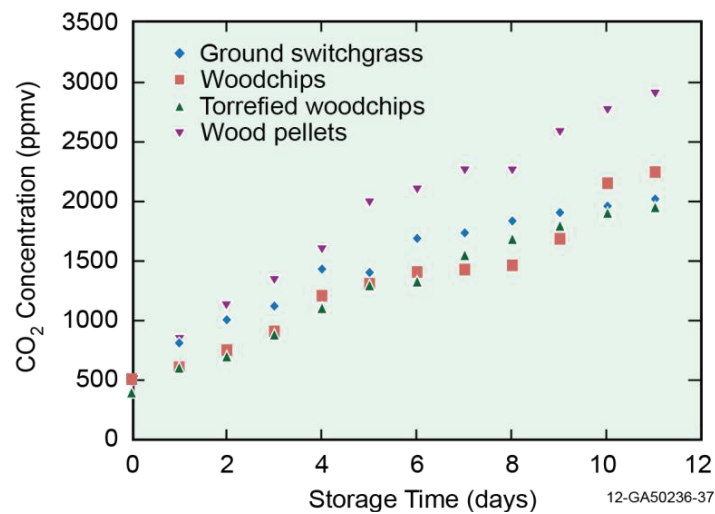**Figure 3.** CO concentration at 40 °C storage temperature.

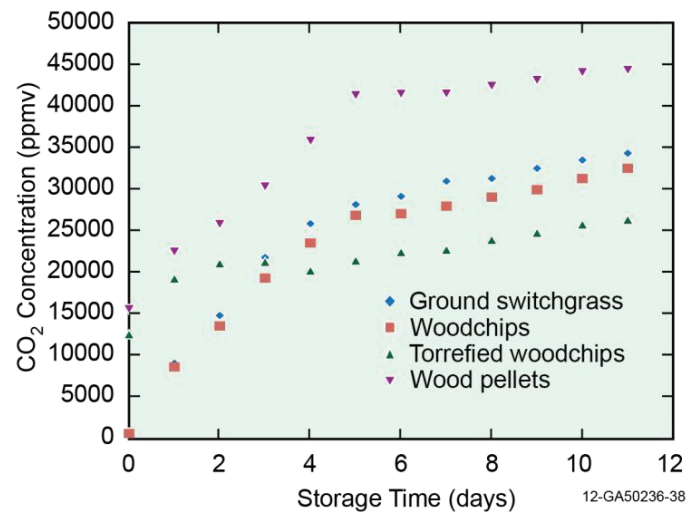
Figure 4. CO_2 concentration at 20 °C storage temperature.

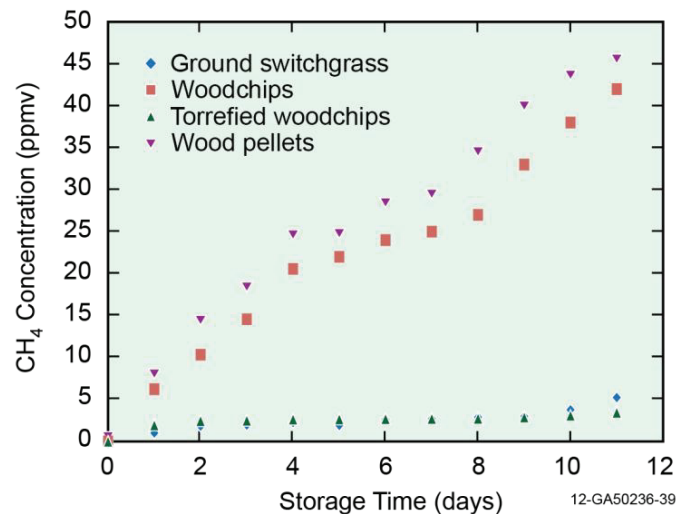**Figure 5.** CO$_2$ concentration at 40 °C storage temperature.

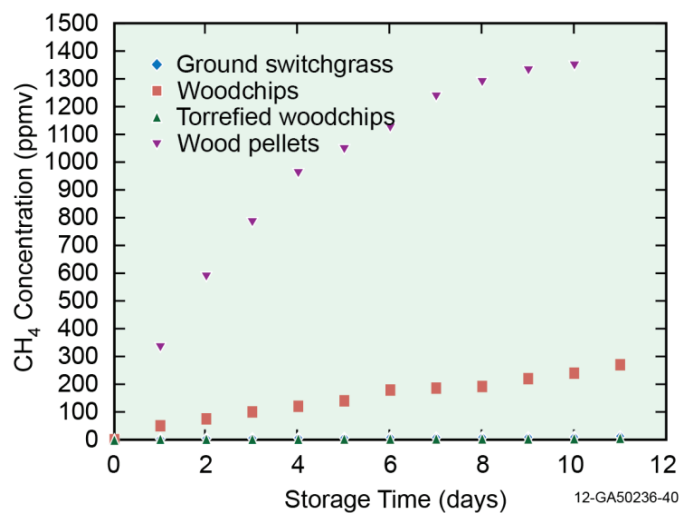**Figure 6.** CH$_4$ concentration at 20 °C storage temperature.

Figure 7. CH$_4$ concentration at 40 °C storage temperature.

3.3. Emission Factor (mg/kg)

Based on the concentration data, emissions factors were calculated for CO, CO_2, and CH_4 from ground switchgrass, wood chips, torrefied wood chips, and wood pellets stored at both 20 and at 40 °C for an 11-day period. A maximum CO-emission factor of about 10.60 and 6.96 mg/kg was recorded by wood pellets and wood chips, respectively. The lowest CO-emission factor for ground switchgrass was recorded at about 2.67 mg/kg at 40 °C, whereas in the case of torrefied woodchips and ground switchgrass it was about 4.85 and 2.68 mg/kg at the end of the 11-day storage period. At 20 °C, the highest CO-emission factor of 1.81 and 1.43 mg/kg were recorded for wood chips and wood pellets, whereas ground switchgrass and torrefied woodchips recorded 0.38 and 0.85 mg/kg at the end of the 11-day storage period.

For CO_2 stored at 40 °C, a maximum emission factor was recorded for ground switchgrass at about 318.72 mg/kg, followed by 123.50 and 118.68 mg/kg for wood chips and torrefied wood chips, respectively, whereas wood pellets recorded the lowest at about 55.45 mg/kg at the end of the 11-day storage period. At 20 °C, the trend was similar, where ground switchgrass recorded the highest value of 19.98 mg/kg, followed by torrefied and regular wood chips of about 9.39 and 9.09 mg/kg, respectively. Wood pellets recorded the lowest of 3.86 mg/kg at the end of the 11-day storage period. The calculated CH_4-emission factor indicated that at 20 °C, the values are very low for all the feedstocks, whereas, at 40 °C, wood pellets recorded the highest emission factor of about 0.76 mg/kg, and torrefied wood chips, the lowest, at about 0.0104 mg/kg. The emission-factor data for CO, CO_2 and CH_4 calculated for wood pellets has corroborated observations reported in the literature [32]. The same authors indicated that the emission factors calculated for off gases like CO, CO_2, and CH_4 from wood pellets for two different-sized storage containers (5200 L and 45 L) were close and also matched closely with the present observations. We have learned from this study that the emission factor calculated based on the concentrations, is strongly dependent on physical properties like bulk and particle density and porosity, which determines the gas volume in the storage container.

3.4. Discussion

In the present study, torrefied wood chips emitted less CO and CH_4 at both 20 and 40 °C than ground switchgrass, woodchips, or wood pellets. Tumuluru *et al.* [19] suggested that, during torrefaction, the biomass loses some of the low-volatility components and extractives, resulting in a hydrophobic product low in moisture content. These changes in the biomass might result in reduced biomass reactivity in the storage environment and fewer chemical-oxidation reactions during storage. Emissions from torrefied biomass reported in this paper indicate that microbial degradation may not be the reason for off-gas emission, because torrefied biomass has less moisture (Table 2) and absorbs little moisture during storage [19]. The measured emissions could have occurred mainly due to chemical oxidation of the chemical components present in the biomass. According to Yazdanpanah [33], torrefied pellets adsorbed about 20% more CO_2 compared to regular pellets. This may be explained by the rate of reaction between off-gas and biomass solid, which is generally proportional to the accessible surface area of the solid. The lower CO_2 emission detected by torrefied samples in this study could be attributed to the higher adsorption of CO_2 by torrefied samples. The speculation is that the torrefaction process causes

dehydration and thus initiates and propagates cracks in the lignocellulosic structure of material. The mass loss also induced changes in density and porosity.

Our earlier studies on off-gases from woody pellets at lower ($\leq$20 °C) and higher ($\geq$30 °C) temperatures indicated that CO and CO_2 emissions and O_2 depletion in the headspace of the storage container are significantly lower at low storage temperatures compared to higher storage temperature. This study has helped us conclude that it is mostly chemical oxidation that results in off-gas emissions from stored wood pellets [7,13], where higher storage temperature accelerates the rate of the oxidation process. The CO, CO_2, and CH_4 off-gas emissions observed from different biomass in the present study can be due to auto-oxidation of the chemical compounds in the biomass. The storage temperature acts as a catalyst to accelerate the chemical oxidation process. Research studies conducted by Back and Allen [14], Höll and Pieczonka [15], and Piispanen and Saranpää [16] on woody biomass (Scots pine and Norway spruce) indicated that triglycerides undergo auto-oxidation in the presence of temperature and emit off-gases like CO and hexanal. Springer and Hajny [34], Kuber *et al* [35], and Kuber [36,37] have established that auto-oxidation of unsaturated fatty acids and other extractives leads to spontaneous heating of wood chips and sawdust during storage. According to Levitt *et al*. [38], when stored at room temperature (particularly in the presence of air and light), organic matter emits small amounts of CO and the emissions are accelerated at elevated temperatures. Svedberg *et al*. [11,12] and Tumuluru *et al.* [13] reported that the emission of these off-gases during storage is due to chemical oxidation of fatty acids, leading to the formation of free radicals. These types of reactions are accelerated by: (a) the environmental conditions of storage, such as temperature and relative humidity; and (b) the biomass-feedstock moisture content and chemical composition. Also, the present study indicates that the off-gas emission concentration varies with the type of the biomass. One major reason for different concentrations observed for different raw and thermally-pretreated biomass feedstock can be different chemical composition (*i.e.*, woody biomass has higher fatty acids and lignin compared to herbaceous biomass). On the other hand, herbaceous biomasses are lower in lignin and free fatty acids [39,40]. Further research is needed to understand the chemistry behind different quantities of off-gas emissions from different biomass feedstocks.

At present, there is a great need to understand the biomass storage losses in terms of dry matter and greenhouse gas fluxes to assess biomass storage options to ensure the design of the biomass supply logistics system which can meet the greenhouse gas reduction requirements for biofuel production. According to Steele *et al*. [41], CO_2 gas emitted during storage due to decomposition process can be used to estimate the dry matter loss. According to their analysis the dry matter breakdown into simple sugars during storage and emits CO_2. Also, the off-gas emission data collected for different woody, herbaceous, and pretreated biomass will help design storage silos by taking into account the hazards associated with off-gases that are emitted and avoid fatal accidents that have been reported in pellet warehouses. This will help mitigate the risks, adopt active control measures, and implement safe working strategies. The off-gas data on herbaceous and thermally-pretreated biomass (like torrefied biomass presented in this paper) will also support developing material safety data sheets for safe storage and transportation of woody, herbaceous and thermally pretreated biomasses.

4. Conclusions

The present experimental study demonstrates that there is off-gassing from stored wood pellets, wood chips, ground switchgrass, and torrefied wood chips posing potential hazards that require mitigation by the proper design of silos and development of safe handling procedures. CO emissions for all the feedstocks at room temperature (20 °C) are above the threshold-level exposure guidelines of 35 ppmv for an occupational setting and 9 ppmv for homes. At the elevated storage temperature of 40 °C, the off-gases CO and CO_2 increase to levels where they could produce fatal accidents within short exposure times. The results indicate that torrefied wood chip emits less CO, CO_2, and CH_4 when compared to wood pellets, untreated wood chips, and ground switchgrass. At 20 and 40 °C, wood pellets recorded the maximum CO concentrations of 1600 and 13,000 ppmv, whereas torrefied wood chips emitted less than 200 and 2000 ppmv. CH_4 emissions recorded for all the feedstocks were less than 100 ppmv at both 20 and 40 °C, except for wood pellets, which recorded 1300 ppmv at 40 °C. The calculated CO emission factors (based on the bulk and particle density and porosity) indicate that wood pellets have the highest emission factor (10.60 mg/kg) at 40 °C, whereas in the case of CO_2, the wood pellets recorded the lowest value (55.46 mg/kg), and switchgrass the highest value (318.72 mg/kg).

Author Contributions

Jaya Shankar Tumuluru conducted the experiments, collected and analyzed the off-gas data, and prepared the draft manuscript. Xingya Kuang and Fahimeh Yazdanpanah supported the experimental work and data analysis, Shahab Sokhansanj, C. Jim Lim, and Xiaotao T. Bi are research advisors on biomass storage, and Staffan Melin is research advisor on wood pellet storage.

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Conflicts of Interest

The authors declare no conflict of interest.

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