

Rate and Peak Concentrations of Off-Gas Emissions in Stored Wood Pellets—Sensitivities to Temperature, Relative Humidity, and Headspace Volume

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Wood pellets emit CO, CO₂, CH₄, and other volatiles during storage. Increased concentration of these gases in a sealed storage causes depletion of concentration of oxygen. The storage environment becomes toxic to those who operate in and around these storages. The objective of this study was to investigate the effects of temperature, moisture, and the relative size of storage headspace on emissions from wood pellets in an enclosed space. Twelve 10-l plastic containers were used to study the effects of headspace ratio (25, 50, and 75% of container volume) and temperatures (10–50°C). Another eight containers were set in uncontrolled storage relative humidity (RH) and temperature. Concentrations of CO₂, CO, and CH₄ were measured by gas chromatography (GC). The results showed that emissions of CO₂, CO, and CH₄ from stored wood pellets are more sensitive to storage temperature than to RH and the relative volume of headspace. Higher peak emission factors are associated with higher temperatures. Increased headspace volume ratio increases peak off-gas emissions because of the availability of oxygen associated with pellet decomposition. Increased RH in the enclosed container increases the rate of off-gas emissions of CO₂, CO, and CH₄ and oxygen depletion.

Keywords: biomass; emission factors; headspace ratio; moisture effect; off-gassing emission; storage; temperature effect; wood pellets

INTRODUCTION

Wood pellets are used for heat and electricity production. More than 800 000 tonnes of wood pellets were exported from Canada to Europe in 2008, mainly from British Columbia. The reaction mechanisms for biomass combustion and emissions from wood pellet combustion have been extensively investigated (Chen and Workman, 1990; Dinu, 2006; Wadso, 2007). Recently, more attention has been given to the emissions from wood pellets during their storage and transportation because these emissions can become a potential health risk (Svedberg *et al.*, 2008).

It is well known that a biomass gradually decomposes chemically and biologically and during these

processes it slowly releases toxic gases, leading to depleting oxygen (Reuss and Pratt, 2000; Johansson *et al.*, 2004; Arshadi and Gref, 2005). Svedberg *et al.* (2004) has reported the composition of the off-gas emissions from stored wood pellets, with CO, CO₂, CH₄, and non-methane organic compounds being commonly identified in the off-gases from biomass (Johansson *et al.*, 2004). Kuang *et al.* (2008) developed a kinetic model of off-gas emissions from wood pellets in sealed containers to predict the evolution of emission rate factors at different storage temperatures. Many factors may contribute to the buildup of gas pollutants emitted from wood pellets in storage. Pellets made from aged sawdust might generate less volatile organic compounds (VOCs) than pellets made from fresh sawdust. The level of off-gas emissions was also found to depend on wood species. Pellets made from spruce sawdust emitted less VOCs

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than pellets made from pine (Arshadi and Gref, 2005). Although the chemical/physical property changes of wood pellets influence the amounts of emissions, the storage environment and conditions should also be fully considered in the development of off-gassing mechanisms and characterization of emissions from wood pellets in storage.

The objective of this study was to investigate the effect of temperature, relative humidity (RH), and storage headspace on the off-gas emissions from wood pellets in an enclosed storage space.

METHODS

Materials and equipments

Twelve 10-l plastic containers (200 mm diameter and 320 mm high) were used to study gas emissions by loading different weights of wood pellets at different temperatures. Three containers were filled with 1.75, 3.5, and 5.25 kg of wood pellets to fill 25, 50, and 75% of the container volume. The average bulk density of pellets was 700 kg m^{-3} . A pellet mill in British Columbia supplied the pellets. The raw material for wood pellets was fresh pine sawdust and planer shavings from mountain pine (*Pinus contorta* Douglas) beetle-infested trees with an estimated 2 years beyond mortality. The moisture content of pellets as received was 5.1% (wet mass basis).

Four containers having the same head space ratio were each placed in one of the four temperature controlled ovens. Each oven was set at 10, 23 (room temperature), 35, or 45°C. These temperature treatments were repeated for each of the three head space ratios. Ten milliliters of gas samples were drawn daily from the containers by a gastight syringe. The composition of the sampled gas was analyzed by a gas chromatographic method [hydrogen flame ionization detector, (FID) and thermal conductivity detector (TCD)] using a GC-14A (SHIMADZU Corporation, Japan) to quantify concentrations of CO, CO₂, CH₄, O₂, and N₂. Prior to measurements, the temperatures of TCD and FID were set at 100 and 200°C, respectively. The gas chromatography (GC) was calibrated with standard CO, CO₂, and CH₄ gases. The standard CO, CO₂, and CH₄ gas concentrations were 1000, 5000, and 1000 p.p.m., respectively. The certified corresponding purity for each standard gas was 969 p.p.m. for CO based on HP 6890 method, 4898 p.p.m. for CO based on Carle 400 AGC, and 995 p.p.m. for CH₄ based on HP 6890 method. Argon and compressed air were used as the reference and carrier gases. A fused silica capillary column of inner diameter of 0.1 mm and 50 m long was used. Gas removal from each container at each time step and composition analysis was repeated twice.

Another set of eight 10-l plastic containers was used to investigate the effects RH and temperature had on wood pellet emissions. Two containers were

loaded with 3.5 kg of wood pellets (50% of container volume). A 500-ml dish was filled with water and placed at the bottom of one of the containers to create a humid space. The wood pellets were loaded on a screen (diameter < 1 mm) installed above the water-filled dish. Four groups of containers with the same set were sealed airtight and set at temperatures of 10°C, room temperature (~23°C), 35, and 45°C. A wireless temperature and humidity sensor was placed inside the container on the top of wood pellets. Temperature and moisture were recorded daily. During the first 3 days, 10 ml gas samples were drawn every day. The remaining 27 days, gas samples were drawn every 5 days. A total of 10 samples were removed from each container and measured daily by GC to determine the concentration of CO, CO₂, and CH₄. Tests were run until the concentration of CO, CO₂, and CH₄ did not increase any further, which usually happened after ~30 days.

Data analysis

The concentrations of CO, CO₂, and CH₄ were converted to emission factors using the N₂ balance method (Kuang *et al.*, 2008). As an inert gas, N₂ is assumed not consumed or generated during the storage period. The N₂ concentration measured at the beginning (79%) over that measured after time t is used to calculate the change in the total moles of gas species in the container. Under constant temperature (T) and pressure (P), the concentration can be converted to an emission factor, f_i (in off-gas species per kilogram of pellets), for gas species i by

$$f_i = \frac{P(C_i V_g) M_{wt} C_{n0}}{RT M_p C_{nt}}, \quad (1)$$

where C_{n0} is the initial concentration of N₂, C_{nt} is the measured concentration of N₂ at time t , M_p is the total mass of wood pellets in the container calculated by N₂ balance method, and M_{wt} is the molecular weight of the gas species. V_g is the gas volume in the container which equals the difference between container volume (V) and pellets volume (V_p) (i.e. $V_g = V - V_p$). P is gas pressure. The volume occupied by pellets (V_p) was calculated based on the weight of pellets divided by the average density of a single pellet. The density of a single pellet is calculated as the average values of the weight of single pellets divided by the volume of single pellets. Volume is calculated from measuring diameter and length of the cylindrical pellet.

The previously developed first-order kinetic model (Kuang *et al.*, 2008) for evolution of gas emissions was used to fit the data of each gas species. The concentration (C) and the emission factor (f) for CO, CO₂, and CH₄ were derived from the first-order reaction equation:

$$C_i(t) = C_{i,\infty} [1 - \exp(-k_i t)], \quad (2)$$

$$f_i(t) = f_{i,\infty} [1 - \exp(-k_i t)], \quad (3)$$

where $C_{i,\infty}$ represents the maximum asymptote value for concentration, and $f_{i,\infty}$ represents the maximum asymptote value for emission factor. k_i is the rate constant of the kinetic equation. The time for the emission concentration to reach half of its asymptote value ($\tau_{1/2}$) is calculated to indicate how fast a gas is emitted from the stored pellets.

RESULTS

Headspace volume ratio (V_h/V)

Equation (1) was used to calculate the emission factor for each gas. Figure 1 shows the emission factor for CO_2 measured in 12 containers, three headspace ratios and four temperatures as a function of storage time. The emission factors for CO_2 increase over the storage time, a sharp rise at the beginning but approaching a plateau gradually. At the same

temperature, as the headspace volume increased from 25 to 75% of the container volume, the peak emission factor for CO_2 increased. Under the same headspace ratio, the peak emission factor for CO_2 increased as the temperature increased. Figure 2a,b shows the same time dependence of emission factors for CO and CH_4 . Table 1 lists peak emission factors. These asymptote factors (f_∞) were calculated by least-square fitting of equation (3) to the experimental data.

Figure 3 shows the rate of oxygen depletion with time. At the same temperature, as the headspace volume increased from 25 to 75% of the container volume, the oxygen depletion decreased. Under the same headspace ratio, the oxygen depletion increased as the temperature increased. Therefore, a larger oxygen depletion occurs at a high temperature and at a low headspace.

The peak emission factors for CO_2 , CO, and CH_4 at high temperatures (35 and 45°C) were larger than those at low temperatures (10 and 23°C). A peak emission factor increases monotonously with increasing the headspace. In other words, both

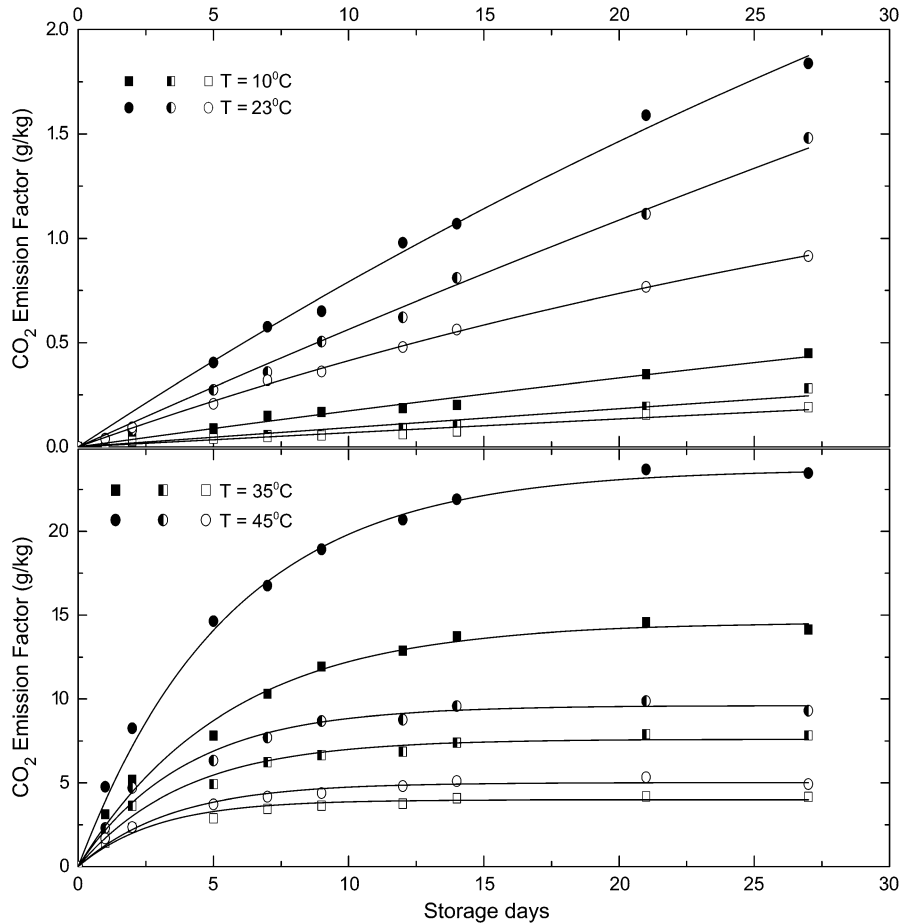


Fig. 1. CO_2 emission factor at different headspaces and temperatures (closed symbols: headspace = 75%; half-closed symbols: headspace = 50%; open symbols: headspace = 25%).

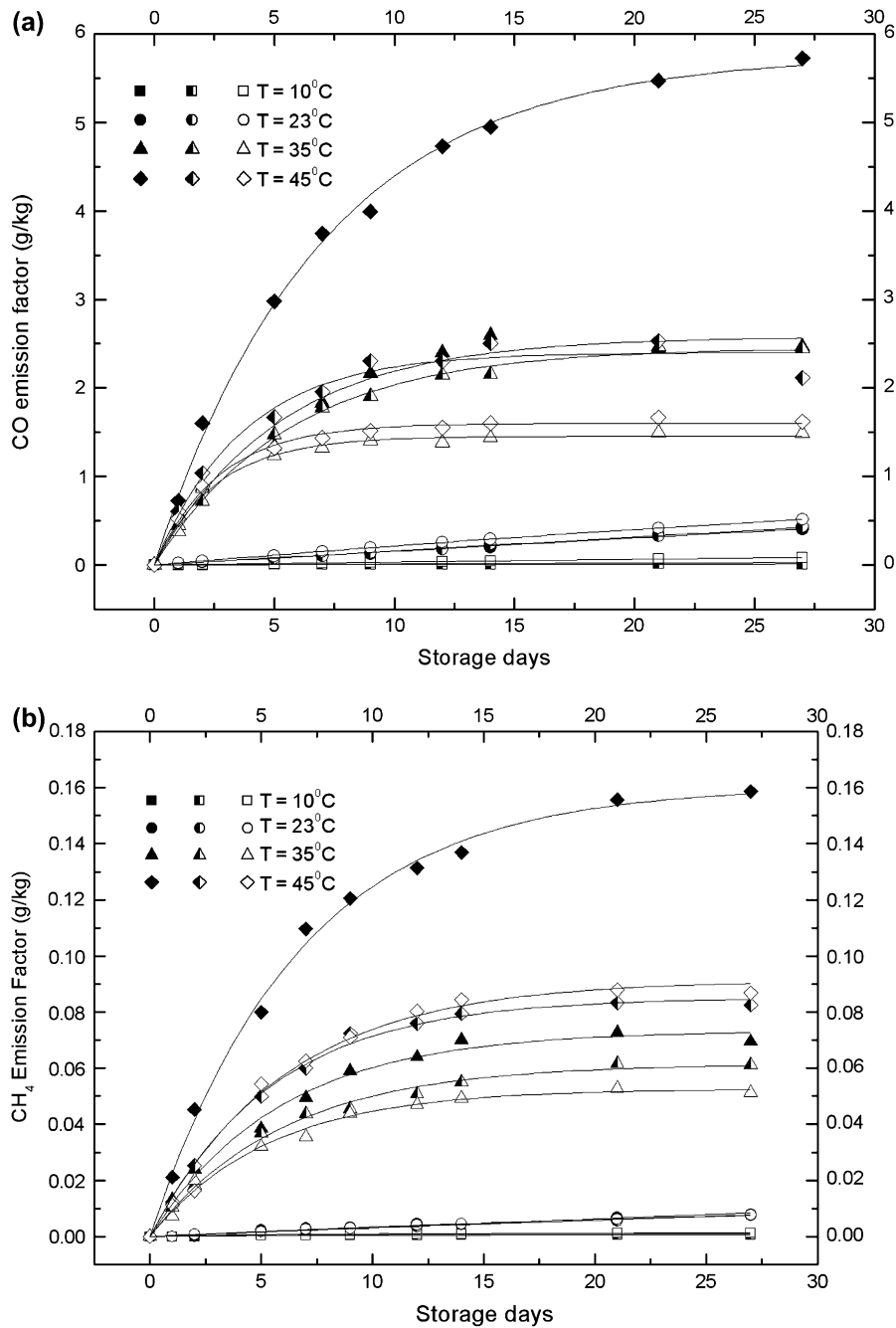


Fig. 2. CO and CH₄ emission factor over time at different headspaces and temperatures (closed symbols: headspace = 75%; half-closed symbols: headspace = 50%; open symbols: headspace = 25%). (a) CO emission factor at different headspaces and temperatures. (b) CH₄ emission factor at different headspaces and temperatures.

temperature and headspaces are important factors affecting the off-gas emissions from wood pellets in storage.

Relative humidity

Figure 4 shows the RH inside each container as a function of storage time. The RH in each container drops sharply initially after loading of wood pellets,

indicating that wood pellets absorb the moisture available in the space. Unfortunately, we did not measure the moisture content of samples after each test. In an earlier experiment, Kuang *et al.*, (2008) found an average of 1% point reduction in moisture content when pellets stored in sealed and heated containers. The RH in the container with water placed at the bottom increased gradually over time, with

Table 1. Maximum emission factors for CO₂, CO, and CH₄ at different temperatures and headspace (HS) ratios (%)

Temperature (°C)	Maximum emission factor, f_{∞} (g kg ⁻¹)								
	CO ₂			CO			CH ₄		
	HS 75%	HS 50%	HS 25%	HS 75%	HS 50%	HS 25%	HS 75%	HS 50%	HS 25%
10	2.84	2.47	2.27	0.09	0.07	0.06	0.00	0.00	0.00
23	3.71	2.27	1.87	0.74	0.62	0.56	0.05	0.03	0.02
35	14.58	7.60	3.99	3.58	2.45	1.45	0.07	0.06	0.05
45	23.73	9.61	5.01	5.77	2.40	1.60	0.16	0.09	0.09

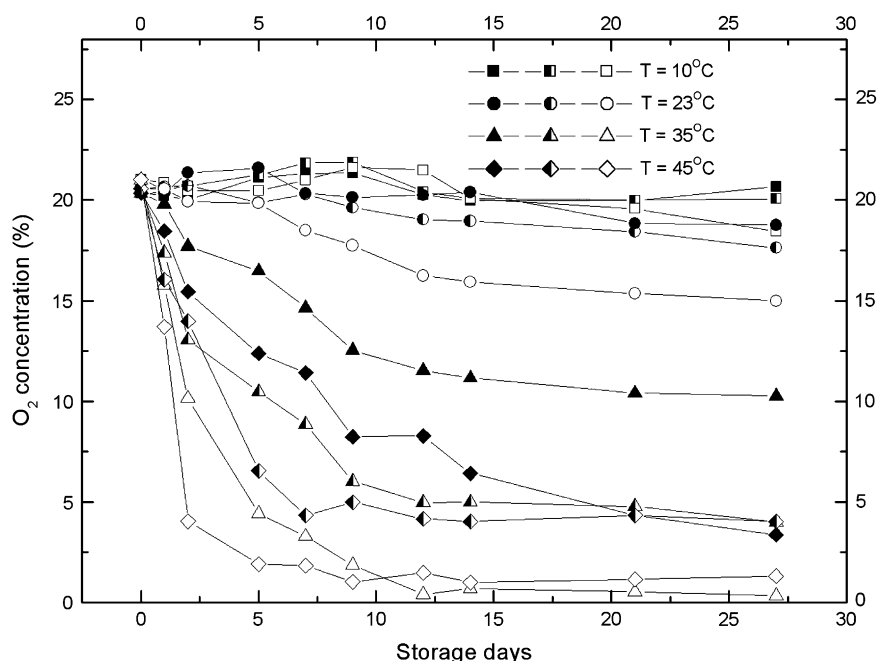


Fig. 3. Oxygen depletion at different headspaces and temperatures (closed symbols: headspace = 75%; half-closed symbols: headspace = 50%; open symbols: headspace = 25%).

higher RH at higher temperatures. Although the RH did not remain constant, the average RH in the container with water was generally higher than that in the container without water at the same temperature.

Figure 4a–c shows emission factors for CO₂, CO, and CH₄ measured in the eight containers at different temperatures and RH as a function of storage time. Emission factors increased over time, faster at the beginning but slower when approaching a plateau. The values of peak emission factor (f_{∞}) and the time to reach the half peak emission factor ($\tau_{1/2}$) are obtained by least-square fitting of experimental data using equations (2) and (3). Table 2 lists the results. The peak emission factor of CO₂, CO, and CH₄ increased as the temperature increased from 10 to 45°C regardless of the RH level. It is also seen that the peak emission factor was higher at high RH at the same temperature. The differences between low and high RH were more significant for CO₂ and CH₄ as tem-

perature increased. Although the peak emission factor did not change a lot between the low and high RH for CO, the time to reach half of the peak emission factor was shorter at high RH than that at low RH.

Figure 5 shows the oxygen depletion over against time in the containers. The oxygen level in the containers decreased more significantly at higher temperatures. The storage RH also affected the oxygen depletion, with a faster oxygen depletion at a higher RH level.

DISCUSSION

The dependence of headspace gas concentrations on temperature has been investigated in our previously published data (Kuang *et al.*, 2008). The current investigation demonstrated that both the headspace volume and the temperature have significant impacts on emission factors and the concentration

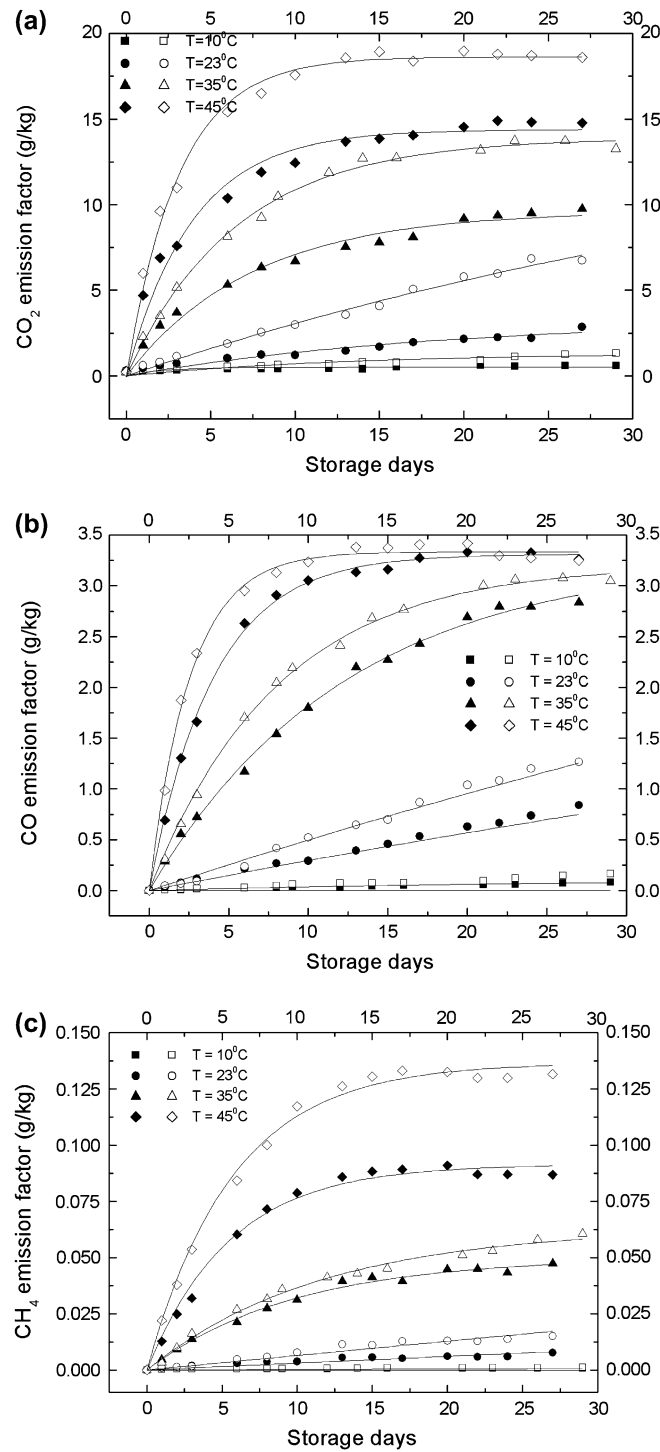


Fig. 4. Emission factors of CO_2 , CO , and CH_4 over time at different temperatures and RH (closed symbols: no water present; open symbols: with water present at the bottom).

buildup of CO , CO_2 , and CH_4 in sealed wood pellet containers. This can be explained by the decomposition mechanism of wood pellets. Biomass decomposes both chemically and biologically. If the thermal degradation is in dominance, the emission factor will

increase with the increase in temperature. However, the biological process may peak at a certain temperature and decrease at higher temperatures at which bacteria and fungi would perish (Agrios, 2004). The results from the current study suggest that chemical

Table 2. Maximum emission factor (f_x) and days to reach half peak emission factor ($\tau_{1/2}$) for CO₂, CO, and CH₄ at different temperatures (T) and moisture (RH)

Temperature (°C)	Maximum emission factor, f_x (g kg ⁻¹)						Half response time $\tau_{1/2}$ (days)					
	CO ₂		CO		CH ₄		CO ₂		CO		CH ₄	
	Low RH	High RH	Low RH	High RH	Low RH	High RH	Low RH	High RH	Low RH	High RH	Low RH	High RH
10	0.51	1.37	0.11	0.19	0.00	0.01	15.40	13.10	17.60	15.90	21.40	17.30
23	3.36	7.17	0.98	1.17	0.02	0.04	13.30	11.60	14.00	11.30	9.40	7.20
35	9.62	13.90	3.28	3.21	0.05	0.06	5.20	4.60	8.60	5.60	6.80	5.10
45	14.39	18.64	3.31	3.34	0.09	0.12	2.70	2.12	3.70	1.80	3.80	4.00

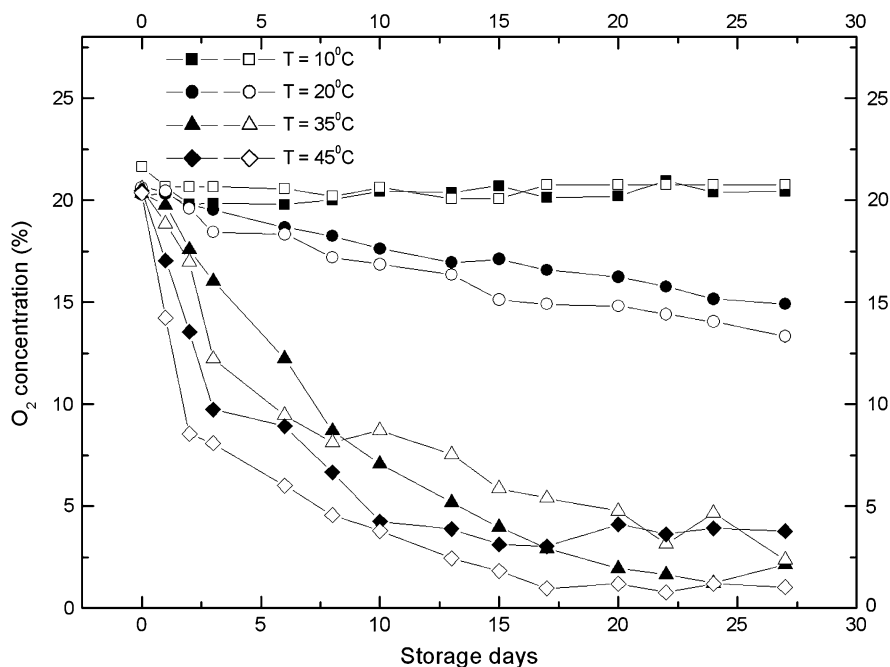


Fig. 5. Oxygen depletion at different temperature and moisture (closed symbols: no water present; open symbols: with water present at the bottom).

process via auto-oxidative degradation of fats and fatty acids (Svedberg *et al.*, 2004; Arshadi and Gref, 2005) may be the dominant mechanism for off-gassing because the emission rate increases monotonously with increasing temperature from 10 to 45°C, although biological process may also contribute to the emissions for moist biomass under a wet environment. Figure 4 shows that CO₂ emission factor is more sensitive to temperature than CO. This sensitivity is more pronounced at higher storage temperatures than at lower storage temperatures.

Moisture is another important factor influencing the off-gas emissions from wood pellets in storage. RH is investigated in this study, whereas the high moisture content of wood pellets (a high water activity in equilibrium with a high RH) could play an important role on the emissions from wood pellets during storage. It is

suggested from the current study that high storage moisture could cause higher emissions of CO₂, CO, and CH₄. Therefore, the control methods such as restricting the storage temperature, RH, or choosing an appropriate headspace ratio in a contained storage space could be effective in reducing the off-gas emissions from wood pellets in order to protect the workers' health.

Further studies of the thermal and biological decomposition of wood pellets under controlled conditions are needed to elucidate to what extent the biological process contributes to the decomposition of woody materials.

CONCLUSIONS

1. Storage temperature is the key factor that affects the off-gassing from stored wood pellets. Higher

- peak emission factors are always associated with higher temperatures.
2. Increased headspace increases off-gas emissions because of the availability of oxygen for pellet decomposition.
 3. Increased humidity in the headspace in the container increases the emissions of CO₂, CO, and CH₄.

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