



Measurement and Modeling of Carbon Monoxide Emission Rates from Multiple Wood Pellet Types

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Supporting Information

ABSTRACT: There is a potential hazard associated with bulk storage of wood pellets because they have been shown to off-gas carbon monoxide (CO). The risk to building occupants from the emission of and exposure to CO from stored pellets has not yet been fully studied. The present study was designed to measure the emission rates from wood pellets and develop a model to predict the CO emission rate. The 20 gallon steel drums were filled to approximately 50% of their volume with wood pellets and CO, and oxygen (O₂), carbon dioxide (CO₂), temperature (*T*), and relative humidity (RH) were measured as a function of time. A variety of conditions were tested including the type of wood, age of the pellets, volume of the headspace, humidity, surface/volume ratio, and temperature. An improved kinetic model was developed to predict the CO emission rate. The model assumes that the reaction generating CO is surface-area-limited. The measurements were well-fit by the mathematical model (*R*² in the range of 0.93–0.99), suggesting that the model is a good predictor of the CO emission rates.

■ INTRODUCTION

Wood pellets, a renewable biomass solid fuel, are becoming a more attractive source of energy for heating and power in the U.S., Canada, and Europe as oil prices rise and/or the need to reduce greenhouse gases increases the use of renewable energy.^{1,2} Wood pellets are made from compacted sawdust from cut trees or wastes from sawmilling and other wood product manufacture. Pellets are formed by extruding the sawdust through a die, resulting in a typical size of 12–20 mm long and 6 mm diameter cylinder. They have a low moisture content (4.5–8.0%) and a low ash content (0.5–0.8) that allows them to be burned with a very high combustion efficiency, resulting in gross calorific values of the order of 8100–8470 Btu/lb.³ In New York State, a series of demonstration projects has been initiated to introduce high-efficiency, low-emission wood pellet boilers based on European designs into homes, schools, and commercial buildings.^{2,4}

After wood pellets are manufactured, they are stored in pellet bins, shipping vessels, boxcars, or at the owner's facility. While in storage, pellets emit a variety of gases, including carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), and volatile organic compounds (VOCs), that can result in CO concentrations and depleted O₂ that can reach toxic concentrations.^{5–8} A recent study has shown that concentrations of CO in domestic and commercial-scale pellet bins can exceed guidance and regulatory limits for CO exposure.⁹ These emissions have also been observed from other hydrocarbon products.^{10,11} The amount of emitted gases will depend upon the temperature (*T*), relative humidity (RH), headspace (HS) volume, surface of pellets available, mass, and type of wood.^{12–17}

The proposed mechanism of CO emission has been studied by Levitt et al.,¹⁰ observing that organic matter, stored at room temperature, particularly in the presence of air and light,

emitted small amounts of CO and the emission rate increases at an elevated temperature (37 °C). The CO emissions ceased under an argon atmosphere. During storage, the extractives or other major components in the wood pellets are reduced and the composition is modified by microbiological and/or oxidative chemical reactions.^{5,6,18,19}

Gauthier et al.²⁰ documented several deaths arising from CO poisoning in large pellet storage areas and reviewed previously reported incidents in marine vessels and commercial and residential pellet and chip storage facilities in Europe. The illness and deaths associated with pellet storage clearly demonstrate risk to human health and the need to fully understand the emission rates and concentrations of CO. Soto-Garcia et al.⁹ showed elevated CO concentrations in a variety of storage facilities but did not observe values in the range of the extremely high values reported by Gautier et al.²⁰

To characterize the off-gassing rate for softwood pellets, Kuang et al.⁷ developed a kinetic model of CO, CO₂, and CH₄ emissions from British Columbia pellets (widely used in Europe) made from *Pinus sylvestris* (Scots pine). This model assumes that the gas formation reaction is first-order because their results showed that the gas concentrations initially increased exponentially over time and then tended to a constant plateau after a few days. Fan and Bi²¹ measured the emission of CO and CO₂ production, considering the depletion of O₂ in the pellet off-gassing reaction. Their kinetic model, which mathematically generated a differential rate expression, included parameters such as the container dimension, spatial scale, bulk density, pellet solid fraction, and interstitial space between the pellets to produce a more complete model of the

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gas evolving into the container. However, this model could not fit the plateau behavior at the end of the reaction period.

To provide further information on the potential safety issues related to the bulk storage of pellets, additional laboratory studies were performed to further characterize the emission kinetics of CO from pellet storage. Pellets made in the northeastern U.S. can differ significantly in their composition from those pellets made in Europe or British Columbia because of the abundance of hardwoods in the northeastern U.S. Thus, this study has examined the off-gassing from hardwood, softwood, and hardwood/softwood blended pellets by storing them in steel drums under different laboratory conditions. In addition, a better model to estimate the rate of emission of CO and depletion of O₂ that includes a surface parameter was developed in this study.

EXPERIMENTAL SECTION

The laboratory studies were conducted in a manner similar to those described by Kuang et al.^{7,8,13} The investigated wood pellets were stored in 20 gallon carbon steel drums that are 20 in. in height and 16 in. in diameter. Two quick connects were inserted through each lid, as shown in Figure 1. The drums were held closed by a metal ring to

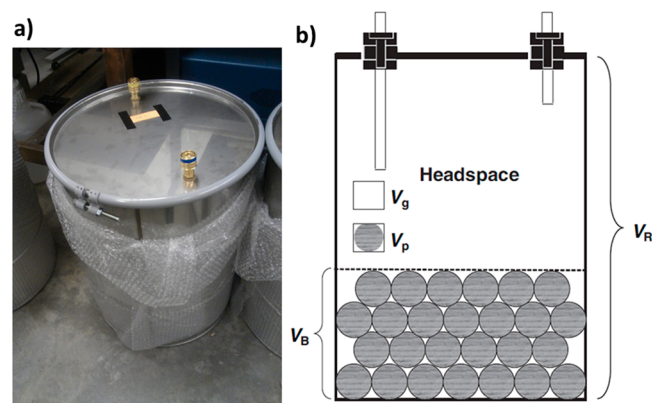


Figure 1. (a) Picture of the steel drums used for most of the pellet storage experiments and (b) schematic view of the drum, which was slightly modify from Fan and Bi.²¹

maintain an airtight fit against the gasket. A recirculating sampling system was constructed to pull air from the drums, through the gas monitors, and return it to the drum. Two types of setups were used. The first setup (see Figure S1 of the Supporting Information) used a brass tube (inside diameter = ~0.4 cm) to connect the units in the recirculating sampling system. Two quick release valves were installed on the lid of the drum. For each sampling event, the vacuum pump (3.6 L/min) was run for at least 30 s and then turned off, drawing approximately 5 L through the system, and after another 30 s, the reading on the sensor was performed. For each drum, CO concentration, O₂ concentration, *T*, and RH was measured.

A modified experimental design was used for the second phase of the testing (see Figure S1 of the Supporting Information). A closed loop was used to pull air from the drums and passed through two boxes [each box was 3.78 L (1 gallon) in volume], each with different types of sensors in them, for 7–10 min (time for sensors to reach equilibrium) and return the air to the drum. The first box contains the CO and O₂ sensors, as the ones used in the first setup. The second box has the CO₂, *T*, and RH sensors from Langan L76n indoor air quality monitor, which uses General Electric Telaire (700 D) to measure CO₂, *T*, and RH.

Measurements from each drum were performed every 24 h. Electrochemical sensors were used to measure the CO (City Tech EZT3F/F) and O₂ (City Tech T7OXV) concentrations. CO provides

a 40–200 mV response to 0–2000 ppm of CO with a sensitivity of 0.10 ± 0.02 mV/ppm. The accuracy of the sensors was verified by calibrating with calibration gas mixtures and a Thermo 146i gas calibrator coupled to a Thermo 110 zero air supply. The oxygen sensor produces an output of 40–200 mV in response to 0–25% oxygen. More detail of these sensors can be found in the study by Soto-García et al.²²

Pellet Samples. Pellets manufactured from fresh wood chips were obtained from a local manufacturer. Because of the greater abundance of hardwood in northern New York, more hardwood pellets and blended softwood/hardwood pellets are sold in this area. Therefore, the kinetic characterizations of hardwood, softwood, and blended pellets were all tested in the drum experiments. The as-received pellets were ~6 mm in diameter and 6–25 mm in length, with a bulk density of ~650 kg/m³ (40 lbs/ft³).

Experiments. Several rounds of drum experiments were performed with different batches of wood pellets. Samples of the commercially available wood pellets including softwood, hardwood, and blended pellets that were considered as freshly produced according to the manufacturer were generally used. Three replicates for each type of pellets were prepared. Measurements of CO, O₂, *T*, and RH were made every 24 h. Each set of measurements was conducted for up to 30 days.

Another round of drum experiments was conducted similar to the previous round, but the pellets were stored at 4 °C (±3 °C) for 3 months (“aged pellets”). Simultaneously, a group of three drums with fresh softwood pellets was used with various HS volume fractions of 50.0, 75.0, and 87.7%, and this experiment were labeled as “HS volume”.

To study the effect of the temperature, two rounds of drum experiments were performed with different batches of hardwood pellets. The drum was heated by placing heating tape around the drum. The heating tape was connected to a variable transformer at approximately 10 V, producing a temperature of ~30 °C. Room temperature measurements were performed by placing the drum in the laboratory at room temperature (~22 °C). The cold condition was obtained by placing the drums in a cold room at 6–8 °C. Drums in the heated and room temperature studies used thermocouples to monitor the temperature. Measurements of CO, CO₂, O₂, *T*, and RH were again made every 24 h. The measurements were collected for at least 11 days and up to 27 days until a clear plateau was reached.

To evaluate the effect of the water content and surface area on the emission rate, a series of experiments was made in 250 mL Erlenmeyer flasks. Pellets were added to four different two-compartment Erlenmeyer flasks as shown in Figure S2 of the Supporting Information. Each chamber had a different moisture condition measured with a Fluke air monitor (model 975). The wood pellets in Figure S2d of the Supporting Information were ground using a Spex 6770 freezer mill to fine particles. All of these experiments lasted 20 days when a plateau in the CO concentrations was obtained.

In addition, a set of experiments was performed to study the effects on the moisture content of the softwood and hardwood pellets under different RH (35, 55, and 85%). The pellets were placed (300 g) in a steel chamber for 48 h and exposed to humidified air (air flow that passed through flasks with distilled water, mixed with dried air). Temperature and humidity was checked periodically (DMT-321 from Tecpel Co., Ltd.). After 48 h, three samples were taken and measured for moisture content.

Characterization of the wood pellets was performed by measuring the gross calorific, moisture, and ash contents using methods ASTM E711-87, ASTM E871-82, and ASTM D1102-84, respectively, as described by Chandrasekaran et al.³

KINETIC MODEL

The model developed in this study was based on the model from Fan and Bi.²¹ The most significant change in our model is the addition of a term to the rate equation recognizing that the generation of CO is a surface reaction. Given the clear plateau behavior seen in the prior work and the results described below,

it is clear that CO is surface-area-limited. Thus, it is necessary to model the amount of reactant remaining on the pellet surface that is able to generate CO. The nature of the reactant(s) is currently unknown. Without the identification of reacting component(s), the off-gassing reaction pathways cannot be understood and future work will be dedicated to this problem. Thus, the CO emission and O₂ depletion kinetics are simplified into half-order rate equations with limiting factors. O₂ is mainly consumed by generating CO with a variety of carbonaceous intermediates contained in the stepwise reaction. Thus, the O₂ depletion, contributing other materials from CO generation, is considered as a first-order reaction.

In the Fan and Bi model, the rate equations are

$$\begin{aligned} \text{pellets} + \frac{1}{2}\text{O}_2 &\rightarrow \text{CO} + \text{other materials}, \\ r_{\text{CO}} &= \frac{1}{m_p} \frac{dn_{\text{CO}}}{dt} = k_{\text{CO}}([\text{O}_2]^{0.5}) \end{aligned} \quad (1)$$

$$\begin{aligned} \text{pellets} + \text{O}_2 &\rightarrow (\text{O}_2^* \parallel \text{pellets}), \\ r_{\text{OD}} &= \frac{1}{m_p} \frac{dn_{\text{OD}}}{dt} = k_{\text{OD}}([\text{O}_2]) \end{aligned} \quad (2)$$

where r_{CO} is the CO emission rate per unit mass of pellets (mol of CO kg⁻¹ of pellets s⁻¹) r_{OD} is the unit first-order O₂ depletion rate per unit mass of pellets (mol of O₂ kg⁻¹ pellets s⁻¹)

$$n_{\text{CO}} = ([\text{CO}]) (V_g) \quad (3)$$

where $[\text{CO}]$ is the gaseous mixing fraction of carbon monoxide, V_g is the total volume of the gas phase inside the drum, k_{CO} is the rate constant of CO off-gassing, k_{OD} is the rate constant for any other O₂ depletion reactions, and m_p is the total mass of stored pellets.

Now, it is assumed that the remaining reactant on the surface is the limiting reagent for the CO emissions. With this modification, the rate equations become

$$w_{\text{R-CO}} = \frac{n_{\text{R-CO}}}{m_p} \left(\frac{\text{mol of reactant}}{\text{kg of pellets}} \right) \quad (4)$$

$$\begin{aligned} \text{pellets} + \frac{1}{2}\text{O}_2 &\rightarrow \text{CO} + \text{other materials}, \\ r_{\text{CO}} &= \frac{1}{m_p} \frac{dn_{\text{CO}}}{dt} = k_{\text{CO}}(w_{\text{R-CO}})([\text{O}_2]^{0.5}) \end{aligned} \quad (5)$$

$$\begin{aligned} \text{pellets} + \text{O}_2 &\rightarrow (\text{O}_2^* \parallel \text{pellets}), \\ r_{\text{OD}} &= \frac{1}{m_p} \frac{dn_{\text{OD}}}{dt} = k_{\text{OD}}([\text{O}_2]) \end{aligned} \quad (6)$$

where $w_{\text{R-CO}}$ is the unit amount of reactant (generating CO) on the pellet surface. The units for each of the parameters and variables in the model are provided in Table S1 of the Supporting Information.

Equivalent relationship 1: The moles of CO generated equals the moles of reactant consumed.

$$\frac{1}{m_p} \frac{dn_{\text{CO}}}{dt} = -\frac{dw_{\text{R-CO}}}{dt} \quad (7)$$

Combining eq 3 with eq 4

$$\frac{V_g}{m_p} \frac{d[\text{CO}]}{dt} = -\frac{dw_{\text{R-CO}}}{dt} \quad (8)$$

This relationship will also be equivalent to the integral form

$$\int_0^{[\text{CO}]} \frac{V_g}{m_p} \frac{d[\text{CO}]}{dt} = \int_{n_{\text{R-CO,T}}}^{n_{\text{R-CO}}} -\frac{w_{\text{R-CO}}}{dt} \quad (9)$$

In the previous equations, it is assumed that the declining mass of wood pellets, which is consumed in the oxidation processes, is negligible compared to the total mass. Thus, m_p is constant. After solving eq 9

$$V_g[\text{CO}] = \frac{w_{\text{R-CO,T}} - w_{\text{R-CO}}}{m_p} \quad (10)$$

Equation 10 illustrates how the current CO concentration is related to the remaining amount of reactant on the pellet surface. $w_{\text{R-CO,T}}$ is the total potential amount of CO-generating reactant on the pellet surface.

The O₂ depletion rate is assumed to consist of two parts: that consumed in CO generation (half order) and that consumed in CO₂ generation (first order).

$$\begin{aligned} r_{\text{O}_2} &= -(r_{\text{CO}} + r_{\text{OD}}) = -k_{\text{CO}}(w_{\text{R-CO}})([\text{O}_2]^{0.5}) \\ &\quad - k_{\text{OD}}([\text{O}_2]) \end{aligned} \quad (11)$$

Converting the reaction rates to involve mass concentrations

$$r_{\text{O}_2} = -\frac{1}{m_p} \frac{dn_{\text{O}_2}}{dt} = -\frac{V_g}{m_p} \frac{d[\text{O}_2]}{dt} \quad (12)$$

$$r_{\text{CO}} = \frac{1}{m_p} \frac{dn_{\text{CO}}}{dt} = \frac{V_g}{m_p} \frac{d[\text{CO}]}{dt} \quad (13)$$

In addition, the total volume of the gas phase is defined to include the HS volume and the interstitial space between solid pellets. It is also assumed that the solid fraction of the packed bed is 0.621, in accordance with the bulk density and the physical density of the wood pellets

$$\begin{aligned} V_g &= V_{\text{HS}} + (1 - \varepsilon_s)V_p = V_T(HS + (1 - \varepsilon_s)(1 - HS)) \\ &= V_T(1 - \varepsilon_s(1 - HS)) \end{aligned} \quad (14)$$

where V_T is the total volume of the drum.

Combining eqs 1, 2, 11, and 12, the set of differential reaction rate equations is written as

$$\begin{aligned} f_{\text{CO}}(t, [\text{O}_2], w_{\text{R-CO}}) &= \frac{d}{dt}[\text{CO}] = \left(\frac{m_p}{V_g} \right) (k_{\text{CO}})(w_{\text{R-CO}}) \\ &\quad ([\text{O}_2]^{0.5}) \end{aligned}$$

$$\begin{aligned} f_{\text{O}_2}(t, [\text{O}_2], w_{\text{R-CO}}) &= \frac{d}{dt}[\text{O}_2] \\ &= -\left(\frac{m_p}{V_g} \right) (k_{\text{CO}}w_{\text{R-CO}}[\text{O}_2]^{0.5} + k_{\text{OD}}[\text{O}_2]) \end{aligned}$$

$$w_{\text{R-CO}} = w_{\text{R-CO,T}} - \frac{V_g}{m_p}[\text{CO}] \quad (15)$$

This set of differential equations will be fit to the measured CO and O₂ concentrations. V_g/m_p is a constant for a given

Table 1. Information and Characterization of the Wood Pellets Used as Fresh Pellets

pellet type ^a	loading mass (kg)	HS fraction (%)	pellet bulk density (kg/m ³)	calorific value (MJ/kg)	moisture content (%)	ash content (%)
(1) ^b HW fresh	18.28	57.2	652.1	19.341	3.55	0.32
(2) HW fresh	18.33	57.6	672.1	19.070	3.52	0.27
(3) HW fresh	18.33	57.9	646.0	19.258	3.55	c
average				19.223	3.54	0.30
(1) SW fresh	18.19	57.6	643.0	20.970	3.53	0.46
(2) SW fresh	18.28	58.7	653.2	20.641	3.63	0.49
(3) SW fresh	18.19	57.1	653.9	21.065	3.45	c
average				20.892	3.54	0.48
(1) BW fresh	18.37	57.8	658.2	19.633	4.57	0.60
(2) BW fresh	18.33	57.2	647.8	19.346	4.51	0.65
(3) BW fresh	18.33	57.1	646.0	19.243	4.95	c
average				19.407	4.68	0.63

^aHW, hardwood; SW, softwood; and BW, blended wood. ^bNumber denotes one of three replicate samples being measured in each experiment. ^cNot measured.

Table 2. Information and Characterization of the Wood Pellets Used as Aged Pellets and for HS Experiments

pellet type ^a	loading mass (kg)	HS fraction (%)	pellet bulk density (kg/m ³)	calorific value (MJ/kg)	moisture content (%)	ash content (%)
Aged Pellets						
(1) ^b HW old	17.4	58.2	646.0	19.659	3.43	0.69
(2) HW old				19.677	3.85	0.72
(3) HW old				19.709	3.99	
average				19.682	3.76	0.71
(1) SW old	17.20	60.3	646.0	20.398	4.55	0.32
(2) SW old				20.626	4.61	0.32
(3) SW old				20.626	4.37	
average				20.550	4.51	0.32
(1) BW old	16.90	62.8	646.0	19.511	4.69	0.47
(2) BW old				19.802	4.66	0.51
(3) BW old				19.794	5.14	
average				19.702	4.83	0.49
Different HS Volume Fraction						
(4) SW HS 50.0%	22.95	50.0	43.49	20.463	4.50	0.33
(5) SW HS 25.0%	31.50	25.0	39.79	20.761	4.10	0.29
(6) SW HS 12.3%	36.80	12.3	39.76	20.533	4.60	
average				20.586	4.40	0.31

^aHW, hardwood; SW, softwood; BW, blended wood; and HS, headspace. ^bNumber denotes one of three replicate samples being measured in each experiment.

experimental configuration, and k_{CO} , k_{OD} , and $w_{\text{R-CO}}$ are the fitted parameters. A nonlinear, least-squares regression was performed to determine the kinetic parameters. More details of the modeling are given by Huang.²³

RESULTS AND DISCUSSION

Tables 1 and 2 present the measured characteristics of the pellets used in these studies. In general, the pellets are low in moisture (fresh, 3.5–4.7%; aged, 3.7–4.8%) and ash (fresh, 0.3–0.6%; aged, 0.3–0.7%) contents, with high calorific values (fresh, 19.2–20.9 MJ/kg or $8\text{--}9 \times 10^3$ Btu/lb; aged, 19.5–20.5 MJ/kg). The high density, lower moisture, and ash content make them high-quality pellets.

Type of Wood Pellets. Figure 2 shows the evolution of the CO off-gassed with time from different types of pellets. CO emissions plateaued on the eighth day for hardwood pellets at around 400 ppm, blended at 800 ppm, and softwood at 1000 ppm. The oxygen consumption rate was consistent with the CO generation rate. The oxygen curves (Figure 2b) of the hardwood pellets are above the others, meaning that less oxygen is used for the oxidation of hardwood pellets. The

oxygen level for softwood pellets was lowest (~17% in the end) corresponding to the greater capability of the softwood pellets to generate CO. Such differences must be related to differences in the chemical makeup of the hardwood and softwood, but at this time, compositional data are not available and will be the subject of future work.

Aged Pellets. Figure 3 shows comparison of fresh and aged (for 90 days) pellets. The CO concentrations are higher for fresh stored pellets than for old pellets. At the beginning, the emission rate for the softwood pellets was faster and the final concentrations on each curve show a difference of ~20% (Figure 3a). Blended and hardwood pellets show a similar pattern (panels b and c of Figure 3). The stored hardwood pellets started with the lowest emission rate. The observed lower reactivity of the stored pellets might be caused by slow oxidation while in storage, resulting in the CO-producing reactants being consumed. Therefore, the total amount of CO generation was substantially smaller after 90 days of storage.

HS Volume Fraction. To simulate different storage conditions with respect to the HS available, experiments were performed using different HS volumes in drums. Figure S3 of

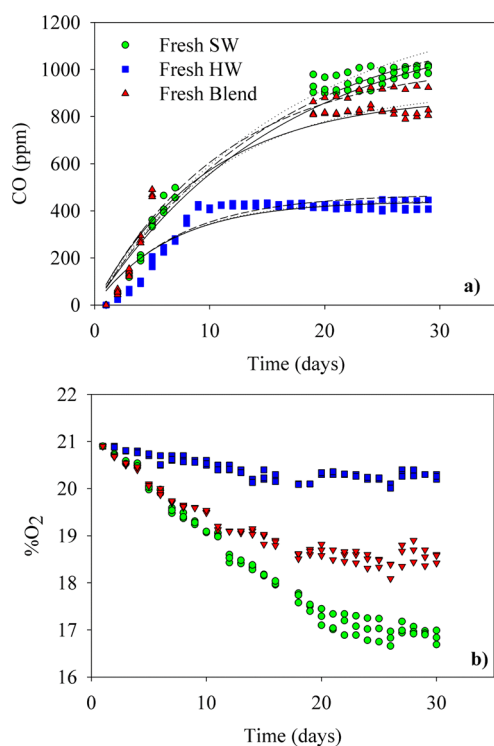


Figure 2. (a) CO concentration and (b) percentage of O₂ as a function of time in the sealed 20 gallon drums containing ~18 kg of pellets.

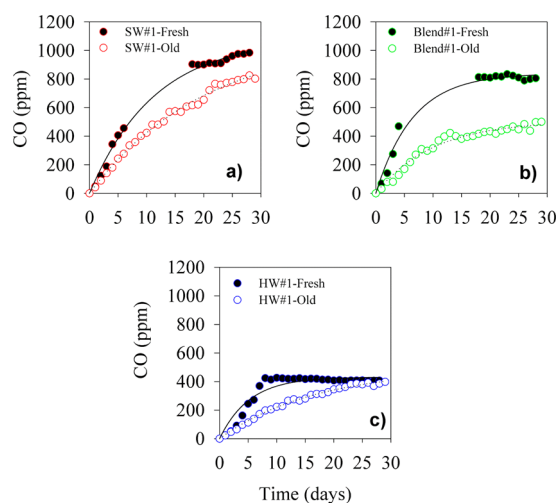


Figure 3. Comparison of the fresh pellets versus the same batch stored for 90 days (old): (a) softwood (SW) fresh versus old, (b) blended wood (BW) fresh versus old, and (c) hardwood (HW) fresh versus old.

the Supporting Information shows the CO concentration and percentage of O₂ as a function of time for different HS volumes. The CO concentration increases for the drums with less HS (12.3 > 25 > 50% HS). However, the mass per unit mass of pellets was lower for smaller HS values, similar to the trends observed by Kuang et al.⁸ The oxygen depletion rates were the same as expected with higher depletion in the lower HS drums. The experiment shows that the CO concentration is positively related to the loading mass of wood pellets and that the oxygen depletion rate is directly related to the HS fraction. Thus, increasing the amount of pellets would increase the off-gassed

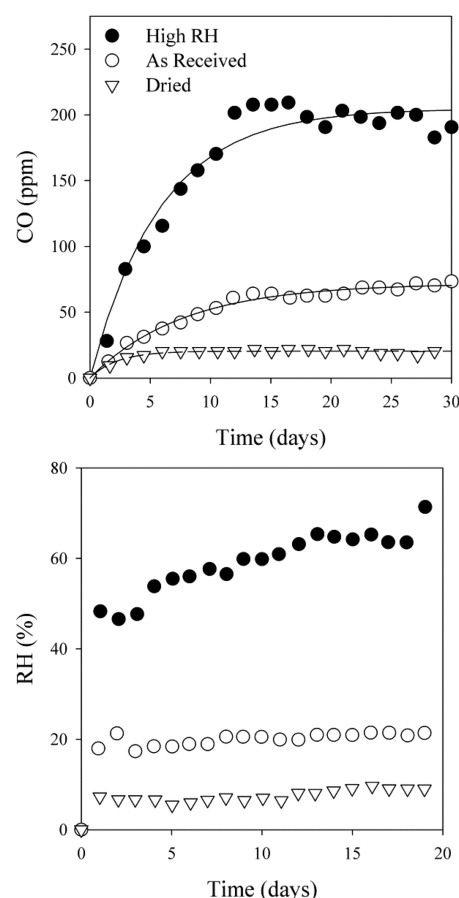


Figure 4. CO concentration emitted and percentage of RH measured from the three different conditions in the moisture content experiment.

Table 3. Pellets Exposure to Different RH (%) Environments and Their Water Uptake (Percentage of Moisture Content)

pellet type ^a	RH (%)	moisture content (%)	all samples moisture content (%)	standard deviation
HW	35 ± 2	4.84	4.9	0.3
SW		5.01		
HW	55 ± 3	8.51	8	1
SW		7.11		
HW	85 ± 5	10.86	10	2
SW		9.99		

^aHW, hardwood; SW, softwood.

CO concentration only when additional oxygen is available because the gas volume would concentrate CO. The increase of pellet mass would accelerate the depletion of the oxygen level because the ratio of the reactive hydrocarbons and interstitial oxygen is greater, as reported by Kuang et al.⁸ and Yazdanpanah et al.¹⁵

Water Content. The relationships between the moisture content and the off-gassed CO concentrations were measured at room temperature using three different moisture conditions: as-received pellets, dried (105 °C) pellets, and pellets exposed to a high-humidity environment (100% RH). At room temperature, there is a significant increase of CO emission for pellets exposed to high humidity and lower emission for the dry pellets (Figure 4a). For pellets exposed to high humidity, the CO concentrations increased from 25 to 200 ppm, whereas

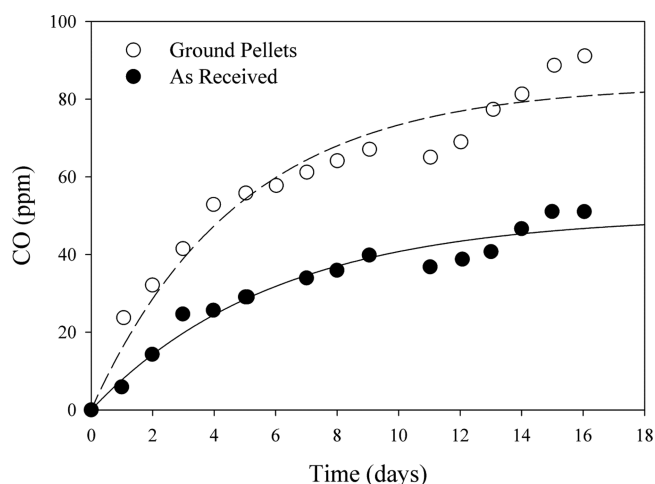


Figure 5. CO concentration as a function of time for as-received and ground wood pellets.

as-received pellets produced values in the range of 15–65 ppm. Dry pellets produced only 10 ppm during the entire experiment. Also, the emission rate for the pellets at high humidity was faster than the other two. These results are also similar to those reported by Kuang et al.⁸ These results (Figure 4b) show that dried and as-received pellets produce a low and fairly constant humidity (10–20%), while the pellets in the

humid environment increased from around 40 to 60%. This result shows that pellets in a humid storage environment will absorb water and will increase their CO off-gassing²¹ to the point where it may exceed the recommended or regulatory guidelines [50 ppm for 8 h, Occupational Safety and Health Administration (OSHA) regulation].²⁴ The humidity typically causes the pellets to break up, and thus, the increased CO emissions may result in an increased surface area that can lead to more CO emission, as postulated in our model.

More detailed information on the moisture absorption is presented in Table 3. In general, at higher relative humidity, the wood pellets tend to absorb more water (observed with a higher moisture content), and as a consequence, high storage humidity will cause higher emission rates of CO via biological activity^{13,18,21} or because water facilitates the oxidation of main components of wood and/or degrades the pellets.²⁵ For pellets aged for 6 months in environments of 35, 55, and 85% RH, the moisture content in the pellets reached 5, 8, and 10%, respectively. It was observed that hardwood pellets absorb more moisture than the softwood pellets (around 10–20% more). This result is likely an effect of differences in chemical composition and the hygroscopicity of the wood components existing in pellets.

Surface/Volume Ratio. To increase the surface area, the wood pellets were ground. The masses of ground pellets and as-received pellets were identical (the difference in mass was less than 0.01 g). Figure 5 shows the emission of CO from ground

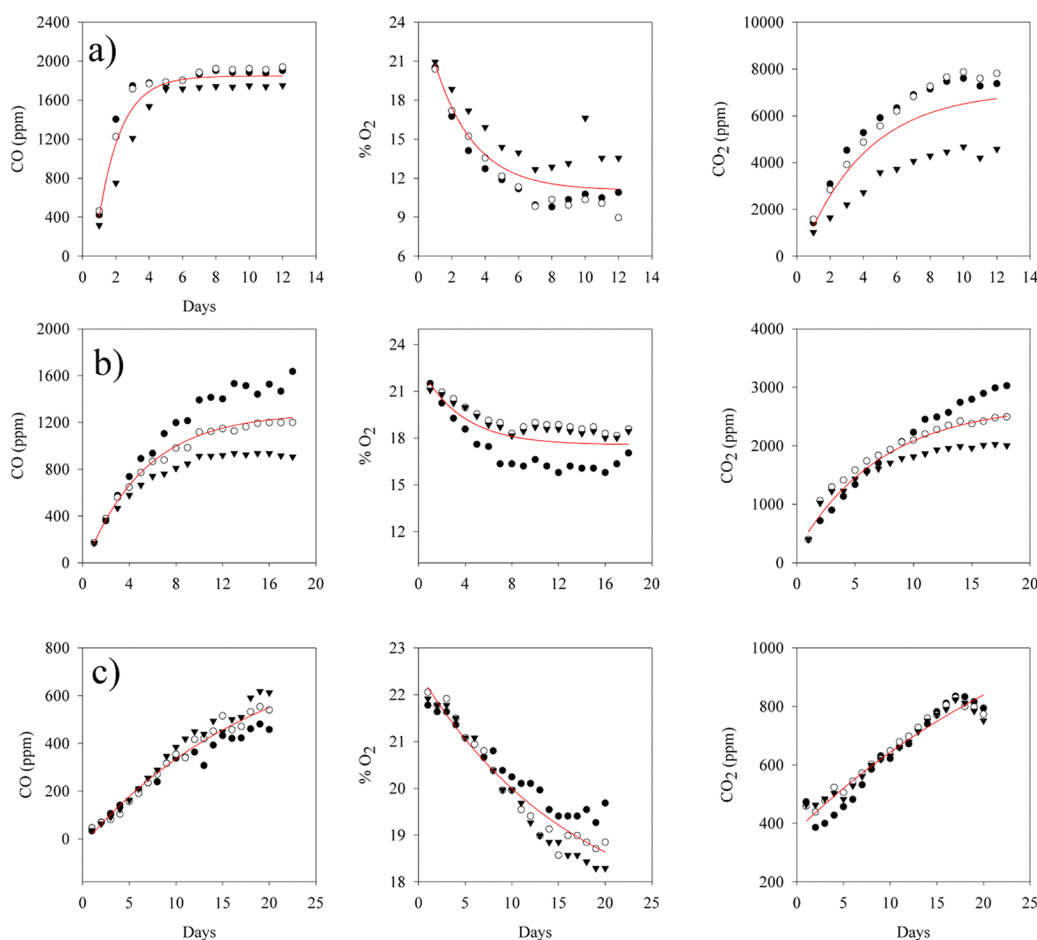


Figure 6. CO, O₂, and CO₂ concentrations as a function of time for pellets under three different temperature conditions: (a) 30 °C, (b) 22 °C, and (c) 6–8 °C.

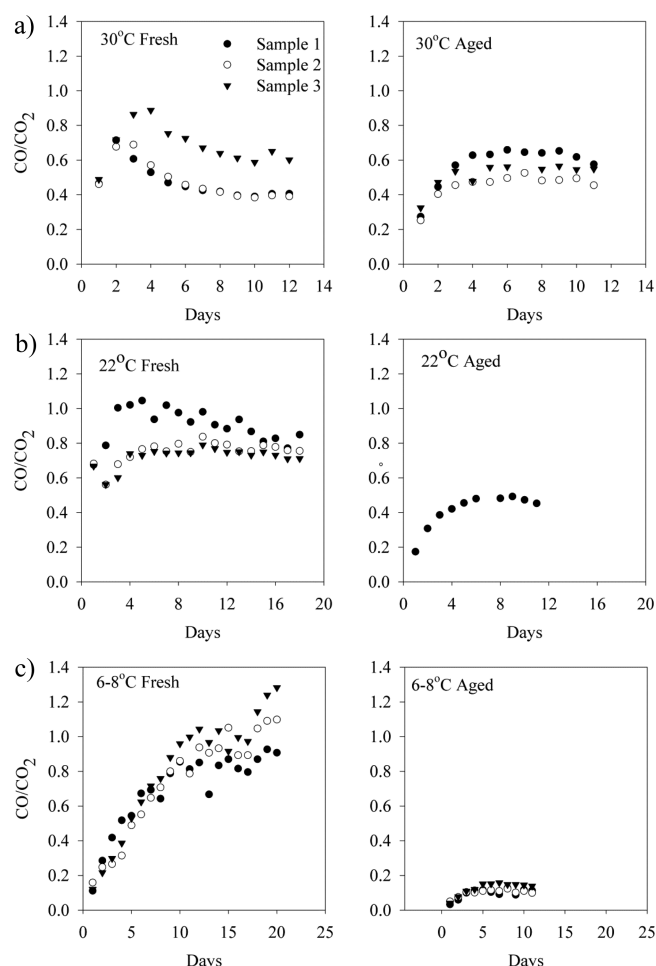


Figure 7. Ratio of the CO/CO₂ concentration (ppmv) as a function of time (days) measured for fresh and old hardwood pellets under (a) heated, (b) room, and (c) cold temperature conditions.

pellets compared to as-received wood pellets. Ground pellets were more than doubly active than as-received pellets in emitting CO. These results support the assumption that the off-gassing from the pellets is a surface reaction process,²¹ because increasing the surface area of pellets will increase the amount of reactants on the surface and increase the reaction rate.

Temperature. Temperature had a strong influence on the pellet off-gassing.⁷ Figure 6 shows the results of the hardwood pellets at elevated (30 °C), room (22 °C), and cold (6–8 °C) temperatures.

The heated pellets (Figure 6a) produce more CO (up to ~1800 ppm) and CO₂ (up to 8000 ppm) gases, with faster emissions reaching a plateau on the fifth day, and a higher depletion of oxygen (from 21 to 13%). Also, it is observed that fresh pellets at room temperature (Figure 6b) produce significant amounts of the CO concentration in the HS of the drums. One sample at 2 days reached ~1500 ppm, and two other samples reached ~1000 ppm at 10 days. Pellets that had aged for 1 month at room temperature showed reduced emissions, especially the pellets that were measured under cold temperature conditions (see Figure S4 of the Supporting Information). Kuang et al.^{7,8} attributed the increase in the emission rate with increasing temperature as a result of enhanced chemical reactions rather than biological activity. Guo et al.²⁶ in their study of wood pellet self-heating and exposed to

30–50 °C show that aged pellets require a higher activation energy to release heat.

Figure 7 shows the molar concentration [parts per millions per volume (ppmv)] ratios of CO/CO₂ in the HS as a function of time. In general, as the temperature rises, the emissions of CO and CO₂ increase as well as the CO/CO₂ ratio. This behavior is clearly observed during the initial period during which the pellets were heated to 30 °C (Figure 7a) and continues during the entire time of the cold experiment (Figure 7c). This behavior indicates that CO is being favored as the product of wood pellet degradation, especially at cold and room temperatures and for aged pellets. CO₂ production is being favored only after 3–4 days at 30 °C and for fresher pellets at room temperature, as observed by the decrease of the CO/CO₂ ratio. This behavior was also observed by Kuang et al.⁷ as the temperature increased to 50 °C. This difference in CO/CO₂ values might be due to a different reaction pathway for the pellets exposed at higher temperatures. This possibility needs to be explored in future work. Yazdanpanah et al.¹⁵ observed an increase of the CO/CO₂ ratio with time at room temperature until it reached a constant value at the end of the storage experiments. Also, the results presented here show that aged pellets have significantly lower ratios (almost half lower) than fresh pellets, and it is probably because there is less reactant available for the off-gassing reactions. From the magnitude of these ratios, we can conclude that the temperature is a stronger driving force for CO production than the age of the pellets.

Kinetic Modeling. The improved kinetic model results from fitting eqs 5 and 6 to the data are given in Table 4. Panels a–c of Figure 8 show the predicted concentrations of CO and O₂ from the modeling with the actual data measured in drum experiments for one set of data (fresh pellets). The predicted concentrations were calculated using eq 15 with the fitted regression parameters. The differential equations were integrated with a Runge–Kutta method using an 0.25 day step length. The estimated concentrations were calculated using the results of the kinetic model. The measured oxygen concentration curves appear to follow an exponential decay, but the model predictions show a linear decay. Although the model does not always follow the observed decay for oxygen (*R*² values for hardwood in the range of 0.65–0.69; Table 4), it does show good fits for CO emission rates.

The results show that the reaction rate constants for CO are of the order of 10^{−7} (m³/mol)^{1/2} s^{−1} and did have a limited variability with the temperature. The rate constants for O₂ depletion are around 10^{−10} m³ kg^{−1} s^{−1} and again showed some temperature dependence. For various types of pellets, the reactivity and areal densities of reactants on the surface are different. The differences in the parameter replicate estimates for each type of pellet are less than 10%. However, the prediction for hardwood is less precise than those for the softwood and blended pellets. In addition, the initial emission rate magnitude calculated for the different factors that influence the off-gassing of CO (Table 4) shows that higher temperatures, following aged, together with HS are the major factors for a high concentration of CO. The percentage of RH and surface were not measured in the drums; thus, there are no model predictions performed for these experiments. Also, the softwood and blended wood pellets are the pellets that produce more CO.

A comparison between the CO emissions as a function of volume (g_{CO}/kg_{pellets} L) from different models shows very different predictions of CO emission rates. The predictions by

Table 4. Results of the Kinetic Model, Calculated Initial Emission Rate, and Percentage of CO Emission Contributing to O₂ Depletion

sample ID	$k_{\text{CO}}^{1/2}$ ((m ³ /mol) ^{1/2} s ⁻¹)	k_{OD} (m ³ kg ⁻¹ s ⁻¹)	$w_{\text{R-CO}}$ (mol of reactant kg ⁻¹ of pellet)	calculated initial emission rate (mol of CO kg ⁻¹ of pellet day ⁻¹)	calculated initial O ₂ consumption rate (mol of O ₂ kg ⁻¹ of pellet day ⁻¹)	percentage of CO emission contributing to O ₂ depletion (%)	RQS ^a CO/O ₂
HW (1) ^b	7.23 × 10 ⁻⁷	3.92 × 10 ⁻¹¹	4.79 × 10 ⁻⁵	8.81 × 10 ⁻⁶	2.93 × 10 ⁻⁵	13.1	0.92/0.65
HW (2)	7.09 × 10 ⁻⁷	3.83 × 10 ⁻¹¹	4.85 × 10 ⁻⁵	8.75 × 10 ⁻⁶	2.87 × 10 ⁻⁵	13.2	0.93/0.69
HW (3)	6.73 × 10 ⁻⁷	4.05 × 10 ⁻¹¹	5.12 × 10 ⁻⁵	8.76 × 10 ⁻⁶	3.03 × 10 ⁻⁵	12.6	0.95/0.66
average	(7.0 ± 0.3) × 10 ⁻⁷	(3.9 ± 0.1) × 10 ⁻¹¹	(4.9 ± 0.2) × 10 ⁻⁵				
SW (1)	3.44 × 10 ⁻⁷	2.59 × 10 ⁻¹⁰	1.21 × 10 ⁻⁴	1.06 × 10 ⁻⁵	1.94 × 10 ⁻⁴	2.7	0.99/0.96
SW (2)	3.41 × 10 ⁻⁷	2.80 × 10 ⁻¹⁰	1.30 × 10 ⁻⁴	1.13 × 10 ⁻⁵	2.09 × 10 ⁻⁴	2.6	0.99/0.95
SW (3)	3.65 × 10 ⁻⁷	2.67 × 10 ⁻¹⁰	1.21 × 10 ⁻⁴	1.13 × 10 ⁻⁵	2.00 × 10 ⁻⁴	2.8	0.99/0.99
average	(3.5 ± 0.1) × 10 ⁻⁷	(2.7 ± 0.1) × 10 ⁻¹⁰	1.24 ± 0.05 × 10 ⁻⁴				
BW (1)	6.05 × 10 ⁻⁷	1.64 × 10 ⁻¹⁰	9.28 × 10 ⁻⁵	1.43 × 10 ⁻⁵	1.23 × 10 ⁻⁴	5.5	0.99/0.82
BW (2)	5.53 × 10 ⁻⁷	1.65 × 10 ⁻¹⁰	9.48 × 10 ⁻⁵	1.33 × 10 ⁻⁵	1.23 × 10 ⁻⁴	5.1	0.99/0.86
BW (3)	5.30 × 10 ⁻⁷	1.71 × 10 ⁻¹⁰	1.05 × 10 ⁻⁴	1.42 × 10 ⁻⁵	1.28 × 10 ⁻⁴	5.3	0.99/0.90
average	(5.6 ± 0.4) × 10 ⁻⁷	(1.70 ± 0.04) × 10 ⁻¹⁰	(9.8 ± 0.7) × 10 ⁻⁵				
HW old	2.34 × 10 ⁻⁷	6.95 × 10 ⁻¹¹	5.78 × 10 ⁻⁵	3.44 × 10 ⁻⁶			0.99/0.87
SW old	1.93 × 10 ⁻⁷	6.82 × 10 ⁻¹¹	1.34 × 10 ⁻⁴	6.56 × 10 ⁻⁶			0.99/0.87
BW old	3.71 × 10 ⁻⁷	7.30 × 10 ⁻¹¹	6.52 × 10 ⁻⁵	6.15 × 10 ⁻⁶			0.97/0.87
HS 50.0%	1.88 × 10 ⁻⁷	7.83 × 10 ⁻¹¹	6.28 × 10 ⁻⁵	3.01 × 10 ⁻⁶			0.98/0.95
HS 25.0%	1.98 × 10 ⁻⁷	6.70 × 10 ⁻¹¹	4.83 × 10 ⁻⁵	2.44 × 10 ⁻⁶			0.98/0.97
HS 12.3%	2.62 × 10 ⁻⁷	5.70 × 10 ⁻¹¹	3.47 × 10 ⁻⁵	2.31 × 10 ⁻⁶			0.99/0.97
Fresh HW Pellets at Different Temperatures							
heated 1	NM ^c	NM	NM	NM	NM	NM	
heated 2	NM	NM	NM	NM	NM	NM	
heated 3	NM	NM	NM	NM	NM	NM	
average							
room (1)	3.81 × 10 ⁻⁸	5.85 × 10 ⁻⁸	1.20 × 10 ⁻⁶	1.17 × 10 ⁻⁸	NM	NM	
room (2)	7.30 × 10 ⁻⁷	4.32 × 10 ⁻¹⁰	1.71 × 10 ⁻⁴	3.17 × 10 ⁻⁵	NM	NM	
room (3)	9.31 × 10 ⁻⁷	4.74 × 10 ⁻¹⁰	1.29 × 10 ⁻⁴	3.06 × 10 ⁻⁵	NM	NM	
average	5.67 × 10 ⁻⁷	1.98 × 10 ⁻⁷	1.00 × 10 ⁻⁴				
cold (1)	2.20 × 10 ⁻⁷	3.06 × 10 ⁻¹⁰	1.03 × 10 ⁻⁴	5.91 × 10 ⁻⁶	NM	NM	
cold (2)	1.07 × 10 ⁻⁷	3.75 × 10 ⁻¹⁰	1.96 × 10 ⁻⁴	5.49 × 10 ⁻⁶	NM	NM	
cold (3)	9.23 × 10 ⁻⁸	4.02 × 10 ⁻¹⁰	2.40 × 10 ⁻⁴	5.80 × 10 ⁻⁶	NM	NM	
average	1.40 × 10 ⁻⁷	3.61 × 10 ⁻¹⁰	1.80 × 10 ⁻⁴				

^aRQS = squared Pearson product moment correlation coefficient between the measured data and the model predictions. ^bNumber denotes one of three replicate samples being measured in each experiment. ^cNM = not measured.

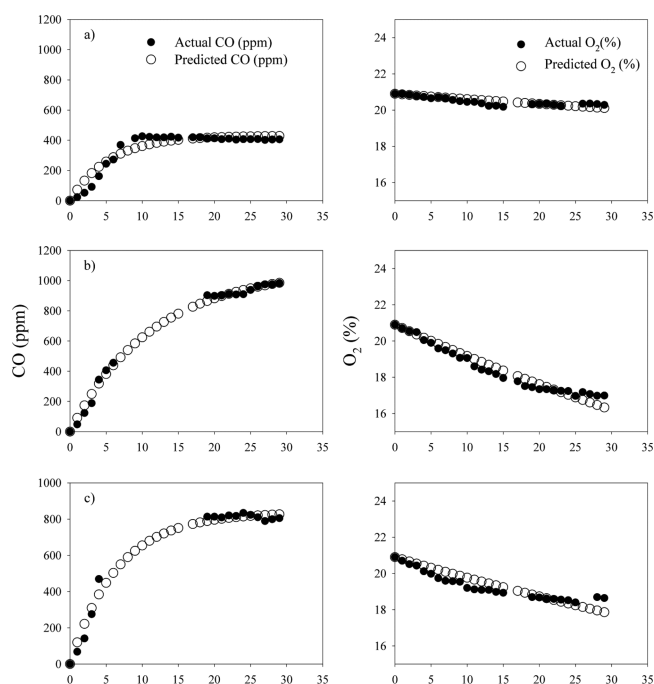


Figure 8. (a–c) Actual concentrations versus predicted concentrations of CO and O₂ for (a) hardwood, (b) softwood, and (c) blended pellets.

Fan and Bi were 1 order of magnitude lower (0.004 76, 45 L) than the models used by Yazdanpanah et al.¹⁶ (0.0191, 5200 L) and Kuang et al.¹³ (0.0124, 45 L). The model developed in this study predicts higher concentrations of CO (0.0403, 68 L), as much as 2 times more than the model used for the effect of pellets inside silo storage.^{15,16} Future work will be conducted to model the CO behavior that has been observed in in-use pellet bins.⁹

CONCLUSION

This experimental study shows that CO emission and O₂ depletion are related to a surface reaction on wood pellets, described here by the parameter of w_{R-CO} , fitting very well with the experimental measurements in drums, especially for CO.

The storage temperature is a factor that affects the off-gassing from stored wood pellets, more than the age. Higher concentrations and faster emission rates were observed with higher temperatures (more than 30 °C). For this reason, it is recommended to store pellets in a cool temperature space or, even better, at colder temperatures, such as outdoor storage commonly used during the winter season. External storage facilities will always reduce the indoor exposure from off-gassed CO.

Pellets stored under high relative humidity had a faster and higher CO emission rate. For almost saturated storage conditions, the final CO concentration was about 3 times as high as that for a normal humidity condition. Dried wood pellets were less active in CO off-gassing compared to as-received wood pellets. It is recommended that wood pellets be stored under low-humidity conditions. In terms of types of pellets produced in the northeastern U.S., hardwood pellets was observed to have the less CO off-gassing, but caution should be taken because these hardwood pellets had the tendency to absorb more moisture than softwood pellets.

ASSOCIATED CONTENT

Supporting Information

Nomenclature, units of parameters or variables in the improved model development (Table S1), recirculation system to obtain air samples used for the off-gassing experiments (Figure S1), photographs for the testing of moisture content and surface area effects in pellets using Erlenmeyer flasks as storing chambers (Figure S2), CO concentration and percentage of O₂ as a function of time for 50, 25, and 12% HS (Figure S3), and CO, O₂, and CO₂ concentrations as a function of time for aged pellets (1 month old) under three different temperature conditions: (a) 30 °C, (b) 22 °C, and (c) 6–8 °C (Figure S4) (PDF). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.5b00347.

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Notes

The authors declare no competing financial interest.

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