Studies of Carbon Monoxide (CO) Off-Gassing from Stored Pellets

Final Report

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Studies of Carbon Monoxide (CO) Off-Gassing from Stored Pellets

Final Report

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Abstract

Emissions of carbon monoxide (CO) and volatile organic compounds (VOCs) arising from stored wood pellets have been previously reported. In some instances, the reported CO concentrations were extremely high and fatalities were reported, but even for lower observed concentrations, residential guidance values and occupational standards have been exceeded. All of the prior research on wood pellet off-gassing was related to bulk pellet storage. This study was initiated to also determine if there is substantial off-gassing of CO from bagged pellets since pellet bags are perforated so they can be easily stacked on pallets for shipment. In addition, the mechanism of CO formation was studied to identify why dry wood pellets would produce unacceptable concentrations of CO under typical storage conditions. To determine the CO concentrations produced by bagged pellets, two 40-pound bags of fresh pellets were placed in 55-gallon drums along with a CO monitor and allow to sit for 20 days at room temperature, at 30ºC and between 0 and 6ºC and two relative humidity (RH) values (~30% and 70%). CO concentrations increased with increasing temperature and moisture in the container. Emission factors were calculated from the measured concentrations. The highest CO emission factors were 9.66 ± 0.52 mg/kg for softwood pellets at 30ºC and 30% RH and 10.41 ± 0.49 mg/kg at 30ºC and 70% RH. Bagged pellets stored under cool to cold conditions resulted in lower concentrations compared to the emissions at higher storage temperatures.

The mechanism for the production of CO from wood pellets was hypothesized to be driven by a multistep process initiated by the autoxidation of unsaturated compounds including fatty acids and terpenes by molecular oxygen. As a byproduct of these reactions, hydroxyl radicals are formed. Then, the bulk of the CO results from reactions of hemicellulose with hydroxyl radicals. The mechanism was tested in a series of experiments in which off-gassed CO was measured and evolved organic compounds were analyzed using gas chromatography-mass spectrometry (GC-MS). These studies identified short- and long-chain aldehydes in the evolved gases that had to derive from the autoxidation process. However, measurements showed there was too little mass of these unsaturated compounds in the wood to produce the observed mass of off-gassed CO. The role of hydroxyl radicals was then investigated using a radical scavenger and its role in CO production was confirmed. Thus, if the autoxidation initiation can be eliminated, then CO off-gassing from pellets would be substantially reduced. Destruction of the reactive compounds with ozone (O_3) led to a suppression of CO formation suggesting an approach to process the wood fiber that would result in low or no CO emission wood pellets.

Additional studies were then undertaken to provide the kinetic data necessary to develop a practical process for elimination of the off-gassing from pellets. Using a small materials auger, the reaction was found to follow a pseudo first order reaction such that the reduction in CO emissions was linearly proportional to the ozone exposure (concentration x time). The exposure needed to reduce or eliminate the formation of CO from the exposed fiber was around 42,000 ppm-minutes at a flow rate of 0.57 kg/minute of fiber or approximately 0.032 g of O_3 per kg of fiber to be passivated. The VOCs produced during the ozonolysis of fiber were analyzed with GC/MS. Aldehydes such as nonanal and decanal were identified, indicating oleic acid, linoleic acid, and linolenic acid in the fiber were ozonized. To determine any changes in the wood characteristics following exposure to ozone, thermogravimetric analysis was performed, and no major changes to the wood properties were observed. To establish the industrial viability of the process, trials were conducted at scale in a commercial pellet mill. Wood pellets produced through this process showed no measurable CO off-gassing given enough ozone exposure thereby confirming the viability of the process. The fuel properties of the resulting pellets were measured and found that the wood pellets produced from the treated fiber exhibited similar calorific content but somewhat different moisture and ash contents as the non-treated wood pellets.

Keywords

Carbon monoxide, off-gassing, outgassing, bagged wood pellets, pellet manufacturing

Acknowledgments

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Acronyms and Abbreviations

ACGIH	American Council of Governmental Industrial Hygienists
ASHRAE	American Society of Heating, Refrigerating, and Air-Conditioning Engineers
hr	hour
CO	carbon monoxide
CO_2	carbon dioxide
kg	kilogram
kW	kilowatt
m^3	meter
MMBtu/h	million British thermal units per hour
NIOSH	National Institute of Occupational Safety and Health
NYS	New York State
NYSERDA	New York State Energy Research and Development Authority
O_2	oxygen
O_3	ozone
OSHA	Occupational Safety and Health Administration
PM	particulate matter
ppm	parts per million
RH	relative humidity
T	temperature
VOC	volatile organic compound

1   Introduction

When fuel oil prices rose sharply in the fall of 2008, NYSERDA initiated demonstration projects to introduce advanced European biomass heating technologies into New York State (NYS). Following these initial projects, commercial scale systems were deployed at institutions in northern NYS. The substantial increase in wood pellets being used as a heating fuel within NYS has led to increased bulk delivery and storage of wood pellets to fuel these systems.

However, a problem exists with respect to the safe handling of wood pellets. There is off-gassing of CO into bulk pellet storage bins and shipping vessels (Svedberg et al., 2004; Arshadi and Gref, 2005; Kuang et al., 2008; Hagström et al., 2008; Arshadi et al., 2009; Granström, 2010; Soto-Garcia et al., 2015a). Fourteen fatal accidents have been reported since 2002 resulting from the storage or transport of bulk wood pellets (Gautier et al., 2012). Svedberg and Galle (2001) investigated complaints of eye irritation and odor in a pellet factory in Sweden. They identified the presence of hexanal, pentanal, methanol, acetone and carbon monoxide. A subsequent study (Svedberg et al., 2004) investigated and described the presence and formation of carbon monoxide and volatile compounds (VOCs), particularly hexanal, from the storage of wood pellets. They also monitored the emissions from kiln drying of wood and determined that the emissions were not specific to wood pellet production but were more general in nature. They concluded high levels of hexanal and carbon monoxide were strongly associated with storage of wood pellets and may constitute an occupational and domestic health hazard. However, this warning clearly was not widely disseminated, and thus, measures were not taken that might have precluded the deaths noted previously.

Additional laboratory studies of CO off-gassing were undertaken by Kuang et al. (2008; 2009a; 2009b) to examine the effects of storage temperature (T), headspace volume, and relative humidity (RH) on the extent of CO off-gassing. Increased temperature produced higher CO concentrations. These studies focused on softwood pellets as commonly produced in western Canada.

Arshadi et al. (2009) examined the VOC emissions from pellets made of blends of pine and spruce. The fatty and resin acid concentrations were measured using gas chromatography-mass spectrometry for newly produced pellets and those aged for 2 and 4 weeks. The concentrations of aldehydes and ketones were determined by high performance liquid chromatography (HPLC) at 0, 2, and 4 weeks to explore the relationships between the acid content and the resulting carbonyl emissions. They found a strong correlation between the pine fraction in the pellets and the fatty/resin acid content, but the

influence decreased over storage time. The fatty and resin acid concentrations decreased by 40% during the 4-week storage period. The drying temperature also influenced the aldehyde and ketone emissions of fresh pellets. The amounts of emitted aldehydes and ketones generally decreased by 45% during storage as the fatty/resin acids oxidized. Thus, they conclude that it is the oxidation of the fatty acids that is the primarily mechanism for the observed off-gassing of VOCs. However, they do not relate any of these quantities to CO emissions.

Alternatively, Ferrero et al. (2011) measured the temperature and gas concentrations in a newly established pine-wood chip pile (20 m × 15 m × 6 m containing approximately 400 tons of fresh weight material) for 150 days. The temperature was measured at ten positions within the pile, and concentrations of CO_2, O_2, CO, and CH_4 were made at four locations. There was a substantial rise in temperature within the first 10–12 days of storage. The analysis of the gas samples collected in this period suggests that the temperature increase was caused by aerobic microbial processes.

Soto-Garcia et al. (2015a) examined the 8-hour rolling average concentrations of CO in actively used pellet bins. Peak concentrations in these pellet storage locations ranged from 44 ppm in a basement residence to 155 ppm inside the storage silo at an elementary school. One-hour average CO concentrations in the boiler rooms were typically 10 to 15 ppm. The measured concentrations were compared to Occupational Safety and Health Administration (OSHA) regulatory standards of 50 ppm, the National Institute of Occupational Safety and Health (NIOSH) recommended occupational guideline of 35 ppm, and the American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE) guidance of 9 ppm for nonworking environments. The concentrations at the three locations in a middle school never exceeded the 35 ppm, 8-h average guideline. At a museum, the CO concentrations after pellets delivery did reach a maximum of 55 ppm for a 1-h average, but did not exceed the 8-h average regulatory limit. High concentrations only remained for 4 days after pellet delivery due to the natural ventilation in this storage location. Storage areas for pellets that exceeded the 50-ppm limit must be considered confined spaces and require appropriate entry procedures. As heating with wood pellets becomes more prevalent, improved designs for storage bins must be considered to minimize the risk of exposure to CO to building occupants.

However, most pellets used for residential heating in the northeastern U.S. are sold in 40-pound (18.1 kg) plastic bags. None of the prior studies examined the issue of emissions from bagged pellets. Although the pellets are placed into bags, the bags are not airtight. They are perforated to allow effective stacking on pallets. Thus, there is the potential for release of CO and other contaminants in a manner similar to bulk pellets.

Soto-Garcia et al. (2015 b,c) performed laboratory studies in which they found substantial emission rates of CO and VOCs. They found that dry pellets off-gassed CO without resulting in increased temperatures and did not appear to be biological in origin. They found that although there were compounds emitted that suggested autoxidation of fatty acids, the fatty acids concentrations were too low to be the origin of the CO. Thus, the mechanism of CO production has not been determined. Thus, the objectives of this project were:

- Obtain additional information on the dynamics of CO concentrations in wood pellet bins that are in use over a variety of bin sizes,
- Determine the extent of CO emissions from bagged pellets and the effect of storage conditions such as temperature and relative humidity on their off-gassing potential, and
- Obtain a better understanding of the mechanism of CO formation and whether the pellet production process has an influence on the CO off-gassing rate.

2   Off-Gassing from Bagged Pellets

2.1   Methods

2.1.1   Laboratory

CO measurements were made using 55-gallon drums that could hold two 40-pound bags of pellets. The drums were sealed with a gasket and metal ring to provide an airtight seal. Two sealed bags of fresh pellets (acquired less than two days since manufacture) were inserted into each drum for each experiment. Then a CO monitor (Model ZDL-500, Environmental Sensors Co. USA) and a temperature (T)/Relative Humidity (RH) (EL-USB-2+, EasyLog, LASCAR electronics, China) monitor were attached to the inside bottom of the cover (Fig. 1). Each drum was sealed for 20 days to continuously monitor the resulting CO concentrations as well as temperature and relative humidity.

Figure 1. Experimental setup of the bag-pellets drum experiment

To study the effects of the temperature and moisture, experiments were performed with different batches of bagged-softwood, hardwood, and blended pellets. For the high RH experiments, the moisture content inside the drum was increased by spraying ~20 mL water into the drum. To help maintain the higher RH, a beaker holding an additional 20 ml of water was placed in the drum. To obtain 30ºC, the drums were heated using heating tape around the drum. The heating tape was connected to a variable transformer set at approximately 10 V, producing a measured temperature of ~30ºC. Room temperature measurements were performed by keeping the drum inside the in the laboratory at room temperature (~22ºC). The cold conditions were obtained by placing the drum outside on the roof of the building during colder weather. It was possible to maintain the 22ºC and 30ºC temperatures at quite constant values over the duration of the experiments. However, the low temperatures were studied outdoors and the test temperatures did vary from 0 to 6ºC (over a 20-day test period), mimicking what would occur in an unheated garage or shed.

The CO emission factors were calculated from the data collected from drum experiments. At constant temperature (T) and pressure (P), the concentration of CO off-gassing was converted to emission factor, f (milligram of off-gas per kilogram of wood pellets) using the following equation (Yazdanpanah et al., 2014; Tumuluru et al., 2015).

$$f = \frac{PCV_gM_{wt}}{RTM} * 1000$$

Equation 1.

where T = temperature (K); R=Gas constant (8.31 J/mol.K); M_{wt} = gas molecular weight (g/mole); M= mass of the pellets in the drum (kg); V_g=volume of the gas in the drum (m³); and P= pressure in the container.

2.1.2 Field Study

To explore if off-gassing from bagged pellets resulting in concentrations that presented a hazard or violated regulatory standards, measurements were made in the warehouse of a pellet mill where they stored pallets of bagged pellets until they are shipped to market. The study was conducted from April 25 to July 21, 2016 as the warehouse was being filled with approximately 5500 tons of pellets in anticipation of the 2016-17 heating season. Rahman et al. (2017) measured aldehyde emissions at the same time and found high concentrations of several aldehydes including formaldehyde and hexanal. CO was measured at 5-minute intervals in the middle of the storage area at ~3.5 m above the floor level with another Lascar CO monitor for 6 months.

2.2 Results

2.2.1 Laboratory

Figure 2 shows the CO concentrations in the drum for blended pellets for the 3 temperatures and an average RH of 30%. The CO concentrations from all of the experiments are summarized in Table I. From such data, the CO emissions rates from the different pellet types were determined for the different temperatures (0 to 6ºC, 22ºC and 30ºC) at 30% RH. This concentration of water vapor was controlled by the equilibrium of the moisture content in the pellets with the water vapor in the drum. The maximum CO emission factors are presented in Table 2. The results show that CO emissions increase with temperature at 30% relative humidity for all types of bagged pellets. However, the emission rates are higher for blended wood (70% softwood, 30% hardwood) and softwood compared to hardwood (100%) pellets at all temperatures. These results clearly indicate that temperature has a significant effect on CO production for all 3 types of wood pellets at constant relative humidity, as with previous studies done with bulk

storage (Soto-Garcia et al., 2015b). The maximum CO emission factors for hardwood, softwood, and blended wood pellets were 4.47 ± 0.22 mg/kg, 9.66 ± 0.52 mg/kg and 9.95 ± 0.53 mg/kg at 0 to 6ºC, 20ºC, and 30ºC and ~30% RH, respectively. Tumuluru (et al., 2015) studied the CO emission factor from softwood pellets at 40ºC and reported the maximum value of 10.60 mg/kg that is comparable with the softwood values in this study.

Figure 2. CO concentrations in the drum with bagged hardwood pellets as a function of temperature at a constant RH of 30%
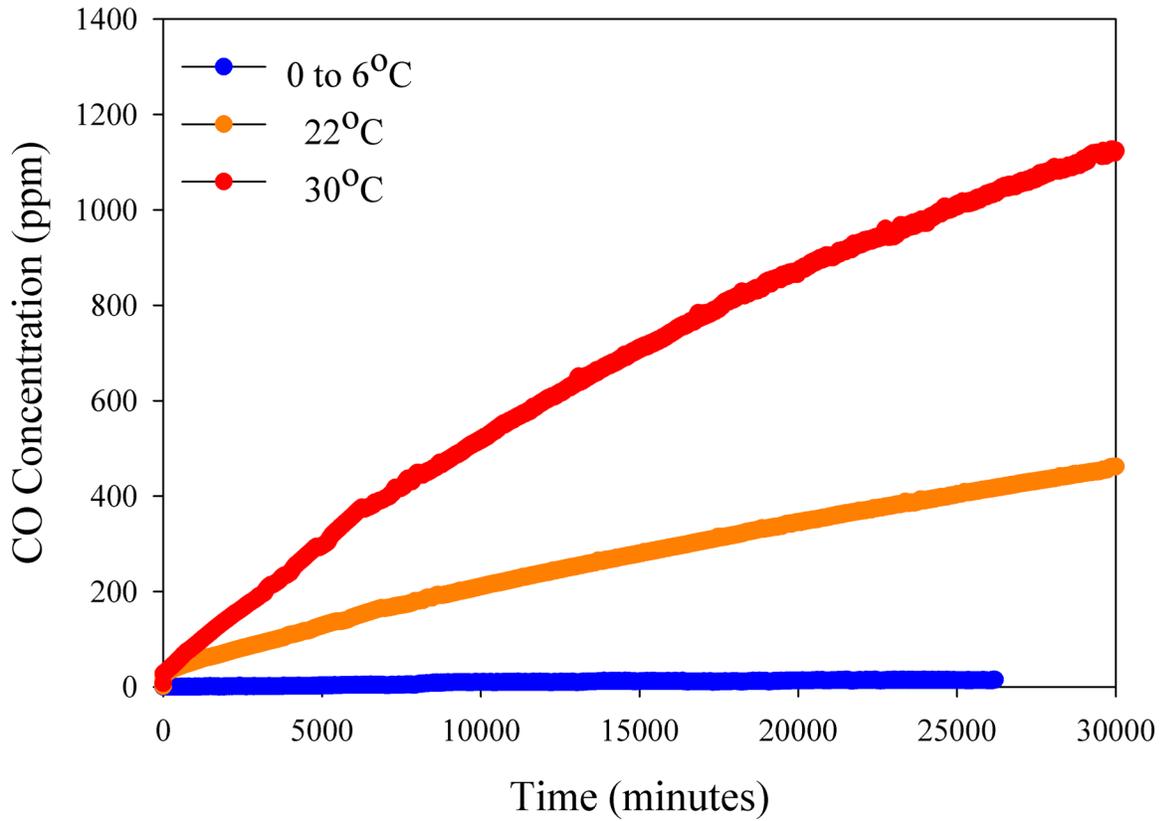
Table 1. Summary of results of the bagged pellet drum experiments

Bag-pellet	Temperature (ºC)	Mean RH: 30%		Mean RH: 70%	
		Maximum CO (ppm)	Std Dev	Maximum CO (ppm)	Std Dev
	0-6	25.0	6.6	193.5	15.7
Hardwood	22	463.0	69.6	502.2	76.8
	30	701.4	64.3	936.2	86.8
	0-6	60.9	13.2	224.7	50.8
Softwood	22	904.7	44.5	1194.2	86.9
	30	1517.0	115.2	1599.8	128.4
	0-6	163.7	30.8	370.6	64.5
Blended wood	22	1467.3	95.5	1599.8	115.5
	30	1822.5	105.9	2000.0	98.6

Table 2. Summary of the maximum CO emission factors at different temperature and moisture

Temperature (ºC)	Hardwood Max. emission factor (mg/kg)		Softwood Max. emission factor (mg/kg)		Blended wood Max. emission factor (mg/kg)	
	30% RH	70% RH	30% RH	70% RH	30% RH	70% RH
0-6	0.35 ± 0.06	1.17 ± 0.08	0.42 ± 0.10	1.88 ± 0.06	0.99 ± 0.11	2.52 ± 0.15
22	3.18 ± 0.12	3.27 ± 0.11	5.73 ± 0.21	7.74 ± 0.41	7.66 ± 0.45	9.52 ± 0.55
30	4.47 ± 0.22	6.10 ± 0.14	9.66 ± 0.52	10.4 ± 0.6	9.95 ± 0.53	10.41 ± 0.49

The CO emission factors at the two different RH values are presented in Table 2. The maximum CO emission factors for hardwood, softwood, and blended wood pellets were 6.10 ± 0.14 mg/kg, 10.39 ± 0.62 mg/kg, and 10.41 ± 0.49 mg/kg, respectively at 30ºC and ~70%. CO emission rates increase with relative humidity (RH) for all wood pellet types but not as dramatically as with temperature. The relative humidity inside the drum initially drops slightly (~4%) after loading the bags of pellets into the drums at all temperatures suggesting that the surface of the pellets absorbs moisture from the closed drum. The RH then rises to a constant value for a given temperature because moisture was provided from the water in a reservoir inside the drum. The moisture content of the pellets was not determined after the drum tests. Kuang et al. (2008) reported that the moisture content reduced about 1% when the pellets were stored in sealed and heated containers. The moisture from the pellets depends on the mass of pellets used in the given experiment. Kuang et al. (2008) used 25 kg of wood pellets for their experiments. Fan and Bi (2013) reported that CO emission increased with moisture as did Soto-Garcia et al. (2015b). In the 0 to 6ºC experiments, the RH values in the drum varied because of the variations in temperature. Increasing relative humidity resulted somewhat higher CO emission rates.

Moisture adsorbs on the pellet surface and increases the surface areas of the active sites by rupturing or cracking. Thus, it helps to provide more of the chemical reactants responsible for CO off-gassing. Therefore, moisture has a smaller contribution to changes in CO emission rates compared to temperature. Kuang et al. (2008) also reported that the emission of CO from stored wood pellets is more sensitive to storage temperature than to RH. Tumuluru et al. (2015) also observed change of CO off-gassing concertation with types of biomass. The CO concentrations for all pellet types at room temperature (22°C) and elevated temperature (30°C) at both RH values were high enough to produce potential in-building concentrations that exceed the ACGIH health based guidelines of 25 ppm and OSHA regulatory concentration of 50 ppm for occupational settings. In addition, the 9 ppm (ASHRAE) guideline for homes could be exceeded.

2.2.2 Field Study Results

Figure 3 presents the time series of 8-hour rolling average CO concentrations measured in the pellet mill warehouse calculated from the 5-minute measurements. The maximum 8-hour average value was 101.5 ppm that were in excess of both the ACGIH TLV (2017) and OSHA (1997) health-based guidelines. Thus, there are times when the CO emitted by the stored pellets creates an occupational hazard and thus, attention needs to be paid to adequate ventilation in spaces where large quantities of pellets are stored in agreement with prior studies of bulk pellets. This work has been submitted for publication in the Annals of Work Exposures and Health (Rahman et al., 2017b)

Figure 3. Time series of rolling 8-hour average concentrations of carbon monoxide measured in the storage warehouse of the pellet mill
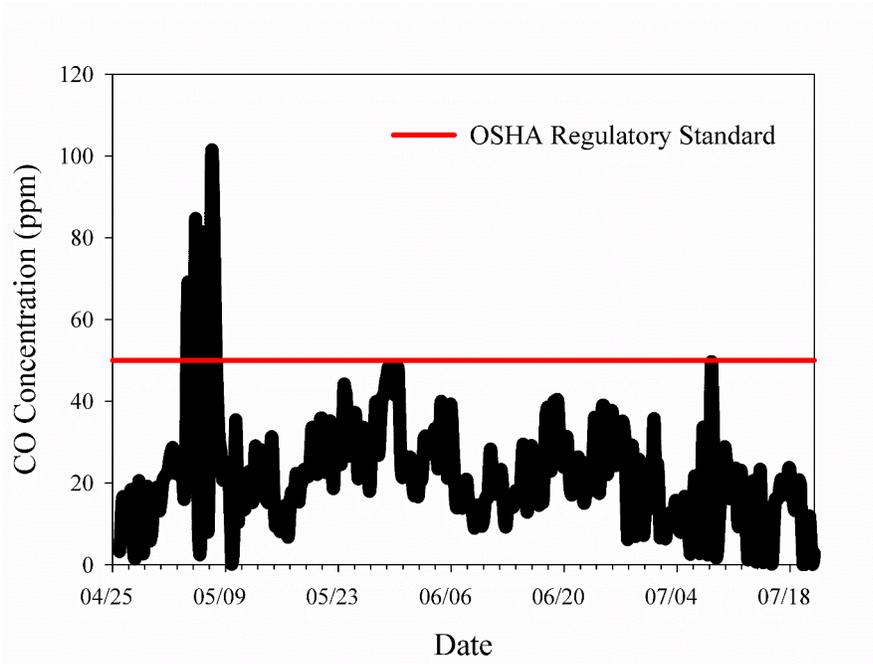
In addition to CO measurements, samples were also collected to measure aldehydes that have been previously reported coming from wood (Svedberg et al., 2002; 2004). Rahman et al. (2017a) report on sampling and analysis of many airborne aldehydes including acetaldehyde, formaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, and hexanal. Using NIOSH method 2539, sampling was conducted in five locations in the warehouse from April–June 2016 when it contained varying quantities of bagged pellets and in two homes with 10-ton bulk storage bins. The aldehyde concentrations were found to increase with the amount of stored pellets. Airborne concentrations of formaldehyde were as high as 0.45 ppm in the warehouse exceeding the NIOSH RELC, and ACGIH TLV-C occupational exposure limits (OELs). The concentrations of aldehydes measured in the residential bins were also elevated indicating emissions may raise indoor air quality concerns for occupants. While exposures to individual aldehydes are of concern, the combined irritant effect of all of the aldehydes further raises concerns for building occupants. Thus, either adequate ventilation or a reduction in emissions from the pellets is needed to reduce the exposure of workers or building occupants to unhealthy CO and aldehyde concentrations.

3 Mechanism of CO Formation

The mechanism of formation of CO is described in detail by Rahman and Hopke (2016). This paper is open access and freely available to everyone at http://pubs.acs.org/doi/pdf/10.1021/acs.energyfuels. 6b00874. Thus, these studies will only be reviewed here briefly. Prior work (Svedberg et al., 2004; Kuang et al., 2008; Arshadi et al., 2009) had suggested that autoxidation of the unsaturated fatty acids present in the wood produced the observed CO and aldehydes. However, analyses of fresh pellet samples showed that there were only enough fatty acids in the wood to account for between 3% and 8% of the observed mass of CO. Thus, an alternative mechanism had to be driving the bulk of the CO formation.

Prior thermogravimetric analysis (TGA) had previously identified that during storage when CO off-gassing would occur, the pellets lost a significant amount of hemicellulose, but did not show loses of cellulose or lignins (Soto-Garcia et al., 2015b). Hemicellulose will not autoxidize, but Porter and Wujek (1984) and Hämäläinen et al., (2001) reported that during autoxidation of unsaturated fatty acids, there is formation of hydroxyl radicals (HO·), a strong oxidizer that is capable of reacting with hemicellulose. It was then hypothesized that HO· played a key role in the CO formation. This hypothesis was tested using a known radical scavenger, and in those experiments, CO production was substantially suppressed. Thus, the process was determined to be a two-step mechanism with autoxidation of fatty acids and terpenes producing HO· radicals that then produces CO in a chain reaction with the hemicellulose in the wood. Once the surface hemicellulose was oxidized, the production of CO stopped producing curves like those shown in Figure 2.

Understanding this mechanism provides a pathway toward eliminating the problem of CO production through the decomposition of those compounds that will autoxidize to initiate the reaction chain. Unsaturated fatty acids and terpenes will react rapidly with ozone (O_3) to decompose. Therefore, exposing pellets or the fiber from which the pellets are made to ozone would reduce or eliminate CO production. Rahman and Hopke (2016) found that exposing the pellets to ozone substantially reduced CO production, but did not eliminate it. It was suspected that compounds from the interior of the pellet could diffuse to the surface over time, autoxidize, and initiate CO production. Exposing the fiber from which the pellets are pressed to ozone completely eliminated CO production. The issue then remained as to whether the ozone exposure could be conducted in a continuous manner such that it could be incorporated into the pellet making process in a practical manner.

4   Development of Process for CO Suppression

To effectively utilize the mechanistic information developed by Rahman and Hopke (2016), it was necessary to determine the process kinetics for the exposure of wood fiber to ozone while being transported in an auger prior to it being pressed into wood pellets. Rahman et al. (2017c) report the results of laboratory and full-scale studies of ozonizing wood fiber and producing material that no longer off-gasses CO or aldehydes. This paper is open access and is available from http://pubs.acs.org/doi/abs/10.1021/acs.energyfuels.7b01093. The first step was the determination of the rate at which the CO production could be reduced by exposure to ozone. Details of the experiments are provided in Rahman |(et al., 2017c).

To continuously expose the fiber to ozone analogously to what might occur in the pellet mill, a lab scale auger system was developed. A single screw extruder with a hopper [capacity: 0.00708 m^3/min (0.25 ft^3/min); conveying distance: 1.83 m (6 ft); internal diameter: 6.35 cm (2.5 inches), auger rotation speed: 360 rpm] was purchased from Hapman Helix Conveyor, Kalamazoo, Michigan, USA. The total volume of the auger is 83.6 l (510 $inch^3$) and the screw volume is 2.57 l (157 $inch^3$). About 4 kg of wood fiber was conveyed from the hopper to the fiber collection drum by the auger in each trial run. Initially, the auger speed was such that the fiber took 7 minutes to traverse the auger. An agitator and vibrator were added that resulted in a faster flow of fiber through the auger and a residence time of 3.5 minutes.

Wood fiber was continuously exposed to ozone in the auger. The experiment was repeated at different ozone concentrations and different exposure times (7 min and 3.5 min), i.e. the time required for moving the wood fiber from the hopper to the collector. After ozone exposure, the concentrations of CO emitted from the fiber was monitored in sealed drum experiments similar to the bagged pellets but with much smaller drums. The resulting CO concentration curves are shown in Figure 4. Only exposure to 6000 ppm O_3 for 7 minutes produced fiber that did not off-gas CO.

Figure 4. CO off-gas emission of wood fiber exposed at different ozone concentrations in the continuous process
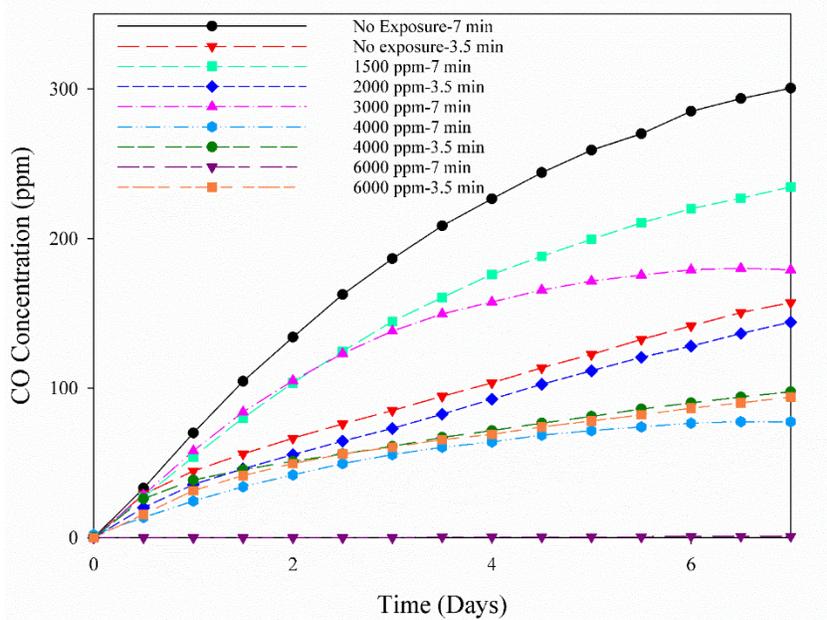
Since the experiments were conducted with two different fiber samples showing different CO formation rates, the results can be compared by calculating the remaining fraction of the maximum CO produced and plotting this fraction against the ozone exposure given in ppm-minutes (Figure 5). There was an excellent agreement between the two sets of experiments with an overall r^2 of 0.971. Thus, the exposure needed to reduce or eliminate the formation of CO from the exposed fiber was estimated to be around 42,000 ppm-minutes at a flow rate of 0.57 kg/minute of fiber or approximately 0.032 g of O_3 per kg of fiber to be passivated.

To test this process at an industrial scale, two ozone generators with a production rate of 2.8 g/h (Queenaire, USA) and 2.2 g/h (Ozonology Inc.) were used to continuously supply ozone with flow rates of 12 l/min and 2.36 l/min, respectively. The Ozonology generator was connected to an oxygen concentrator that allowed it to produce 4.2 g/h. Ozone was purged through the main auger (~6.1 m (20 ft)) bringing the fiber into the building from the drying and milling processes. The fiber mass flow rate of fiber is 182 kg/min. The fiber is then distributed to individual hoppers for each pellet press (Figure 6). The fiber is then augured from these hoppers to the presses to produce the pellets. In this mill, up to five presses can be operating simultaneously. However, in the trials, only three presses were in operation.

Figure 5. The fractional reduction in the maximum CO produced by the fiber following exposure to O_3

$$Y = -2.47 \times 10^{-5} (\pm 0.15 \times 10^{-5}) X + 1.02$$
$$r^2 = 0.971$$

Legend:
○ No exposure
● 3.5 minutes exposure in auger
● 7 minutes exposure in auger

x-axis: O_3 Exposure (ppm-minutes)
y-axis: Remaining fraction of CO
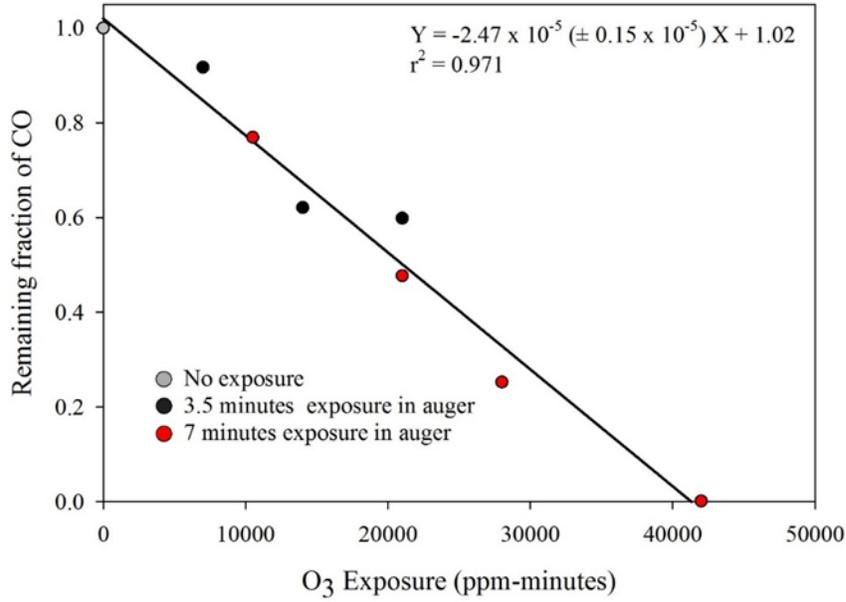
Figure 6. Schematic representation of the areas in the operation where the ozone-fiber reactions occurred (Trial I, Trial-II)
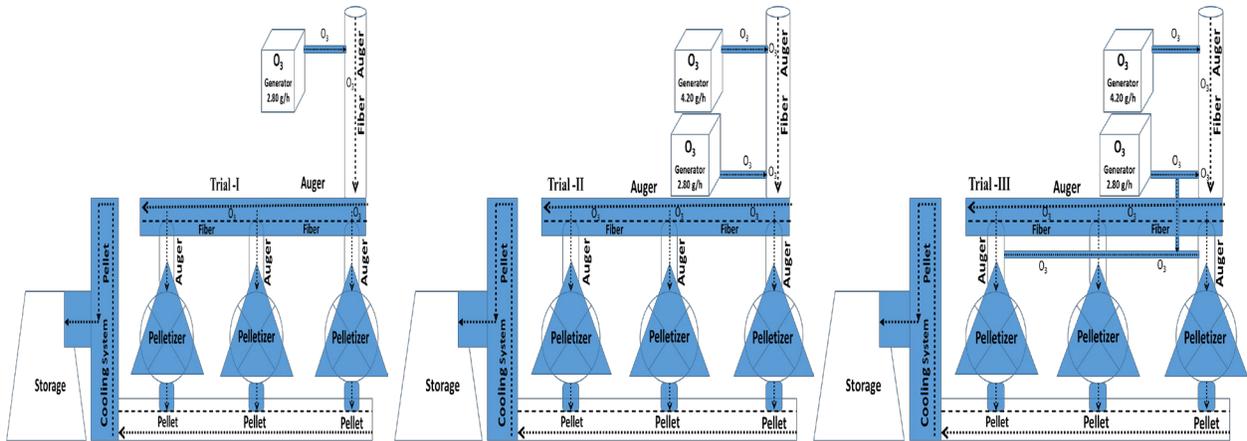
Three trials were performed: 45 min (trial–I), 60 min (trial-II), and 120 min (trial-III), respectively, to try to attain steady-state operation before collecting samples with just the ozone feed to the main inlet auger. The results of the industrial trials are presented in Table 3. The unexposed pellets produced a maximum of CO concentration of 361 ppm. In trial–I, 131 ppm CO was observed with the pellets produced by exposure to 2.80 g/hr ozone. This result indicates that the ozone exposure reduced the CO formation potential but was insufficient to fully passivate all the fiber present in the system. If the residence time in the system is longer than the waiting period, then some unexposed fiber would have been incorporated into the pellets resulting in the observed CO production.

Therefore, trial-II was conducted with a longer waiting period before pellet collection (60 min) as well as an increased total ozone concentration (7 g/hr). The resulting pellets produced in trial-II showed no measured CO. Finally, trial-III was conducted to determine if injecting the ozone through multiple connection points into the auger and the press feed hoppers (Figure 6, right side) and an extended exposure time (120 min), would also eliminate CO production. However, a maximum of 19.66-ppm CO was observed in this trial. Thus, distributing the ozone into multiple points into the process actually reduced the overall exposures since there was less time for the fiber to react with ozone compared to when ozone was injected further upstream in the process.

Table 3. Maximum CO off-gassing by 9 kg pellets/10 days from industrial trials (n=3)

Pellet Sample (Softwood)	Conc. Of O3 used for Exposure (g/h)	Mass of fiber flow rate (kg/min)	Average O3 flow rate (L/min)	Equilibrium Time of O3 Exposure on fiber (min)	Size of the fiber used for Pellets production (mm)	Moisture content in Fiber (%)	Max. Average CO (ppm)	Std. Dev
Unexposed	0.00	182.	-	-	2.00-3.00	10-12	360.50	29.15
O3 Exposed (Trial-I)	2.80 (Queenaire)	182.	12.00 (Queenaire)	45.	2.00-3.00	10-12	130.83	48.41
O3 Exposed (Trial-II)	2.80 (Queenaire) 4.20 (Ozonology)	182.	12.00 (Queenaire) 2.36 (Ozonology)	60.	2.00-3.00	10-12	0.00	0.00
O3 Exposed (Trial-III)	2.80 (Queenaire) 4.20 (Ozonology)	182.	12.00 (Queenaire) 2.36 (Ozonology)	120.	2.00-3.00	10-12	19.66	8.41

Thus, the simpler system of a single injection point produced pellets that did not offgas CO. Given the flow rate of fiber, it was possible to passivate fiber with only 0.00064 g O_3 per kg of fiber, which is 50 times lower, compared to laboratory experiments (0.032 g/kg fiber). This difference can be attributed to several possible causes. In the industrial trials, the fiber experienced much longer reaction times (60 minutes) compared to laboratory experiments (7 minutes). The exact residence time of the fiber between the point at which the ozone is introduced in the main inlet auger and the pellet press is unknown. However, with the holdup in the hoppers that supply fiber to each press, it is approximately 40 to 50 minutes. When the ozone was introduced closer to the presses, the residence time would have diminished resulting in more CO production in the resulting pellets. There was also potentially better mixing in the industrial scale process compared to the laboratory scale auger. The industrial trials confirmed the laboratory studies in that CO off-gassing could be eliminated using a continuous ozonation process. Moreover, this simple kinetics of passivation of the fiber can be easily implemented in conventional wood pellet production with relatively simple ozone generation systems.

The pellets produced from ozone-treated fiber were analyzed for moisture, ash, and calorific content and compared to pellets produced that day prior to the introduction of ozone into the system. Results show significant differences for ash and moisture (p-value < 0.05) but not for the calorific value (p-value = 0.271). However, the exposed fiber pellets met the premium pellet standards of the Pellet Fuel Institute (http://www.pelletheat.org/pfi-standards). Thus, the basic fuel properties of the pellets were not changed sufficiently by the ozone exposure to actually reduce their quality. A patent application covering this process has been filed with the United States Patent and Trademark Office.

5 Conclusions

This project has successfully tested bagged pellets for their ability to produce CO in sufficient quantities to represent a potential hazard to workers and building occupants. Rahman et al. (2017a; b) have shown that exposures to CO and aldehydes in a bagged pellet storage warehouse were sufficiently high that they exceeded regulatory standards. Thus, bagged pellets should be considered as a potential hazard in a similar manner to bulk pellets such that they require active ventilation of the space in which they reside if they are to be stored within an occupied structure.

However, a better alternative would be to move to the production of pellets that will not produce CO and aldehydes. The work of this project has successfully identified the mechanism by which the aldehydes and CO are formed. It is a two-step process in which autoxidation of unsaturated compounds in the wood produce aldehydes and hydroxyl radicals that can go on to react with hemicellulose and produce the CO. Thus, if the unsaturated compounds can be removed from the wood prior to pressing the pellets, formation of these pollutants can be eliminated.

A continuous ozonation process has been developed and tested at the laboratory scale that eliminated CO emissions with sufficient exposure (concentration x time) to ozone. The process was tested at full scale in an operating pellet mill and pellets that did not produce CO were manufactured. The equipment to produce the ozone is relatively inexpensive and apparently easy to install. There will be some adjustments needed to accommodate the ozone. There will need to be changes in rubber and plastic parts to ozone-resistant materials in addition to the acquisition of the ozone generator and oxygen concentrator. It is highly recommended to use an oxygen concentrator to both produce higher quantities of ozone and eliminate the production of nitrogen oxides that would lead to acidic corrosion in the pellet-making systems. Thus, it is now practical to produce wood pellets that do not produce CO or aldehydes without affecting their price. Such pellets would help make it easier to expand the use of renewable wood pellet fuels for residential and commercial heating requirements.

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