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Continuous Ozonolysis Process To Produce Non-CO Off-Gassing Wood Pellets

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ABSTRACT: Prior work on the mechanism of carbon monoxide (CO) formation from stored wood pellets has provided the basis for a continuous process that results in the production of pellets that do not off-gas CO. It had been shown that exposure to ozone eliminated the unsaturated hydrocarbons that autoxidize to produce hydroxyl radicals, which, in turn, react with the hemicellulose to produce CO. To develop a practical process to eliminate the CO formation, a kinetic study of the continuous ozonolysis of wood fiber was conducted 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 × time). The exposure needed to reduce or eliminate the formation of CO from the exposed fiber was around 42 000 ppm min at a flow rate of 0.57 kg/min of fiber or approximately 0.032 g of O_3/kg of fiber to be passivated. The volatile organic compounds produced during the ozonolysis of fiber were analyzed with gas chromatography/mass spectrometry. Aldehydes, such as nonanal and decanal, were identified, indicating that oleic, linoleic, and linolenic acids in the fiber were ozonized. To determine the 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, proving 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 exhibit a similar calorific content but somewhat different moisture and ash contents from the non-treated wood pellets.

■ INTRODUCTION

The off-gassing of carbon monoxide (CO) from stored wood pellets has been identified as a significant problem, potentially resulting in adverse occupational and residential exposures.[1−4] At least, 14 fatal accidents have occurred since 2002 resulting from CO exposure related to the storage or transportation of bulk wood pellets.[5] There have also been problems with smaller scale storage with observed exceedances[6] of the recommended guidelines for homes of 9 ppm of CO averaged over 8 h as proposed by the American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE)[7] and the World Health Organization (WHO).[8] However, the use of wood pellets is increasing in many parts of the world given demands for high-density, renewable energy, concerns about climate change, and long-term decreases in fossil fuel resources.[9] Wood pellets have high energy density, are easy to handle, and are relatively homogeneous in quality.[10] Thus, they are competitive with fossil fuels for heating purposes among wood fuels. In the U.S., there are 188 wood pellet plants producing approximately 13 million metric tons/year of pellets, and there are 42 wood pellet plants in Canada producing about 4 million metric tons/year of pellets.[11] In 2008, the worldwide pellet consumption was about 10 million metric tons, increasing to 13.5 million metric tons in 2010.[12] The European Pellet Council reported that the wood pellet production of the world reached 24.5 million metric tons in 2013.[13] Europe is the largest pellet consumer market, responsible for around 80% of the wood pellet consumption of the world.[14] Estimates from the European Pellet Council indicate that at least 55% of the European pellet consumption is used for residential heating in units of <50 kW.[9] Because global wood pellet production and consumption have risen rapidly over the recent past, there is concern surrounding safety and health issues related to having wood pellets that do not off-gas CO.

Several previous studies investigated the processes that lead to the formation of CO from the stored wood pellets. Svedberg et al.[15−23] suggested that the oxidation of fatty acids could be the reason for the off-gassing of CO. Soto-Garcia et al.[2,3] reported laboratory studies, in which they determined the emission rates of CO and volatile organic compounds (VOCs). They found that, although there were compounds emitted that suggested autoxidation of fatty acids, the fatty acids measured in the pellets were too low in concentration to account for the mass of observed CO. Recently, Rahman and Hopke[24] hypothesized a multiple-step reaction process responsible for the production of CO from wood pellets. The autoxidation of unsaturated compounds, including fatty acids and terpenes, by molecular oxygen initiates the process. As a byproduct of these

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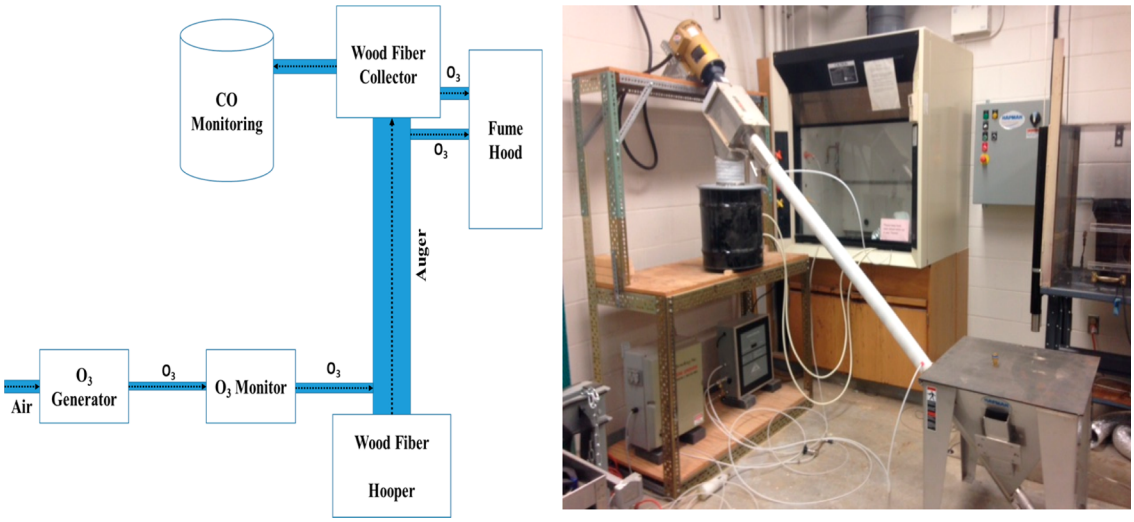

Figure 1. Schematic diagram and picture of the continuous ozonolysis process, including the auger and the ozone generator and monitor (lower shelf).

reactions, hydroxyl radicals are formed. Then, the bulk of CO is formed from the reactions of hemicellulose and hydroxyl radicals. If the autoxidation initiation can be eliminated, the CO off-gassing from the pellets would be substantially reduced or eliminated. It would also reduce or eliminate the terpene smell of softwood or blended pellets. Rahman and Hopke[24] showed that ozonation of wood fiber successfully passivated the reactive hydrocarbons under static conditions. An ozone concentration (>10 ppm) with a flow rate of 2 L/min was passed over the surface of ∼4 kg of wood fiber, and the resulting fiber produced no measurable CO. However, kinetics of the continuous ozonolysis reactions were not determined, and they will be needed to assess the feasibility of a continuous process as would be required in a commercial pellet mill. The present study was conducted to determine the kinetics of continuous ozonolysis of wood fiber and to use that information to apply ozonolysis at an industrial scale. A substantial reduction in CO emissions at a reasonable cost in the pellet production process would remove one barrier to the expanded use of wood pellet fuels at national and global levels.

■ MATERIALS AND METHODS

Freshly ground and dried softwood fiber prepared from pine, fir, and spruce was obtained from a local wood pellet mill. The moisture content of the fiber was 10−12%, and the size of the fiber varied by 1.00−3.00 mm. To continuously expose the fiber to ozone analogously to what might occur in the pellet mill, a lab-scale auger system was developed and is shown schematically in Figure 1. A single screw extruder with a hopper [capacity, 0.007 08 m^3/min (0.25 ft^3/min); conveying distance, 1.83 m (6 ft); internal diameter, 6.35 cm (2.5 in.); and auger rotation speed, 360 rpm] was purchased from Hapman Helix Conveyor, Kalamazoo, MI, U.S.A. The total volume of the auger is 83.6 L (510 $in.^3$), and the screw volume is 2.57 L (157 $in.^3$). 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 min 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 min.

Simultaneously, a flow of 1.4 L/min of 1% by weight O_3 was provided through the auger. An ozone generator (model L-50, Ozonology, Inc., Evanston, IL, U.S.A.) was used to prepare the ozone, and the concentration was monitored with an ozone monitor (model HC-12, PCI Ozone Control Systems, Inc., West Caldwell, NJ, U.S.A.). The sensitivity of the ozone monitor was 1 ppm by volume, and the accuracy was ±3% of reading. The residence time for wood fiber in the auger from the hopper to drum was 7 or 3.5 min. After conveying the fiber to the drum of the collector, the flow of ozone through the auger was stopped. Then, the drum was placed inside a fume hood and left for 30 min, so that ozone and other gaseous products could dissipate. Then, CO off-gassed from the passivated wood fiber was measured.

Off-gassing measurements of the O_3-exposed wood fiber were conducted similarly to those of Soto-Garcia et al.[2] The fiber was placed in 20 gallon steel drums [51 cm (20 in.) in height and 41 cm (16 in.) in diameter]. The drums were sealed with a metal ring and gasket to maintain an airtight fit. A Lascar CO monitor (model EL-USB-CO) was placed in each drum. The accuracy of the sensors was verified by calibration with commercial gas mixtures and a Thermo 146i gas calibrator coupled to a Thermo 110 zero air supply. These CO sensors have a maximum reading of 1000 ppm. The relative standard deviations (RSDs) of the results were 2.5−3.5%. Emissions from the wood pellets obtained from the O_3-exposed wood fiber in the industrial trial were measured in the same manner.

The VOCs produced inside the collection drum as a result of the ozonolysis reactions were analyzed by gas chromatography/mass spectrometry (GC/MS). VOC samples were collected using a 10 mL gastight syringe connected via plastic tubing to a quick release fitting in the top of the drum. Samples were analyzed by injecting 3 μL of sample into a GC/MS system (Thermo Electron TRACE GC with DSQ quadrupole MS and capillary column of 30 m × 0.25 mm × 0.25 μm, Restek, Bellefonte, PA, U.S.A.). Compounds were identified by comparing their mass spectra to the National Institute of Standards and Technology (NIST) MS library. Vapor samples from standards (e.g., hexanal) were analyzed to provide confirmation of the qualitative analyses. Repeatability was confirmed with triplicate analyses of each sample. The RSD of the repeatability was in the range of 2.2−2.5%. To check the quality of the analysis, toluene-d_8 solution in methanol, analytical standard (Sigma-Aldrich, St. Louis, MO, U.S.A.), was used as an internal standard, which was prepared as a vapor by injecting the required amount into a Tedlar bag. The RSD of the results for the internal standard was in the range of 1.5−2.8%.

Pellet quality parameters (lignin, moisture, ash, and gross calorific contents) were determined on both the wood fiber and wood pellets before and after the ozone exposure to ensure that exposure of ozone does not affect the fuel functionality. Thermogravimetric analysis (TGA) is the standard method for determining the major wood components: hemicellulose, cellulose, and lignin.[25−27] TGA was performed using Pyris 1 TGA (PerkinElmer, Waltham, MA, U.S.A.). To mitigate the difference of heat and mass transfer, the sample weight was kept at ∼15 mg. Samples were heated from 25 to 800 °C at a constant heating rate of 10 °C/min and maintained at this temperature

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for 3 min. Purified nitrogen (99.9995%) at a flow rate of 120 mL/min was used as carrier gas to provide an inert atmosphere and to remove the gaseous and condensable products, thus minimizing any secondary vapor-phase interactions. Duplicate samples were analyzed to check the quality of the data.

The moisture content in wood pellets was determined using ASTM E871-82, where about 5 g of sample was heated in an oven at 102 ± 2 °C for 16 h. Three replicates were analyzed for each sample. For the ash determination, the wood pellets were ground in a porcelain mortar. At least 2 g of the ground sample was ashed in a porcelain crucible for 2 h at 580 °C using a muffle furnace according to ASTM D1102-84. Three replicates were analyzed for each sample.

The gross calorific value was determined according to ASTM E711-87. About 1 g of sample was combusted in an oxygen bomb calorimeter. Three replicates were analyzed for each sample.

RESULTS AND DISCUSSION

Continuous Ozonolysis. Wood fiber was continuously exposed to ozone in the auger. The experiment was repeated at different ozone concentrations and different exposure times (7 and 3.5 min), i.e., the time required for moving the wood fiber from the hopper to the collector. After ozone exposure, the concentration of CO emitted from the fiber was monitored in the drum experiments. Figure 2 shows the variation of the CO

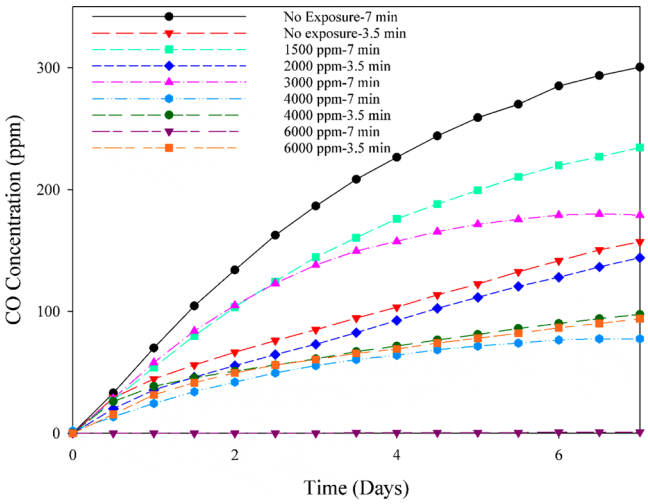

Figure 2. CO off-gas emission of wood fiber exposed at different ozone concentrations in a continuous process.

off-gassing concentration as a function of time for the various ozone concentrations and exposure times. During the first set of experiments with the 7 min residence time (Figure 2), the flow of air containing 6000 ppm ozone yielded processed fiber that produced no CO in the subsequent drum experiment, implying that reactive hydrocarbon compounds in fiber had been passivated. After the ozone exposure, the remaining olefinic compounds were sufficiently low in concentration that they could not initiate CO production following the proposed mechanistic pathways.[24] The second set of experiments (Figure 2) was conducted with the modified auger that carried the fiber in 3.5 min (residence time of fiber in the auger). At the same ozone concentration (6000 ppm), some CO was produced from the exposed fiber, indicating that the lower exposure was not sufficient to fully passivate all of the reactive hydrocarbon content. Therefore, the extent of the reaction of ozone with the reactive hydrocarbons depends upon the total exposure given by the concentration of ozone times the duration of the reaction per unit mass of fiber. Exposures of 2000 and 4000 ppm ozone were insufficient to fully passivate the fiber for both 7 and 3.5 min exposure time.

Because 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 parts per million minutes (Figure 3).

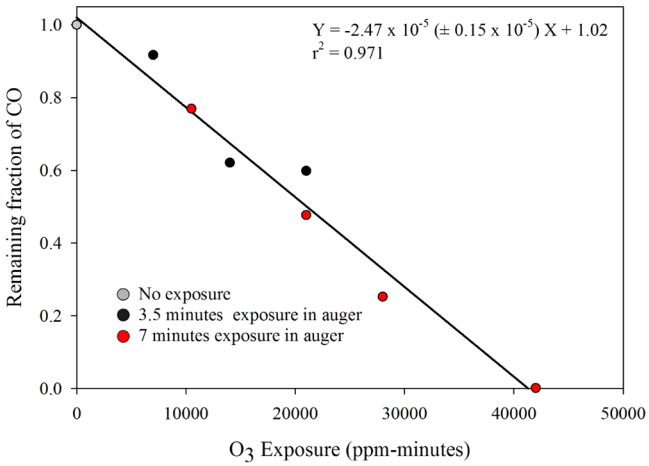

Figure 3. Fractional reduction in the maximum CO produced by the fiber following exposure to O_3.

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 min at a flow rate of 0.57 kg/min of fiber or approximately 0.032 g of O_3/kg of fiber to be passivated.

During the continuous exposure of the fiber to ozone, the vapors produced inside the collection drum from the ozonolysis reactions were collected and analyzed by GC/MS. Figure 4a shows the VOCs produced by the ozonation of the wood fiber. Nonanal and decanal were observed. Thornberry and Abbatt[28] found nonanal as a gas-phase product of the reaction of ozone with oleic, linoleic, and linolenic acids, thus, the ozonolysis of fatty acids in this continuous process. The VOCs produced by the wood fiber without O_3 exposure are presented in Figure 4b. There are a number of VOCs observed in off-gas collected from fiber stored in a sealed drum (3 days). The important VOCs are hexanal, octanal, limonene, α-pinene, β-pinene, 3-carene, etc. The number of VOCs produced with unexposed fibers is higher compared to that with exposed fiber. The differences indicate the removal of compounds by reaction with ozone as well as the difference in sampling times (i.e., 3 days for unexposed fiber and 5−10 min for exposed fibers).

TGA of Exposed Wood Fiber. There was a concern that the exposure of the wood fiber to high concentrations of ozone might oxidize the lignin, which is a natural binder necessary to bind the pellet in the hot press process. Alternatively, it may destroy part of the hemicellulose, resulting in a decrease in the calorific content of the wood.[29] To explore the changes in the wood fiber as a result of ozone exposure, TGA was performed on both unexposed and exposed wood fiber and the thermograms are shown in Figure 5. The thermogram from exposed wood fiber (right panel of Figure 5) is similar to the unexposed fiber thermogram (left panel of Figure 5). The temperature scale is shifted upward, and there may be some

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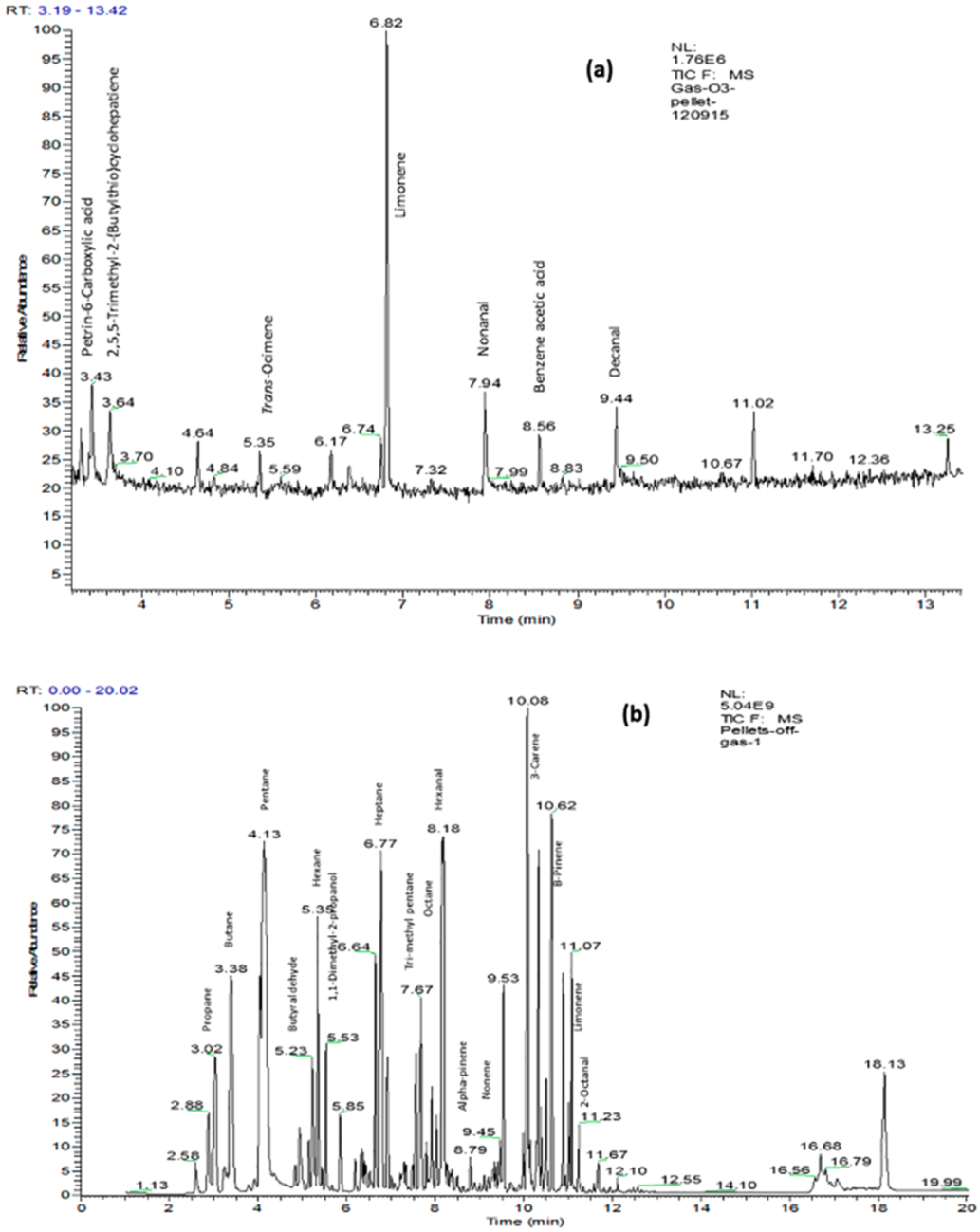

Figure 4. VOCs produced during the (a) ozonolysis process and (b) normal off-gassing process.

degradation of hemicellulose. However, it appears that the ozonolysis reaction does not significantly affect the lignin and hemicellulose contents. Thus, it is expected that the pellets produced from the ozonized fiber will bind to produce pellets similarly to those produced from unexposed fiber.

Industrial Trials. The laboratory-scale tests showed that ozone can effectively passivate the unsaturated hydrocarbons in wood fiber in a continuous process. Thus, the industrial-scale viability of this process needed to be established, and trial experiments were conducted in a pellet mill with a production capacity of 100 000 tons of pellets per year. Two ozone generators with a production rate of 2.8 g/h (Queenaire, Ogdensburg, NY, U.S.A.) and 2.2 g/h (Ozonology, Inc.) were used to continuously supply ozone with flow rates of 12 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 augered from these hoppers to the presses to produce the pellets. In this mill, up to 5 presses can be operating simultaneously. However, in the trials, only three presses were in operation. The hot pellets are carried by a belt to a cooling system and then pneumatically transferred to a storage hopper that feeds the bagging system or can provide bulk pellets to a delivery truck.

Three trials were performed, 45 min (trial I), 60 min (trial II), and 120 min (trial III), to try to attain steady-state operation before collecting samples with just the ozone feed to the main inlet auger (Figure 6). The results of the industrial trials are presented in Table 1. The unexposed pellets produced

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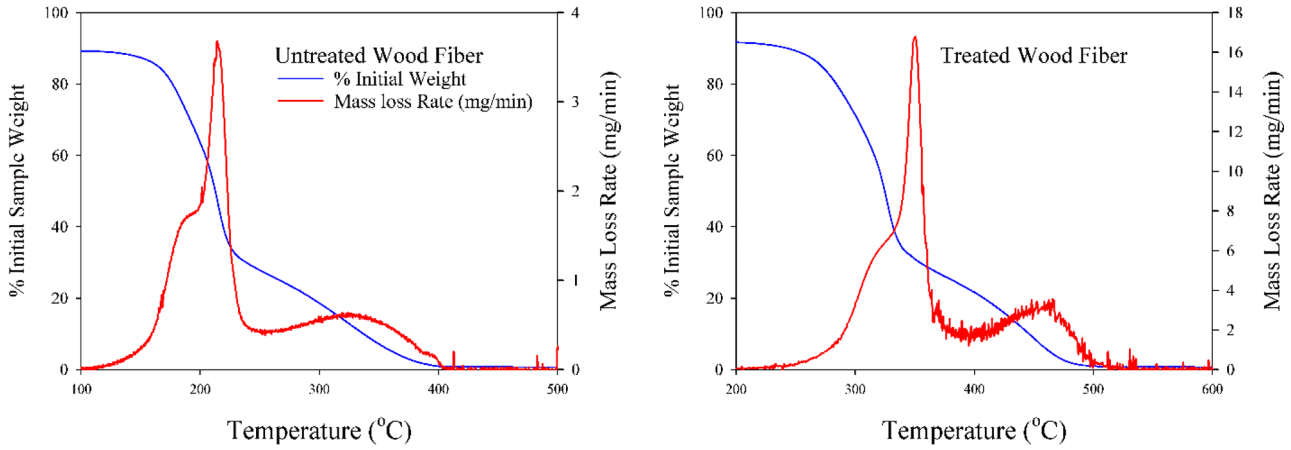

Figure 5. (Left) TGA of wood fiber without O_3 exposure and (right) TGA of O_3 exposed (6000 ppm, 7.0 min) wood fiber.

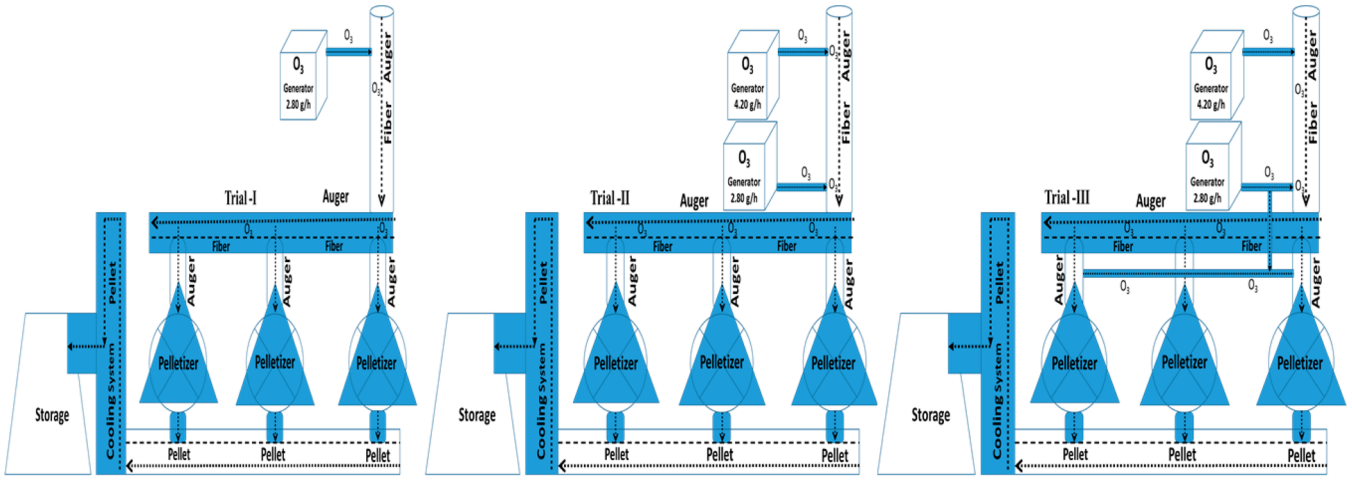

Figure 6. Schematic representation of the areas in the operation where the ozone−fiber reactions occurred (from left to right, trials I, II, and III).

Table 1. Maximum CO Off-Gassing by 9.00 kg of Pellets/10 Days from Industrial Trials (n = 3)

pellet sample (softwood)	concentration of O_3 used for exposure (g/h)	mass of fiber flow rate (kg/min)	average O_3 flow rate (L/min)	equilibrium time of O_3 exposure on fiber (min)	size of the fiber used for pellet production (mm)	moisture content in fiber (%)	maximum average CO (ppm)	standard deviation
unexposed	0.00	182.00			2.00−3.00	10−12	360.50	29.15
O_3 exposed (trial I)	2.80 (Queenaire)	182.00	12.00 (Queenaire)	45.00	2.00−3.00	10−12	130.83	48.41
O_3 exposed (trial II)	2.80 (Queenaire) 4.20 (Ozonology)	182.00	12.00 (Queenaire) 2.36 (Ozonology)	60.00	2.00−3.00	10−12	0.00	0.00
O_3 exposed (trial III)	2.80 (Queenaire) 4.20 (Ozonology)	182.00	12.00 (Queenaire) 2.36 (Ozonology)	120.00	2.00−3.00	10−12	19.66	8.41

a maximum CO concentration of 361 ppm. In trial I, 131 ppm of CO was observed with the pellets produced by exposure to 2.80 g/h ozone. This result indicates that the ozone exposure reduced the CO formation potential but was insufficient to fully passivate all of 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/h). The resulting pellets produced in trial II showed no measured CO. Finally, trial III was conducted to determine if injecting ozone with multiple connection points into the auger and the press feed hoppers (right panel of Figure 6) and an extended exposure time (120 min) would also eliminate CO production. However, a maximum of 19.66 ppm of CO was observed in this trial. Thus, distributing ozone into multiple points into the process actually reduced the overall exposures because there was less time for the fiber to react with ozone compared to when ozone was injected further upstream in the process.

Thus, the simpler system of a single injection point produced pellets that did not off-gas CO. Given the flow rate of fiber, it was possible to passivate fiber with only 0.000 64 g of O_3/kg of fiber, which is 50 times lower, compared to laboratory experiments (0.032 g/kg of fiber). This difference can be attributed to several possible causes. In the industrial trials, the fiber experienced much longer reaction times (60 min)

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Table 2. Properties of the Wood Pellet Samples Produced in the Trial Experiment[a]

sample	moisture (%)	standard deviation	ash (%)	standard deviation	calorific value (MJ/kg)	standard deviation
unexposed	3.83	0.05	0.71	0.01	18.91	0.22
sample 1	3.61	0.07	0.62	0.01	18.91	0.21
sample 2	3.73	0.09	0.70	0.08	19.26	0.32
sample 3	3.97	0.02	0.77	0.02	18.91	0.18

[a]Samples were analyzed in triplicate.

compared to laboratory experiments (7 min). 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 40−50 min. When 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.

Physical Quality Parameter of Wood Pellets Produced by Industrial Trial. Another critical aspect of the study is the characterization of the pellets produced in the industrial-scale trial to ensure that exposure of ozone does not reduce their functionality as a fuel. Thus, pellets from the trial experiments were characterized. The moisture, ash, and gross calorific values were analyzed. The results are shown in Table 2. The data passes tests for normal distributions and equal variance; therefore, a one-way analysis of variance (ANOVA) was performed for each measured parameter to compare the properties of pellets produced from unexposed and exposed fibers. Results show significant differences for ash and moisture ($p < 0.05$) but not for the calorific value ($p = 0.271$). 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. These results further support the viability of the reactive hydrocarbon removal by the continuous ozone treatment.

CONCLUSION

In this work, the reaction kinetics were measured for the passivation of reactive hydrocarbons in wood fiber in a continuous auger. The continuous ozonolysis reaction was observed to follow pseudo-first-order reaction kinetics. In the laboratory experiments, CO production was eliminated with a dose of approximately 0.032 g of O_3/kg of fiber to be passivated. In the industrial-scale process, it was possible to passivate fiber with only 0.000 64 g of O_3/kg of fiber. The pellets produced in the industrial trial showed that their fuel properties were not different from ordinary pellets. Thus, ozonolysis of wood fiber can be used to commercially produce low-CO or essentially CO-free pellets.

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Notes

The authors declare no competing financial interest.

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