Elimination of CO Off-gassing in Stored Wood Pellets

Monday, June 4, 2018
2:30 PM ET
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Agenda:

1. Welcome and Introduction
2. Overview of BTEC & AGH – Peter Thompson & John Ackerly
3. Elimination of CO Off-gassing from Stored Wood Pellets – Dr. Philip Hopke
4. Industry Perspective and Involvement – Kelli Ramsey
5. Q&A – Moderated by John Ackerly
The national trade association for the modern wood heating industry.  
• Engage in technical codes and standards development, public advocacy, and education.  

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Communication Operations, Membership
✓ 501c3 nonprofit
✓ Promotes clean & efficient biomass heaters
✓ National voice for wood heat consumers
✓ Hosts design competitions
✓ Encourages transparency from manufacturers and regulators
• 4\textsuperscript{th} Wood Stove Design Challenge
  • November 9-14, 2018
  • National Mall in Washington DC
• Two Competition Categories:
  • Automated stoves
  • Thermoelectric stoves
Thank you!

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(for thermoelectric issues)

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In support of the Alliance for Green Heat’s 4th Wood Stove Competition in November 2018
Elimination of CO Off-gassing from Stored Wood Pellets Webinar

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THANKS TO

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• New York State Energy Research and Development Authority (NYSERDA) for the financial support of this work
Biomass Heating in the Northeastern U.S

• >80% of the No. 2 oil burned for space heating in the US is burned in NYS and northern NE representing $6 billion dollars leaving the region.

• Substantial sustainable forest resources particularly that which has been left by the decline of the pulp and paper industry.

• 3 x more wood growth than harvested in this region.

• It is possible to have sustainable harvesting of wood.
In 2008, New York State Energy Research and Development Authority (NYSERDA) initiated projects to demonstrate commercial scale European-built or designed pellet boilers.

- High fuel costs for locations off natural gas pipe lines
- Declining budgets for many public entities (schools, hospitals, museums, nursing homes)
- Efforts to develop wood as a fuel by companies like Curran Renewable Energy in Massena, NY

A number of wood pellet boilers were installed in schools and museums in the North Country with NYSERDA support.
Problem Identification

• In August 2012, NYSERDA personnel became aware of a paper reporting incidents in Europe of people going into very large pellet storage bins, encountering CO concentrations of 6500 to 15,000 ppm CO, and dying.
Motivation

Review

Lethal Carbon Monoxide Poisoning in Wood Pellet Storerooms—Two Cases and a Review of the Literature

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Pellet Off-Gassing

• Actually the literature is more extensive, but had not come to anyone’s attention.
Motivation

- High levels of hexanal and carbon monoxide were strongly associated with storage of wood pellets and may constitute an occupational and domestic health hazard.
Motivation

• The results from lumber drying show that the emissions of hexanal and carbon monoxide are not limited to wood pellets but are caused by general degradation processes of wood, facilitated by drying at elevated temperature.

• They postulated that carbon monoxide is formed due to autooxidative degradation of fats and fatty acids.
Motivation

• Subsequently, Svedberg et al. (Ann. Occup. Hyg. 52, 259–266, 2008) reported the study of 5 ocean-going vessels shipping pellets from Canada to Sweden.

• The study was initiated after a fatal accident with several injured during off-loading of the pellets in Sweden.

• Carbon monoxide (CO) concentrations were found to range from 1460–14650 ppm
Motivation


• All victims had entered inadequately ventilated stairways communicating with cargo holds.
Motivation

• Since 2002, there have been 14 reported death related to CO-poisoning related to wood pellets.

• Since we generally store the pellets in occupied structures, there is then a high potential for exposure to susceptible individuals.

• NYSERDA wanted to know if there were unsafe concentrations of CO in in-use pellet bins that had been installed as part of their demonstration projects with one installation of a bin being under three middle school classrooms.
Monitoring Sites

- We have data from
  - A residential basement in Massena
  - Three locations in the Malone Middle School
  - The Saranac Lake Elementary School
  - Energy Cabin at Clarkson University
  - Walker Center at Clarkson University
  - Wild Center in Tupper Lake
Massena Residence Basement
8-hr rolling average

CO (ppm)

Date
Mar  May  Jul  Sep  Nov  Jan  Mar  May

NIOSH-OSHA

ASHRAE

Date
Aug 06  Aug 10  Aug 14  Aug 18  Aug 22

VENTILATION
Residential Concentrations

• It can be seen that there were a number of values that exceeded the ASHRAE guidance level of 9 ppm averaged over 8 hours. This guidance is the same as set as a National Ambient Air Quality Standard (NAAQS) for CO.

• Although the concentrations do not represent an acute threat to health, the elevated levels do represent an unwarranted health hazard to susceptible individuals.
Occupational Settings

• The NIOSH guidance level is 35 ppm for exposures averaged over 8 hours.

• The OSHA regulatory level is 50 ppm for exposures averaged over 8 hours.

• If there are exceedances of these levels, then the space becomes a “confined” space and requires the development of a “confined space” policy and a permitting procedure.
In-Bin Measurements

Bagged Pellets

- All of these studies have been of bulk pellets.
- Most people in the US buy 18 kg (40 lbs) of pellets, typically 1 to 3 tons at a time and store them in their basement or garage.
- In order to be able to stack the bags of pellets on wooden pallets for easy shipment, the bags are perforated so the air can be squeezed out as one bag is stacked on another.
Thus, do bagged pellets off-gas sufficient CO and carbonyls to be a problem?

Yes, See:
Rahman et al., Annals of Work Exposures and Health, 62:2, 248–252, 2018 for the CO results

Bagged Pellets

Graph A: CO Concentration (ppm) over dates from 04/25 to 07/18, with OSHA Regulatory Standard and NIOSH Guideline.

Graph B: CO Concentration (ppm) over dates from 07/25 to 10/17, with a peak at 3.66 m.

Graph C: CO Concentration (ppm) over dates from 04/25 to 07/18.

Graph D: CO Concentration (ppm) over dates from 07/25 to 10/17, with a peak at 1.52 m.
Figure 6. Concentrations of different aldehydes measure at multiple locations in the warehouse.
Lab Studies

• To better understand what we were seeing in the in-use storage bins, we conducted a series of laboratory studies.
Wood Pellet Storage Simulation

Figure 4 A schematic diagram for CO outgassing container
**CO concentrations**

- Off-gassing emission rates were fast during the first few days.
- Off-gassing emissions slowed down after and CO concentrations plateaued.

NAAQs 1-hr exposure limit
Bagged Pellets

• If we put 2 18 kg bags of pellets into a larger drum (55 gallon)
If we put 2 18 kg bags of pellets into a larger drum (55 gallon), CO concentrations in the drum with bagged hardwood pellets as a function of temperature at a constant RH of 30%.
Clearly Pellets Off-Gas CO

- The big question is

WHY?
Clearly Pellets Off-Gas CO

- What in wood would oxidize at room temperature and normal atmospheric oxygen concentrations to produce significant CO?
- Kuang et al. and Fan and Bi suggest it is auto-oxidation of fatty acids in the wood.
- This process causes food to go rancid.
- We had been developing methods for fatty acid analysis as part of our Great Lakes Fish Monitoring and Surveillance Program work.
What Causes Pellets To Off-Gas CO

• We do see some aldehydes emitted by pellets that suggest the presence of fatty acids in the wood, BUT

• Doing the analyses shows that fatty acid oxidation cannot account for more than 3 to 8% of the mass of emitted CO.

• Wood is cellulose, hemicellulose, and lignins typically determined using thermogravimetric analysis (TGA).
What Causes Pellets To Off-Gas CO

![Graph showing the TGA thermogram of biomass from reference willow clone S. dasyclados 'SV1.' Arrow indicates cutoff line for water loss correction (129 °C). Block A: weight loss representative of hemicellulose (245-290 °C). Block B: weight loss representative of cellulose (290-350 °C). Block C: weight loss representative of lignin (350-525 °C).]
What Causes Pellets To Off-Gas CO

• So, we did TGA analyses of fresh and aged softwood pellets.
What Causes Pellets To Off-Gas CO

![Graph showing d(Mass)/dT vs. Temperature (°C) for aged pellets. The graph exhibits a peak at a certain temperature indicating the off-gassing of CO.](chart.png)
What Causes Pellets To Off-Gas CO

![Graph showing the difference in d(Mass)/dT for Fresh Pellets and Aged Pellets vs. Temperature (°C).]
Thus, it appears that it is the hemicellulose that is disappearing as the CO appears and there is certainly sufficient mass to explain the observed concentrations.

However, hemicellulose is not going to react with oxygen at room temperature. There has to be a stronger oxidizer.
Hypothesis

• That is nice, but where does the hydroxyl radical come from?
• Now we do need to remember that we saw hexanal and other carbonyls in the emitted VOCs suggesting autoxidation of fatty acids (and terpenes in they are present such as in softwood pellets).
• Thus, from the mechanism for autooxidation of fatty acids, there is a pathway that produces a strong oxidant, hydroxyl radicals.
Testing the hypothesis

• If it is the autoxidation of the fatty acids that gives rise to OH, we can test if OH is important by adding a chemical to deactivate the free radical. Alcohols do this.

\[ RHCOH + \bullet OH \rightarrow RHCO\bullet + H_2O \]

• The resulting radical is a much weaker oxidizer and thus, we should see the reaction stop
Testing the hypothesis
Is it the unsaturated compounds?

• Is it really a two-stage process where there is autoxidation of the fatty acids (and other reactive olefins) that produces OH and then oxidizes the hemicellulose?

• If so, we can eliminate these compounds by reacting them with ozone.

• First we tried exposing pellets overnight to high ozone concentrations
Is it the unsaturated compounds?

CO monitoring with Ozone and tert-butanol exposed pellets

- Without ozone exposure
- Ozone exposed (Overnight)
- Ozone exposed/tert-Butanol

![Graph showing CO levels over time with different conditions]
Is it the unsaturated compounds?

• This is nice since we reduced the maximum CO by about 80%, BUT why not by 100%

• Pellets are densified sawdust and porous, but the ozone probably could not penetrate very deeply and there is then the opportunity for the fatty acids in the bulk of the pellet to oxidize, out-gas and that material diffuse to the surface and be released.

• We need to have more surface area to passivate with ozone.
Is it the unsaturated compounds?

• Luckily we have a cooperative pellet mill in Massena where we could go and collect the ground wood fiber just before it goes into the press.

• This material was then exposed to high ozone overnight
Is it the unsaturated compounds?
Thus, we believe we have the answer to where the CO derives for the room temperature production.

These results also suggest a way to make a CO-free or Low-CO pellet.

We react the fiber with ozone as it moves to the pellet press.
Creating a Process

• We need to obtain the kinetics of the ozonation under realistic conditions.
• We have acquired an auger and modified it so we can add ozone
• We can adjust the ozone concentrations and determine the time-concentration product necessary to reduce/eliminate CO production
Creating a Process
CO Offgassing after O$_3$ Exposure

O$_3$ exposure time: 7 min, Flow rate: 1L/min, Length of the Auger: 6 feet, Mass of wood fiber: 57 g/min
CO Offgassing after O₃ Exposure

\[ Y = -2.47 \times 10^{-5} (\pm 0.15 \times 10^{-5}) X + 1.02 \]

\[ r^2 = 0.971 \]
Modification of the Wood

TGA of O₃ exposed (6000 ppm) wood fiber (No CO off-gassed by the fiber)
Final Test

- Our final challenge was to modify the auger at an actual pellet mill, inject ozone, and determine if we are making low or no CO pellets.
- This process should be easy to implement and relatively low cost. Low cost is essential since the pellet market is currently depressed due to the low prices of fossil fuels.
Full Scale Tests
Full Scale Tests

Graph showing CO (ppm) levels over time (min) for No Exposure, Sample 1, Sample 2, and Sample 3.
What now?

• The mill in Massena is currently installing the ozone generator to be used routinely in making their pellets. The cost will be less than $10,000.

• NYSERDA is likely to help convert all of the NYS mills to utilizing the process

• Thus, we CAN eliminate the potential for occupational and environmental exposures from stored wood pellets.
Kelli Ramsey

In support of the Alliance for Green Heat’s 4th Wood Stove Competition in November 2018
Elimination of CO Off-Gassing from Stored Wood Pellets

Kelli Curran Ramsey, Marketing Manager
Curran Renewable Energy
Massena, NY
Our Involvement

- Clarkson University of Potsdam, NY with Queenaire Technologies of Ogdensburg, NY and NYSERDA asked Curran Renewable Energy to be their location site for live testing.

- It had been brought to our attention that the storage of wood pellets could be a safety concern.
Why We Are Participating

- As a pellet manufacturer, we face unpredictable weather patterns, volatile oil prices and fluctuating exchange rates...all which affect market conditions in selling wood pellets.

- There has been concern with the carbon off-gassing of ag products like grain and wood pellets where people have been sick or even died.

- If there is a method to make the consumer safe and more confident in using and storing wood pellets, we feel it is essential to protect the consumer and take the steps to alleviate one more possible hurdle in this industry.
Testing

- Bulk wood pellets were tested at Curran residence where there is currently a 9 ton fabric bin/boiler set-up.
- Bagged wood pellets were tested at a CRE warehouse
- The lab scale models were successful in introducing ozone and eliminating the off-gassing of CO as well as a test during production at CRE last fall.
- A full scale commercial system is currently installed and being monitored at Curran Renewable Energy.
Bulk Pellet Storage Testing Site

Curran residence garage basement
Bagged Pellet Storage Site

CRE Warehouse
In photo from left to right:
-Richard Luscombe-Mills of Queenaire Technologies
-Mohammad Rahman of Clarkson University
-Stefania Squizzato
-Phil Hopke, Clarkson University and University of Rochester
Safety Precautions

- The process is eliminating the CO off of the finished product but to do so, Ozone needs to be injected into the production process.
- Proper safety measures are being taken to test ozone levels to assure the ozone is being absorbed properly into the wood fiber and excess is not being exposed to our workforce.
Ozone Monitors

AEROQUAL 500

EZ-1X
Carbon Monoxide Monitors

CO Monitors

10 Gallon Steel Drums

Temperature Monitor
The Process

- Ozone is injected into the wood before it is pelletized.
- The system is designed to shut off automatically if the pellet mill shuts down.
- Samples of pellets are taken and stored steel drums where we test to see that the ozone process has been successful.
  - Very simple to do, not labor intensive.
  - Currently testing every 10 days and it takes about 10 minutes to download the data from the USB monitors.
  - *Interesting find...the dense wood smell in the air has noticeably been removed during the process
Investment

- The investment in the technologies that make this process work are very minimal, less than $10,000.
  - Testing is simple and fast
  - Takes up minimal space
  - Easy to install
Hopes for the Industry

- It is a technology that can be easily adopted by any pellet manufacturer to help the industry as a whole increase market share.

- The outcome from the technology battles any fear regarding the safety of wood pellet storage that could affect the market.
Thank You!

Questions? Please contact me at kelli@curranpellets.com
Questions?

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