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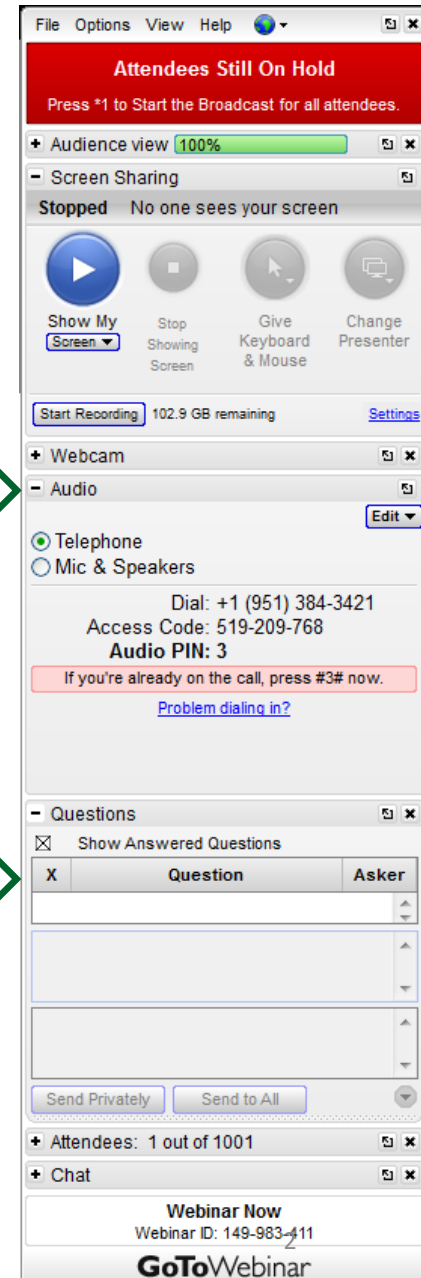


Elimination of CO Off- gassing in Stored Wood Pellets

Monday, June 4, 2018
2:30 PM ET

Quick Notes

- Two Audio Options: Streaming Audio and Dial-In.
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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.

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 - Sellers
 - Installers
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 - Universities
 - Non-profits & NGOs
 - Government agencies



For More Information:

<http://www.biomassthermal.org>

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Executive Director

Peter Thompson- pthompson@ttcorp.com

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

NEXT GENERATION Woodstove DesignChallenge

- 4th Wood Stove Design Challenge
 - November 9-14, 2018
 - National Mall in Washington DC
- Two Competition Categories:
 - Automated stoves
 - Thermoelectric stoves



Thank you!

John Ackerly – jackerly@forgreenheat.org

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(for thermoelectric issues)

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NEXT GENERATION
Woodstove
DesignChallenge



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Dr. Philip Hopke

**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

Philip K. Hopke

Department of Chemical and Biomolecular Engineering and
Institute for a Sustainable Environment, Clarkson University
and

Department of Public Health Sciences
University of Rochester School of Medicine and Dentistry

phopke@clarkson.edu

THANKS TO

- Dr. Lydia Soto-Garcia, Xinrui Huang, Alan Rossner, Mohammed Rahman, and Stefania Squizzato for doing the work being presented here,
- To Pat Curran and Curran Renewable Energy for their collaboration and donation of pellets, and
- 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.

NYSERDA Wood Pellet Boiler Projects

- In 2008, New York State Energy Research and Development Authority (NYSERDA) initialed 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

Ann. Occup. Hyg., Vol. 56, No. 7, pp. 755–763,
© The Author 2012. Published by Oxford University Press
on behalf of the British Occupational Hygiene Society
doi:10.1093/anhyg/mes047

Review

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

SASKIA GAUTHIER^{1,*}, HILDEGARD GRASS², MARTIN LORY³, THOMAS KRÄMER¹, MICHAEL THALI¹ and CHRISTINE BARTSCH¹

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Pellet Off-Gassing

- Actually the literature is more extensive, but had not come to anyone's attention.

Motivation

- Svedberg et al. (*Ann. Occup. Hyg.* 48, 339–349, 2004) investigated the emissions of volatile compounds, particularly hexanal and carbon monoxide, from large- and small-scale storage of wood pellets.
- 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 autoxidative 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

- Svedberg et al. (*Ann. Occup. Hyg.* 53, 779–787, 2009) five fatalities and several injuries in Swedish ports under similar circumstances within a 2-year period.
- All victims had entered inadequately ventilated stairways communicating with cargo holds.

Motivation

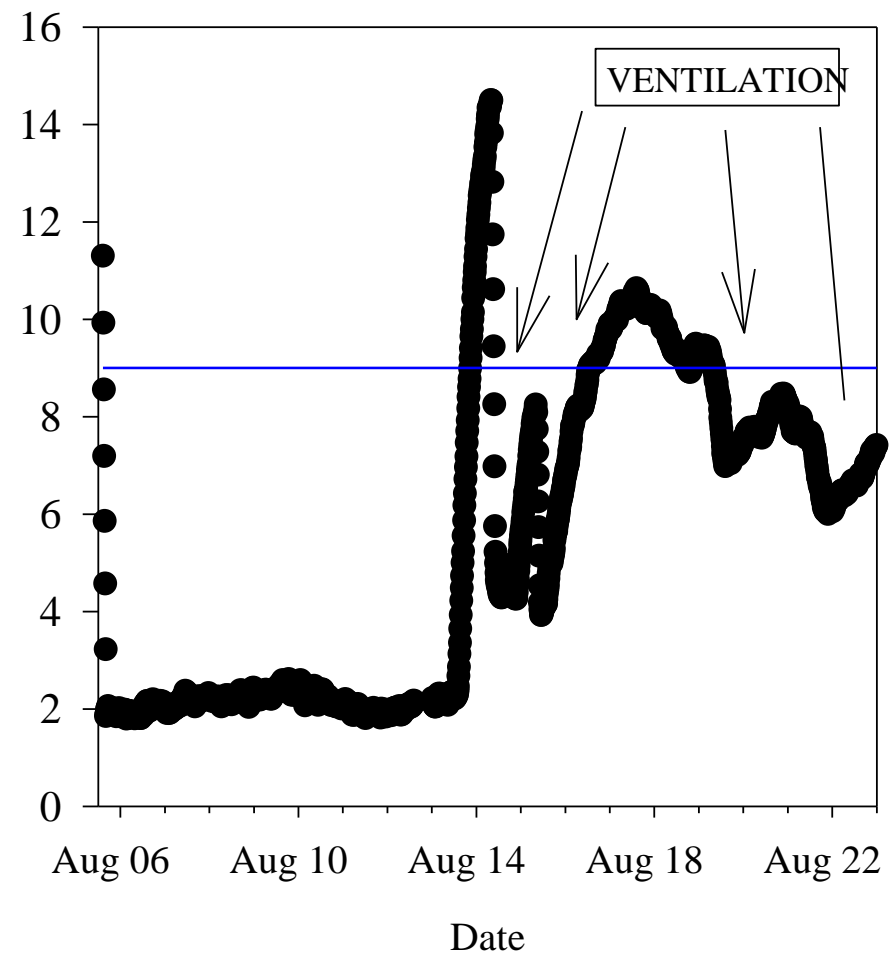
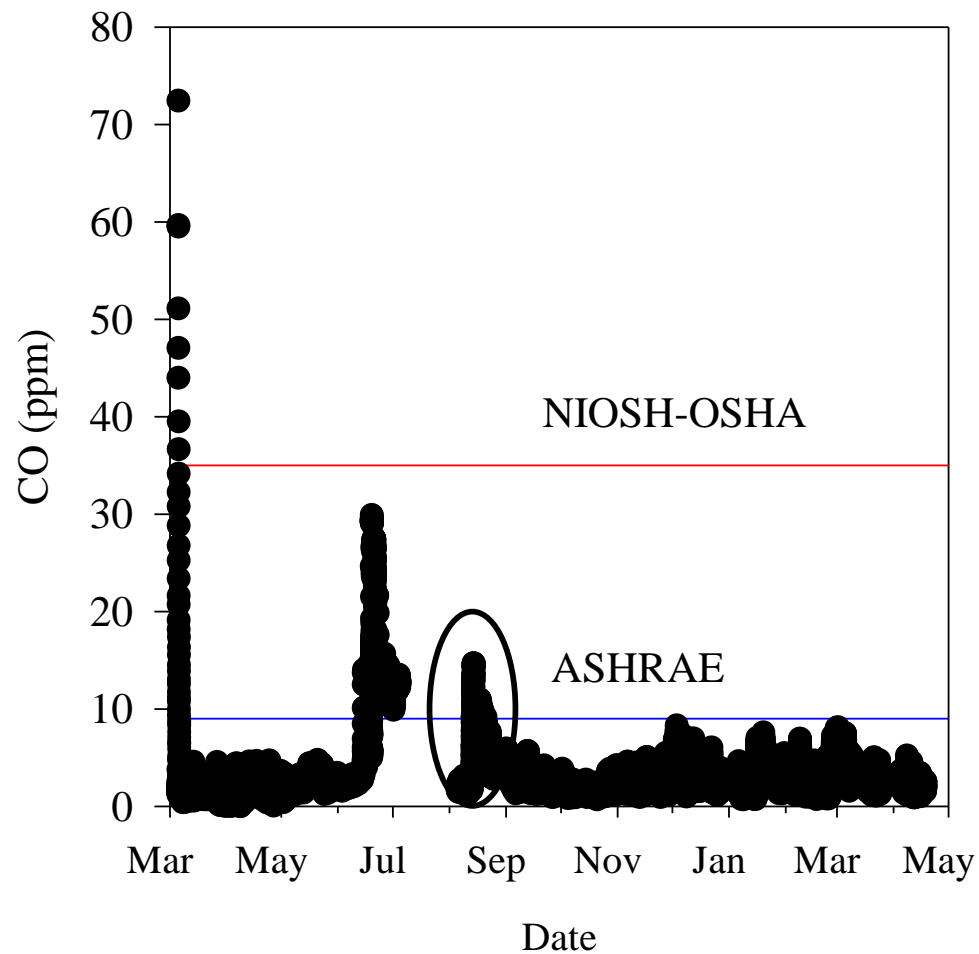
- Since 2002, there have been 14 reported death related to CO-poisoning related to wood pellets.
- Since we generally store the pellets in occupied structures, there is then a high potential for exposure to susceptible individuals.
- NYSERDA wanted to know if there were unsafe concentrations of CO in 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



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

These results have been published in
Exposures to Carbon Monoxide from Off
Gassing of Bulk Stored Wood Pellets, L. Soto-
Garcia, X. Huang, D. Thimmaiah, A. Rossner,
P.K. Hopke, *Energy & Fuels* 29: 218–226
(2015).

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.

Bagged Pellets

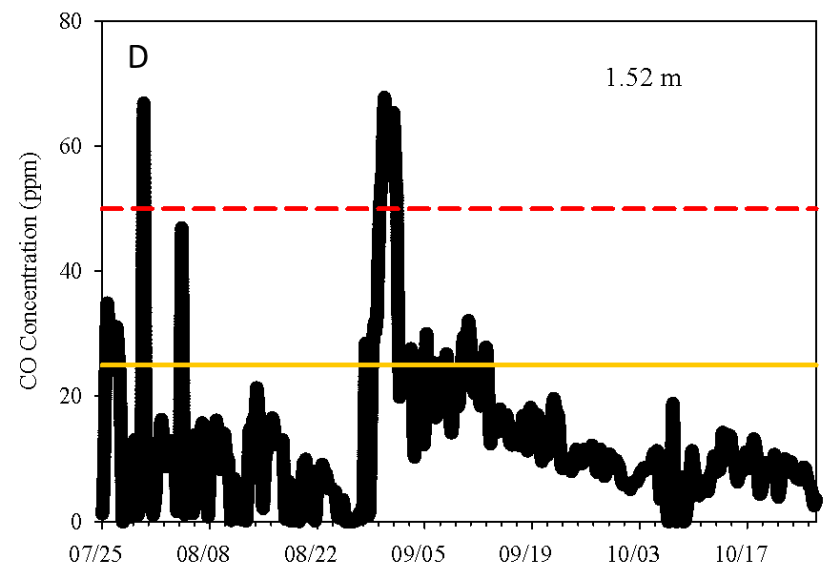
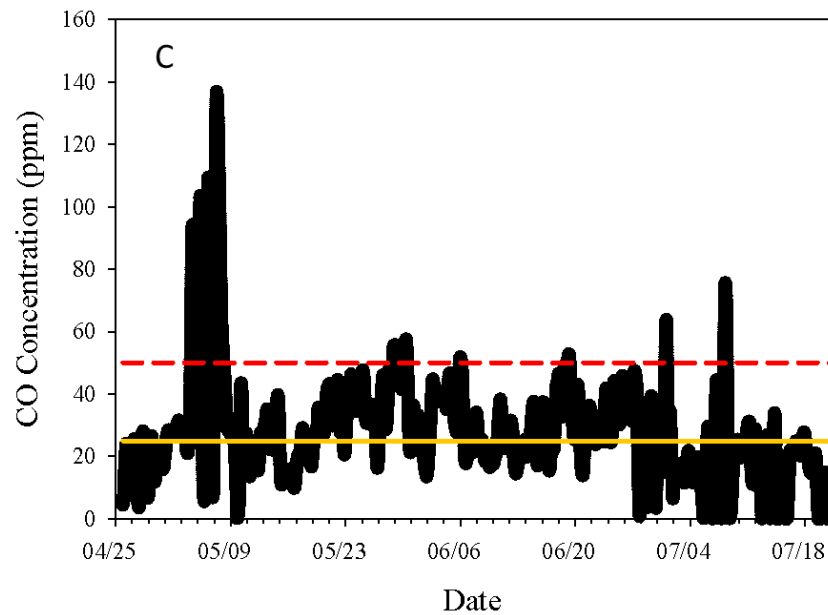
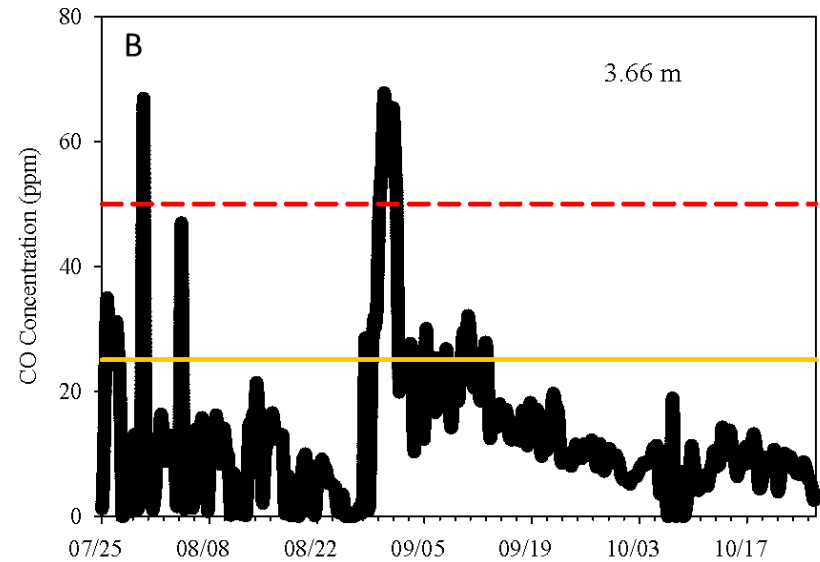
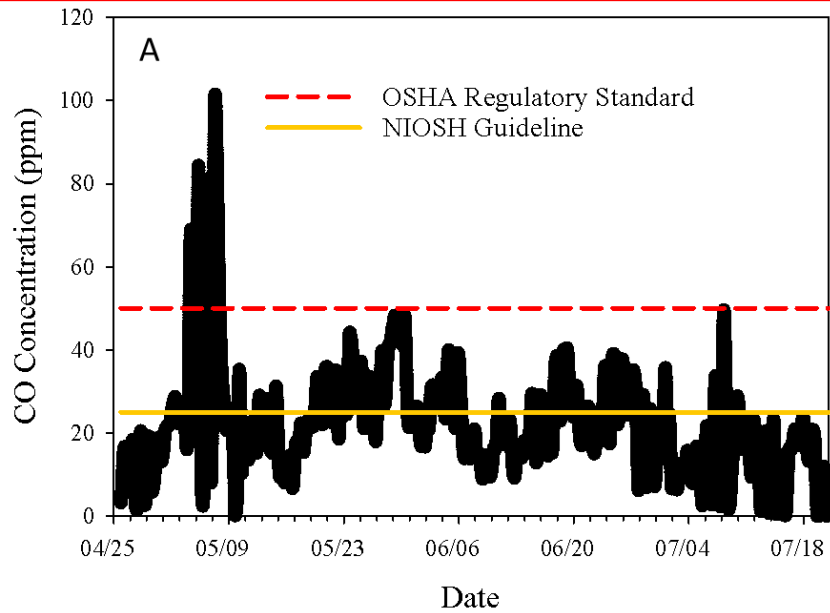
- Thus, do bagged pellets off-gas sufficient CO and carbonyls to be a problem?

Yes, See:

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

Rahman et al., Journal of Occupational and Environmental Hygiene 14:6, 417-426, 2017 for the aldehyde results.

Bagged Pellets



Bagged Pellets

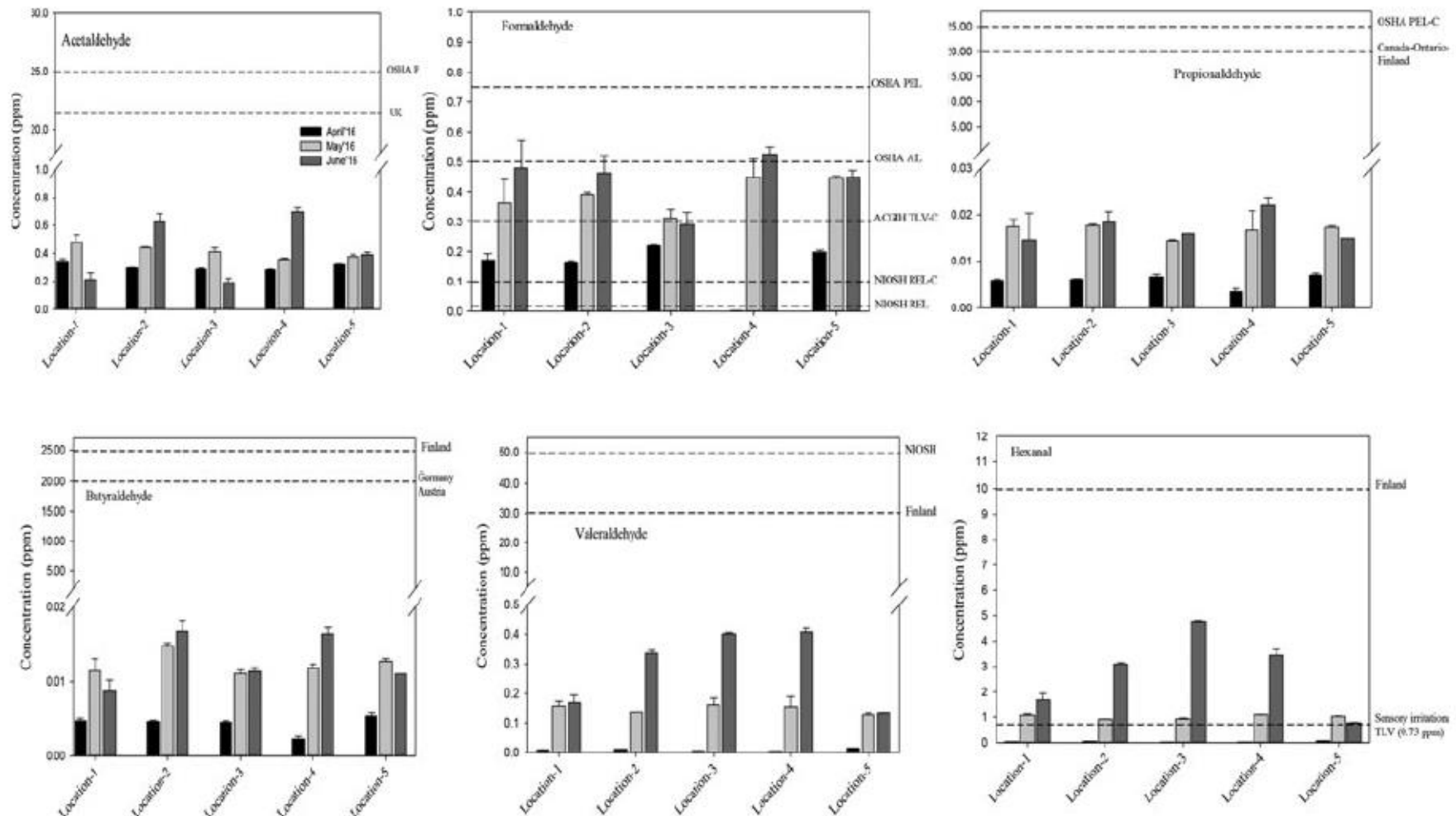


Figure 6. Concentrations of different aldehydes measure at multiple locations in the warehouse.

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

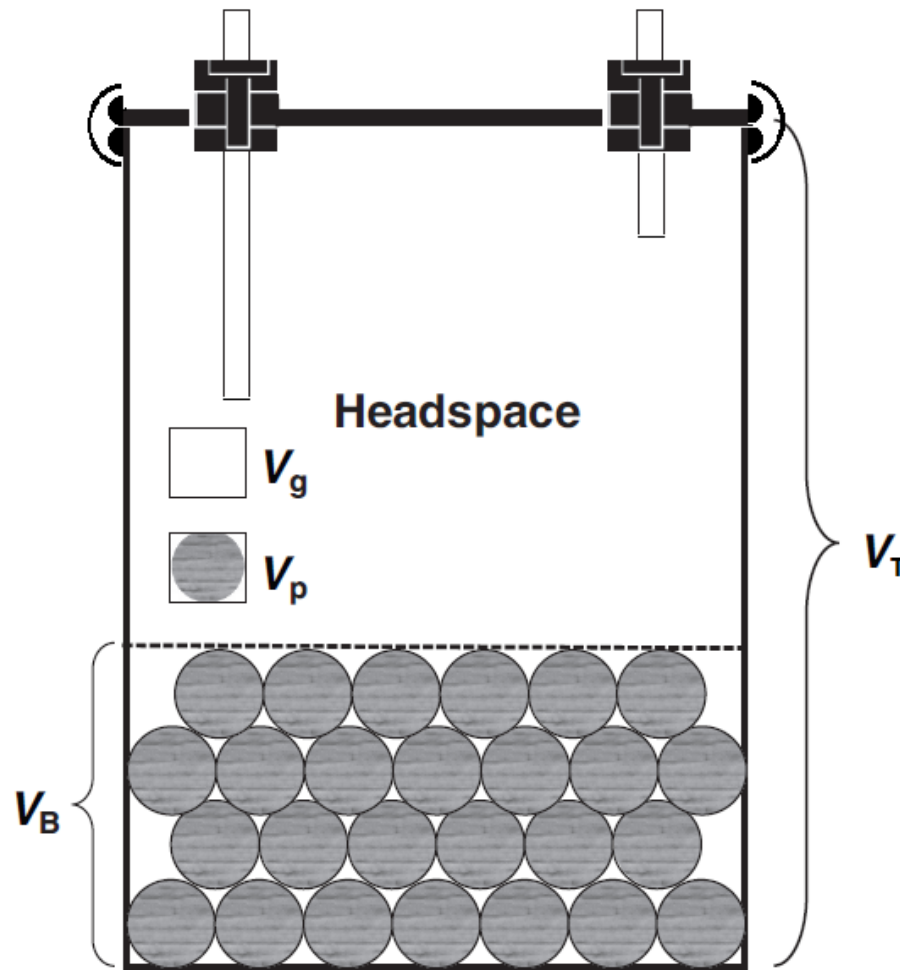
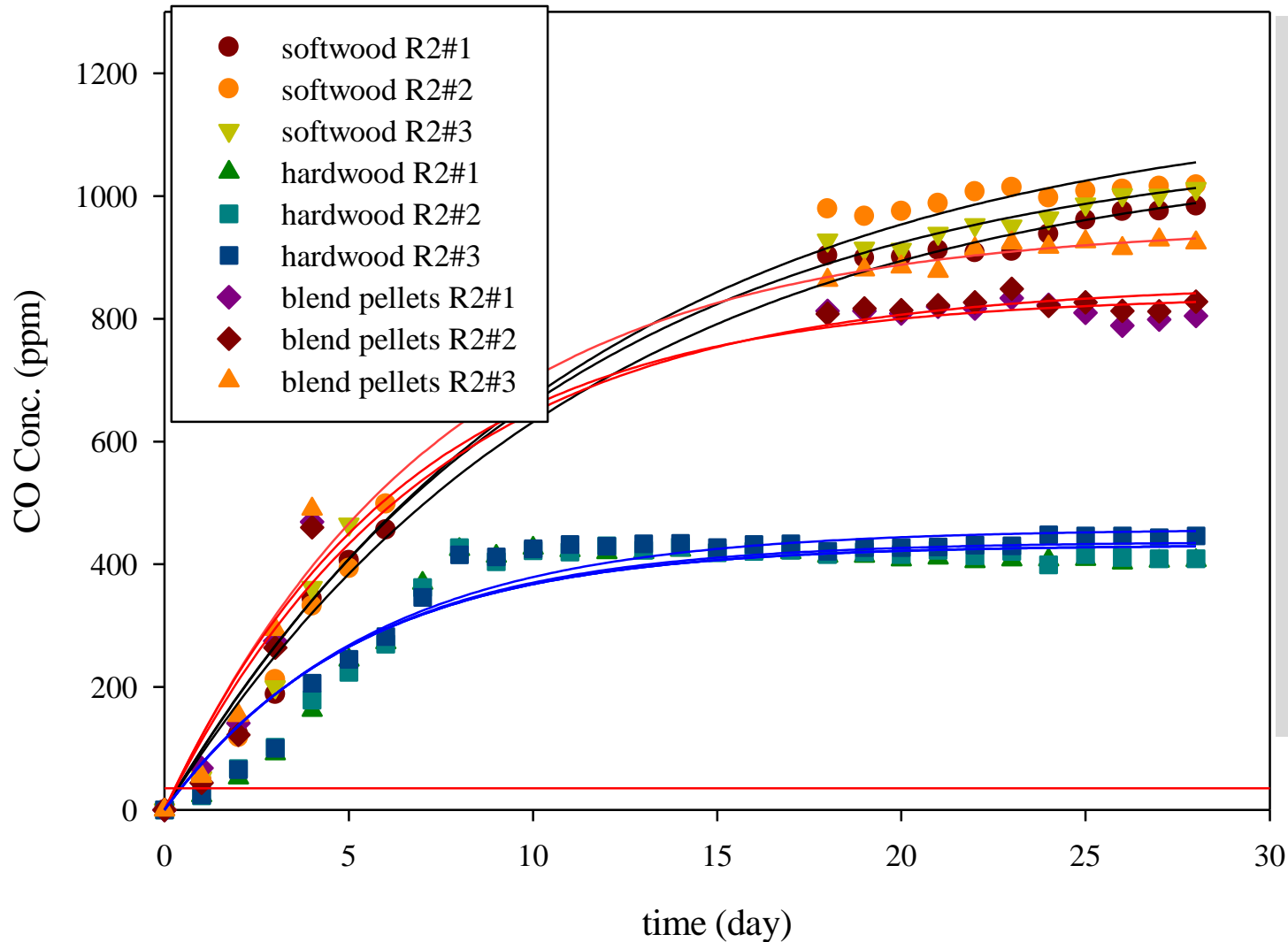


Figure 4 A schematic diagram for CO outgassing container

CO concentrations

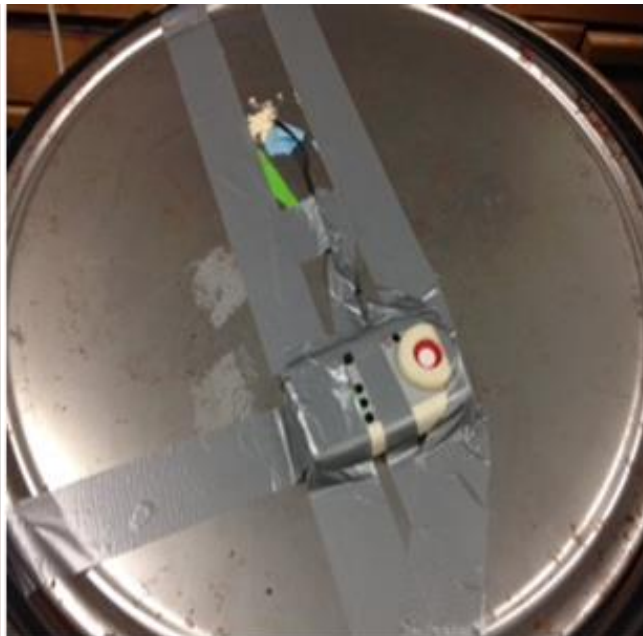


- Off-gassing emission rates were fast during the first few days
- Off-gassing emissions slowed down after and CO concentrations plateaued

NAAQS 1-hr exposure limit

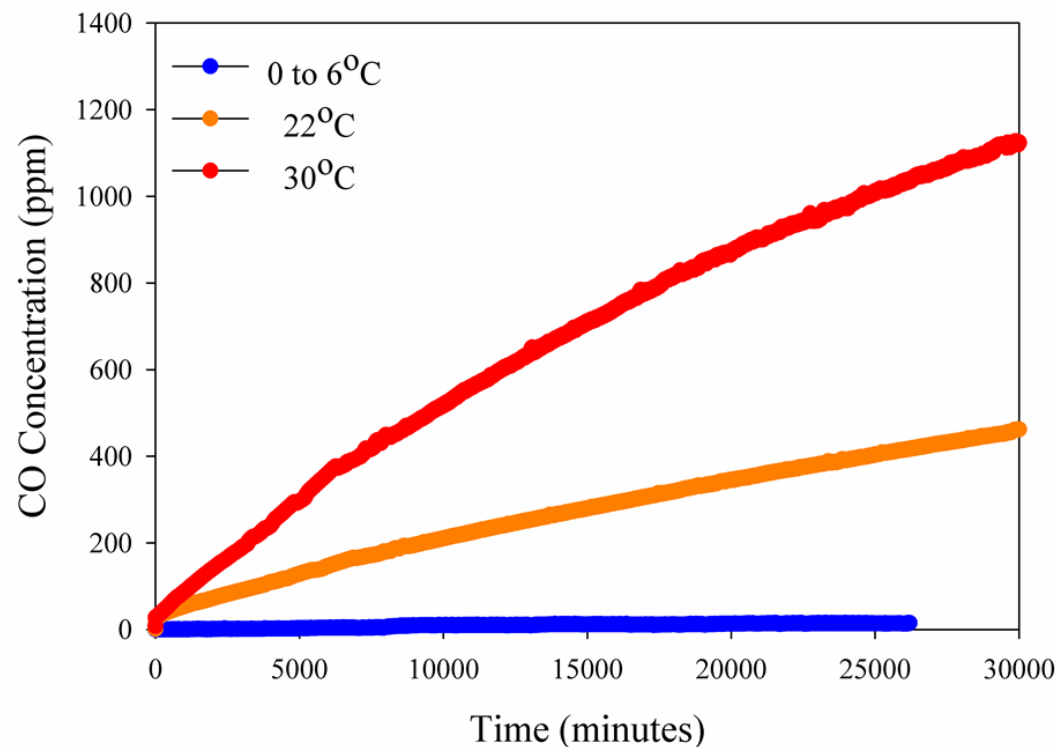
Bagged Pellets

- If we put 2 18 kg bags of pellets into a larger drum (55 gallon)



Bagged Pellets

- 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

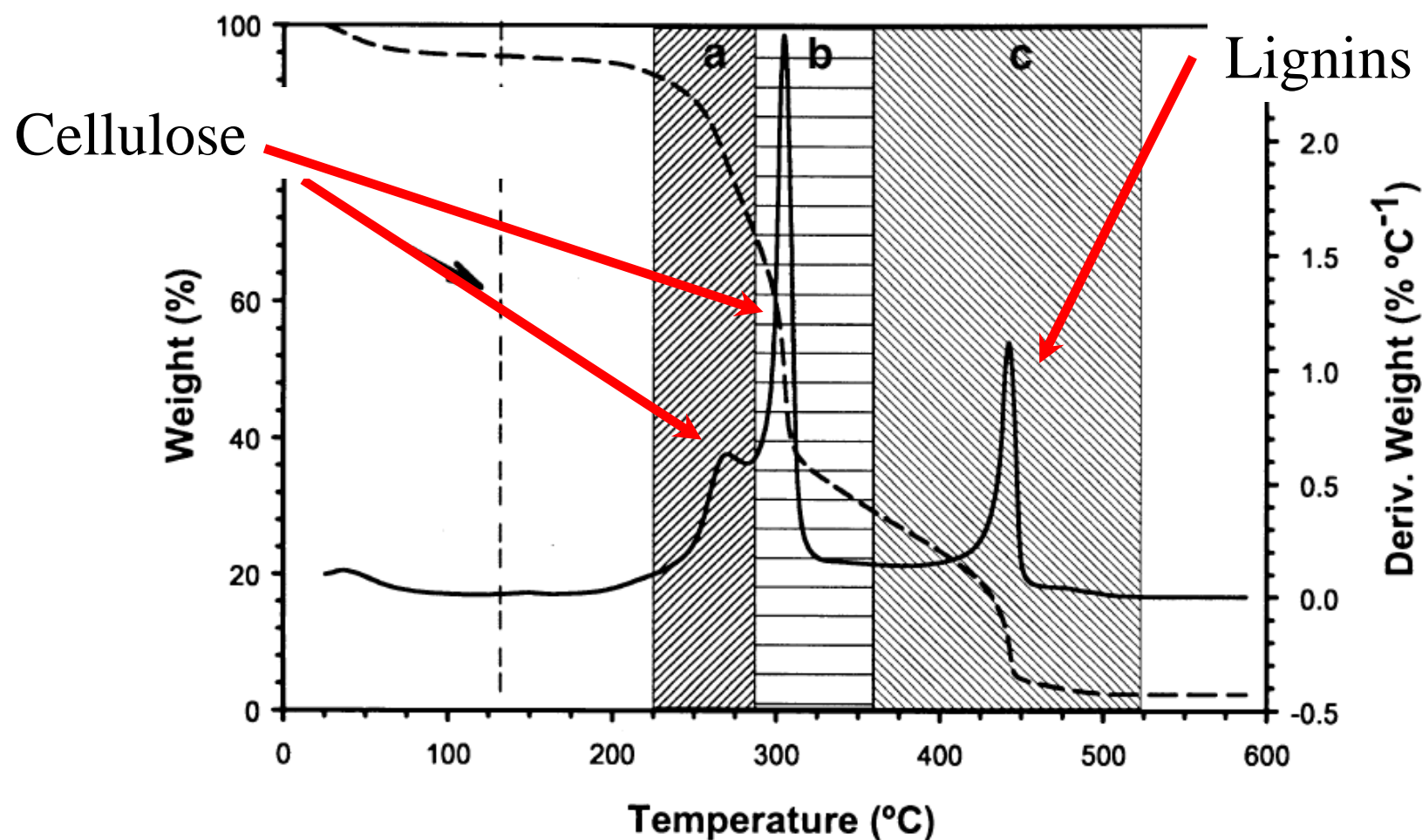
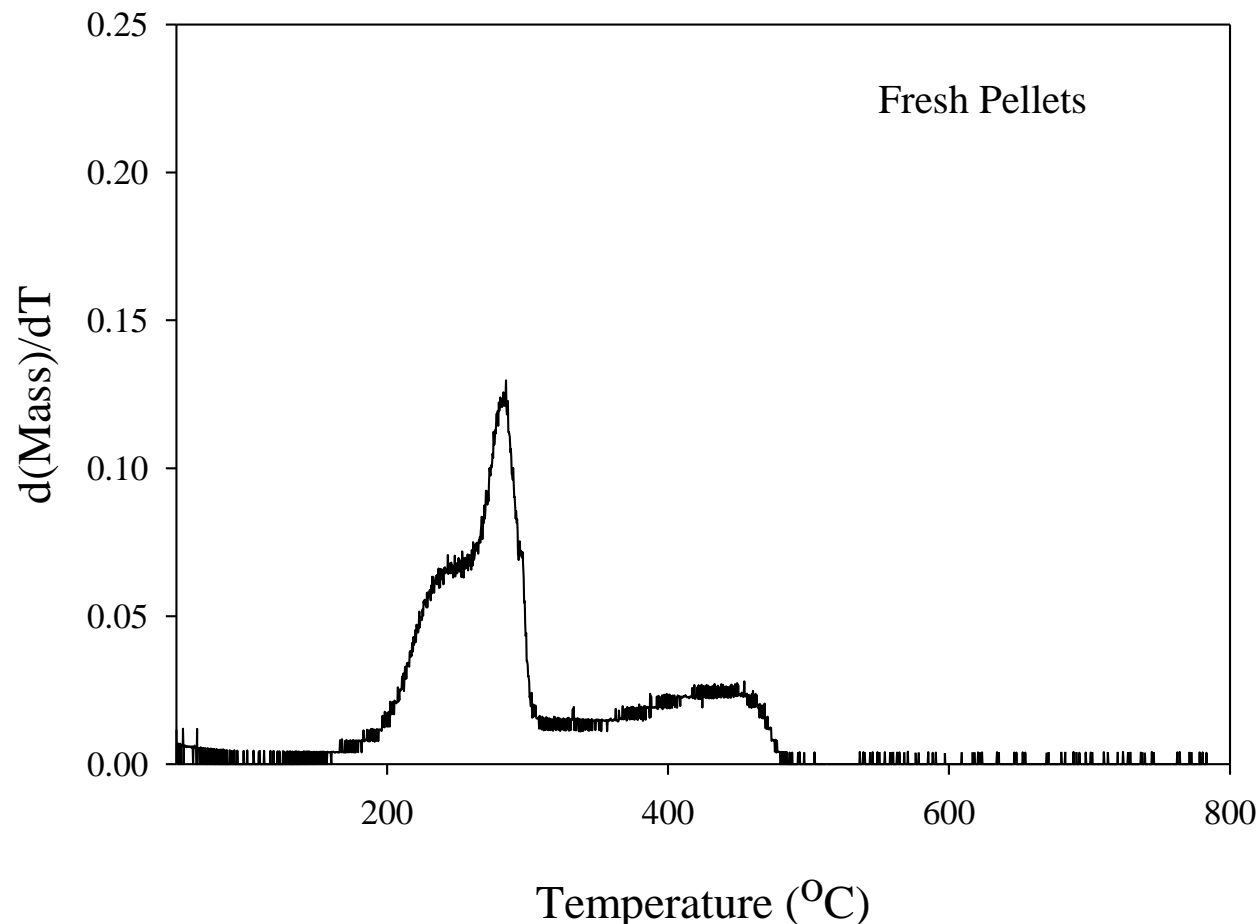


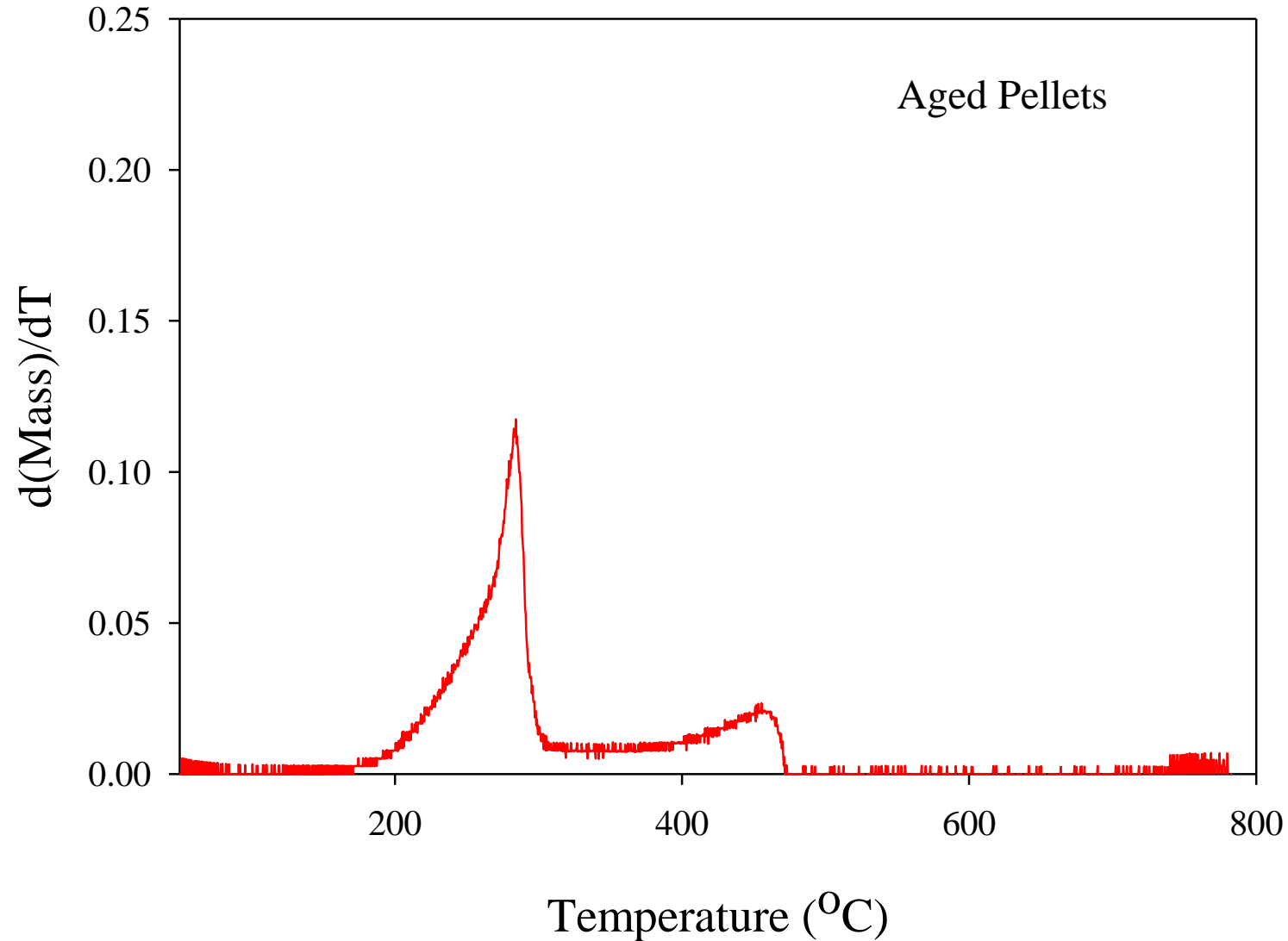
Fig. 1 TGA thermogram of biomass from reference willow clone *S. dasyclados* 'SV1.' Arrow indicates cutoff line for water loss correction (129 °C). Block A: weight loss representative of hemicellulose (245–290 °C). Block B: weight loss representative of cellulose (290–350 °C). Block C: weight loss representative of lignin (350–525 °C)

What Causes Pellets To Off-Gas CO

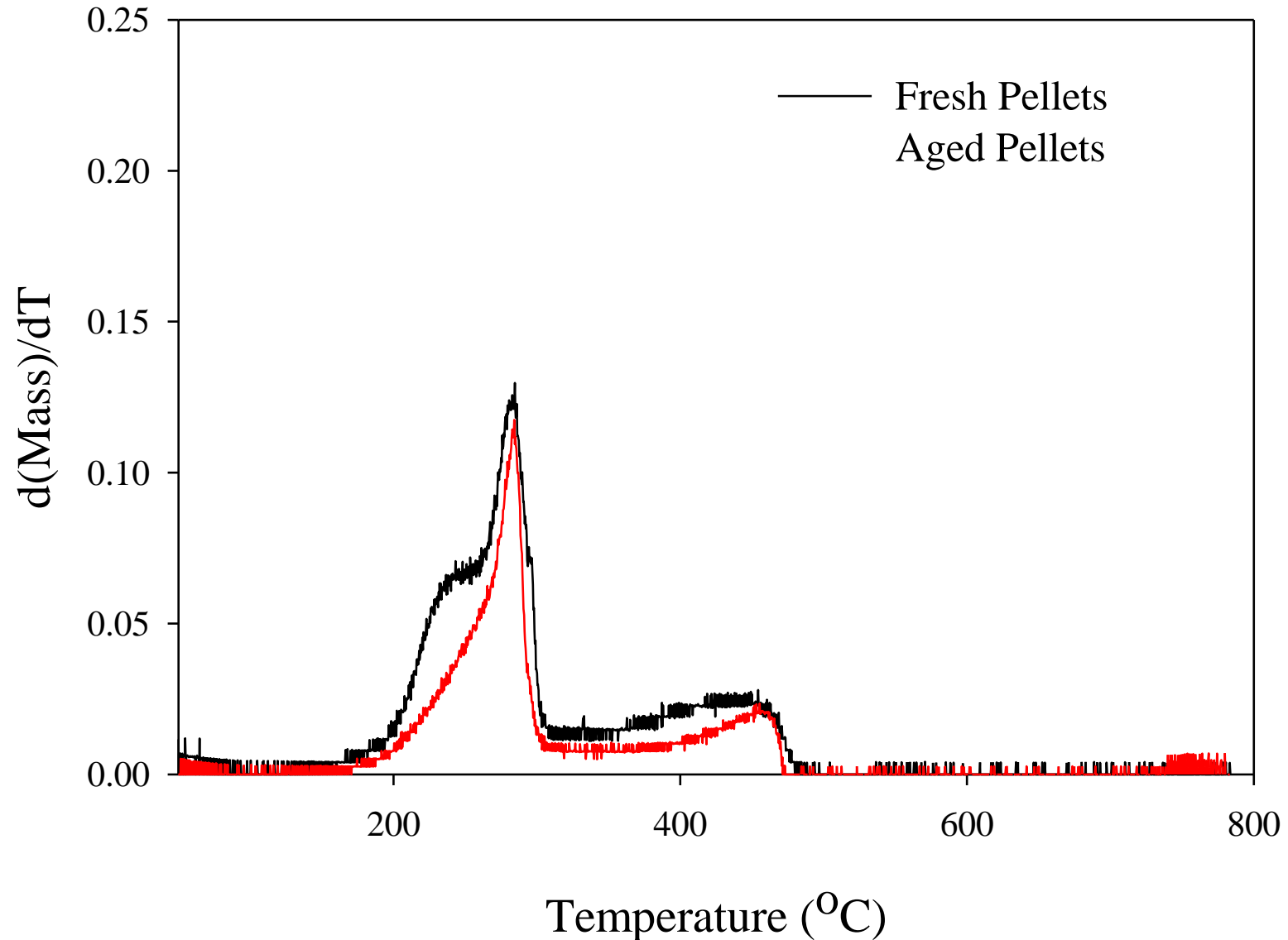
- So, we did TGA analyses of fresh and aged softwood pellets.



What Causes Pellets To Off-Gas CO



What Causes Pellets To Off-Gas CO



Oxidizable Components

- 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 autooxidation 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.

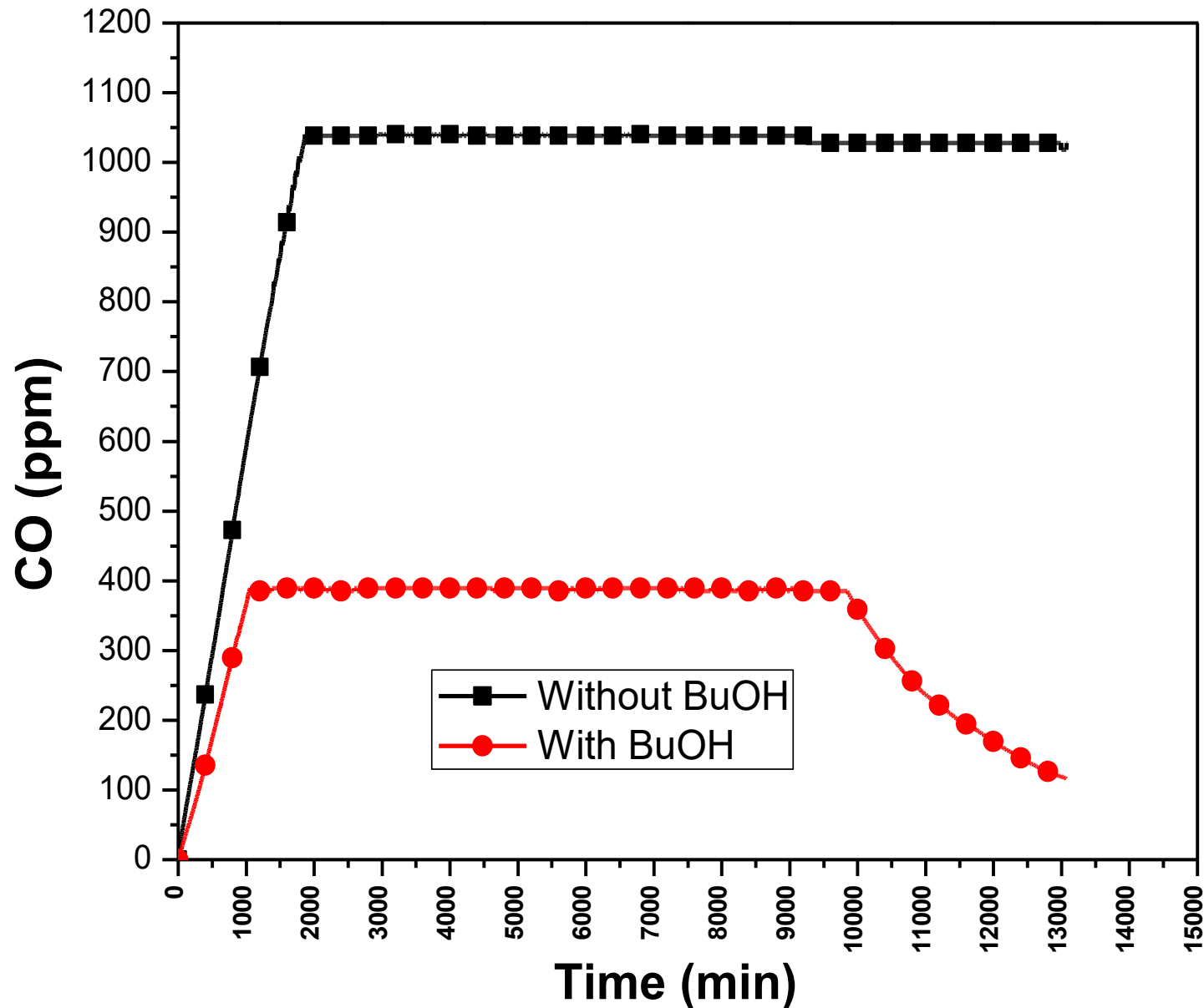
Testing the hypothesis

- 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.



- The resulting radical is a much weaker oxidizer and thus, we should see the reaction stop

Testing the hypothesis

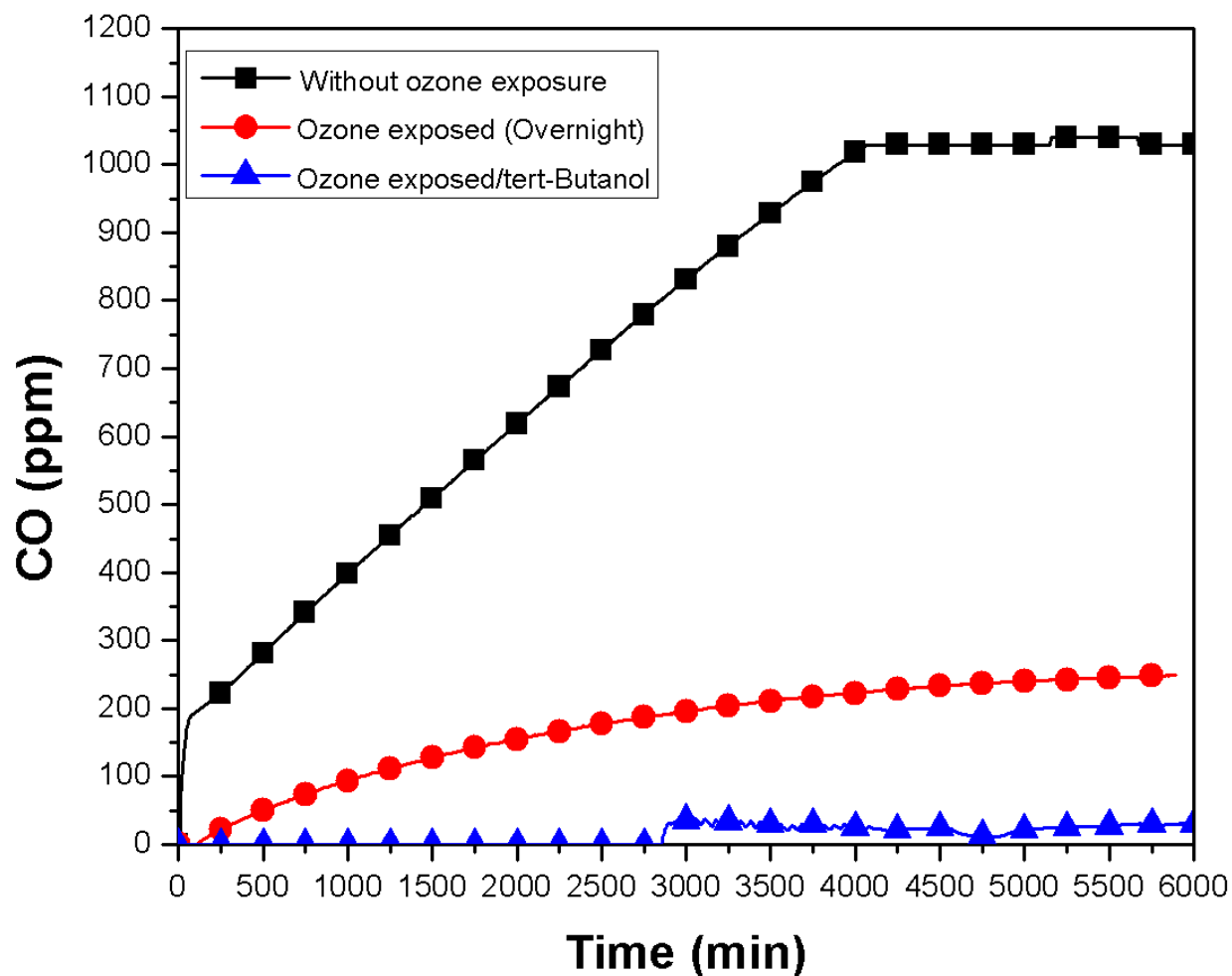


Is it the unsaturated compounds?

- 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



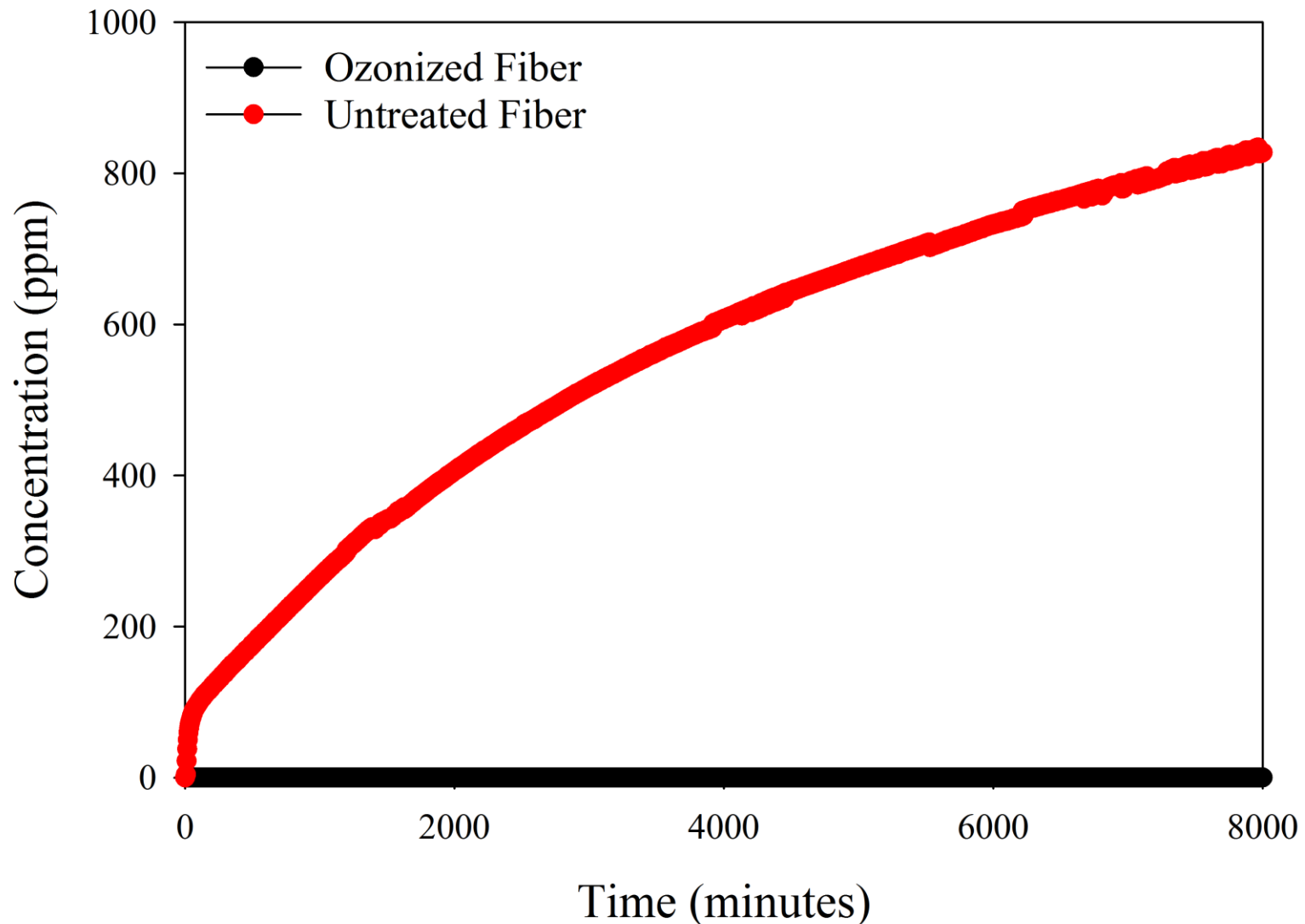
Is it the unsaturated compounds?

- 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?

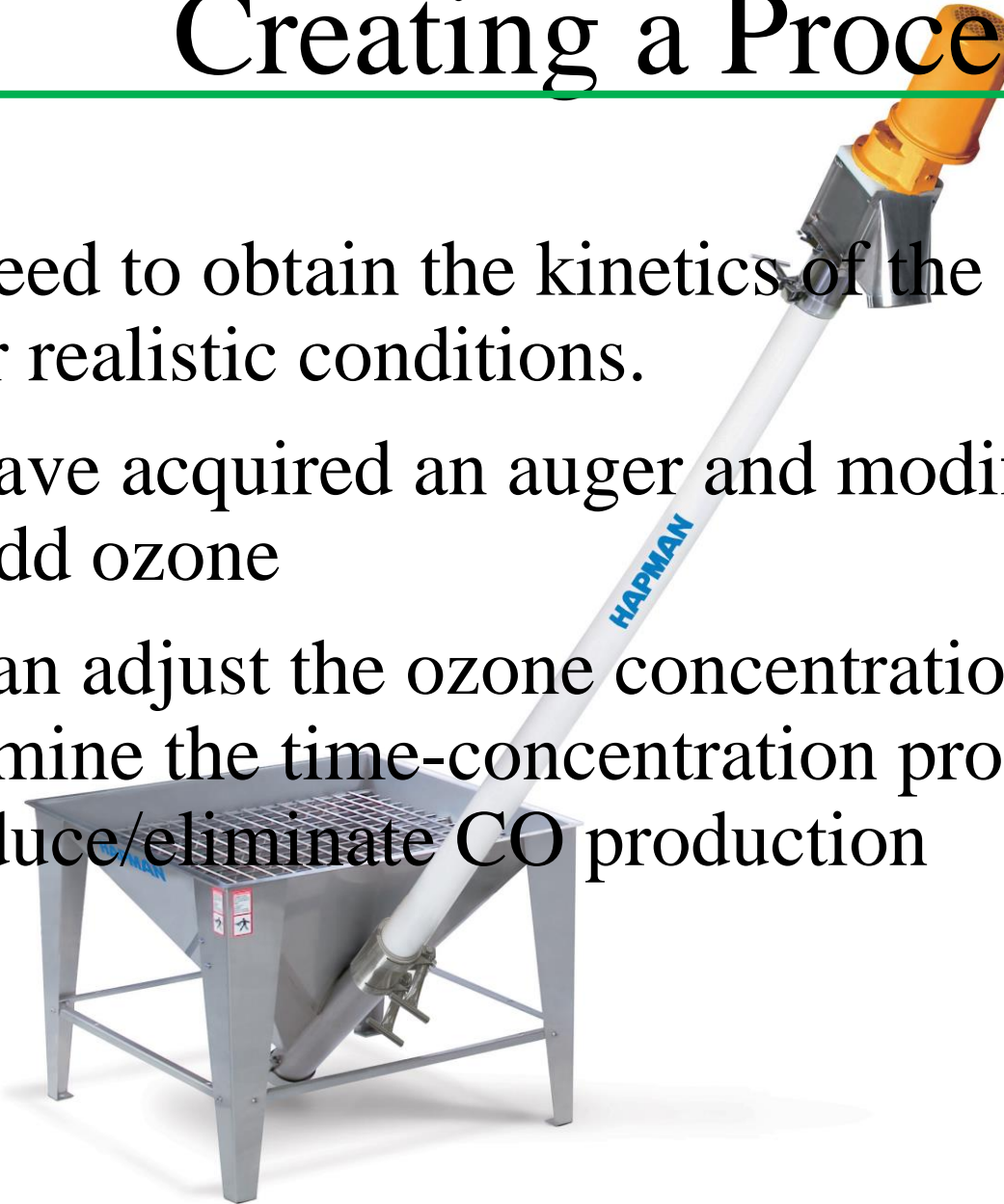


Voila!

- 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

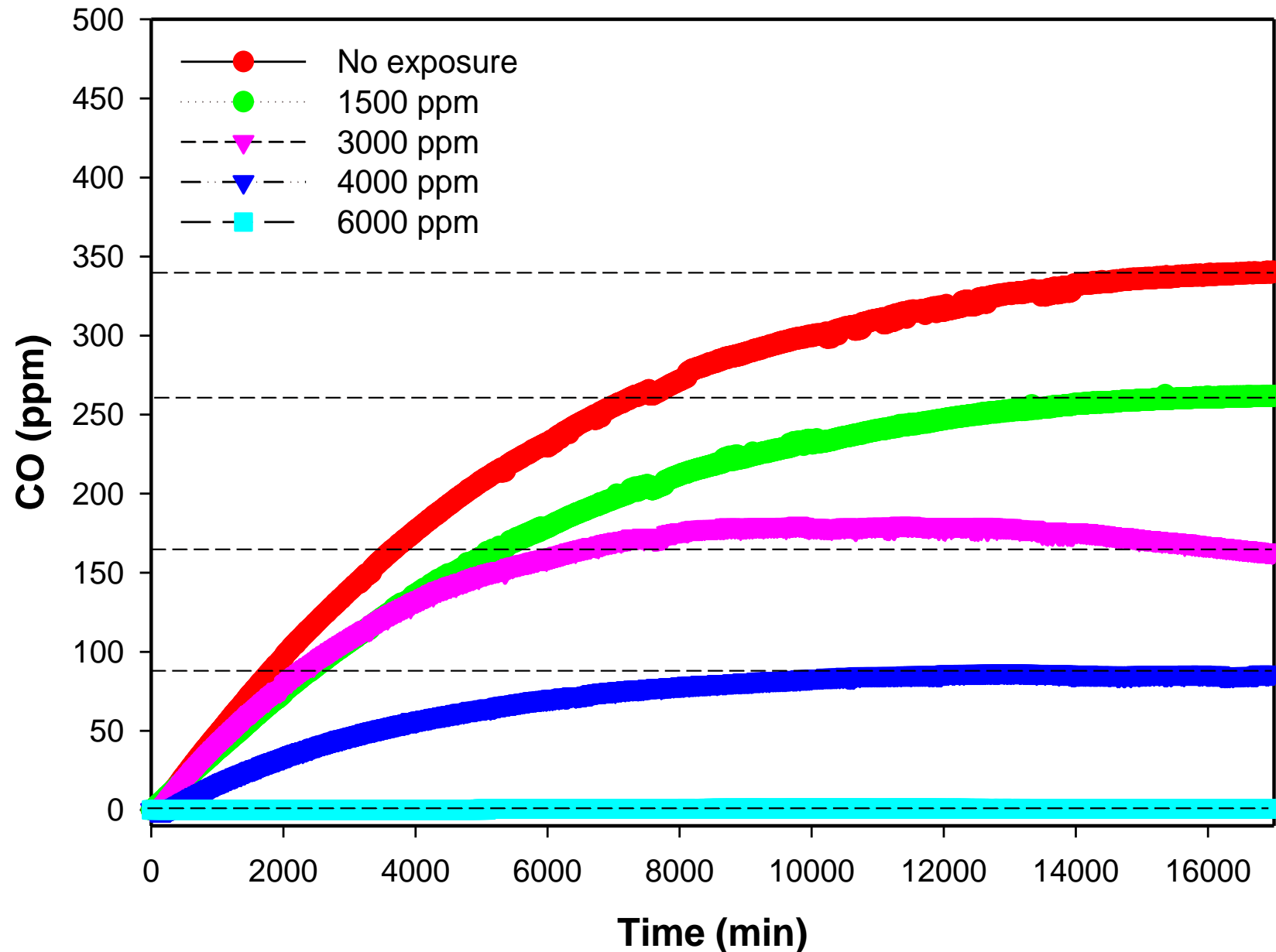
- We need to obtain the kinetics of the ozonation under realistic conditions.
- We have acquired an auger and modified it so we can add ozone
- We can adjust the ozone concentrations and determine the time-concentration product necessary to reduce/eliminate CO production



Creating a Process

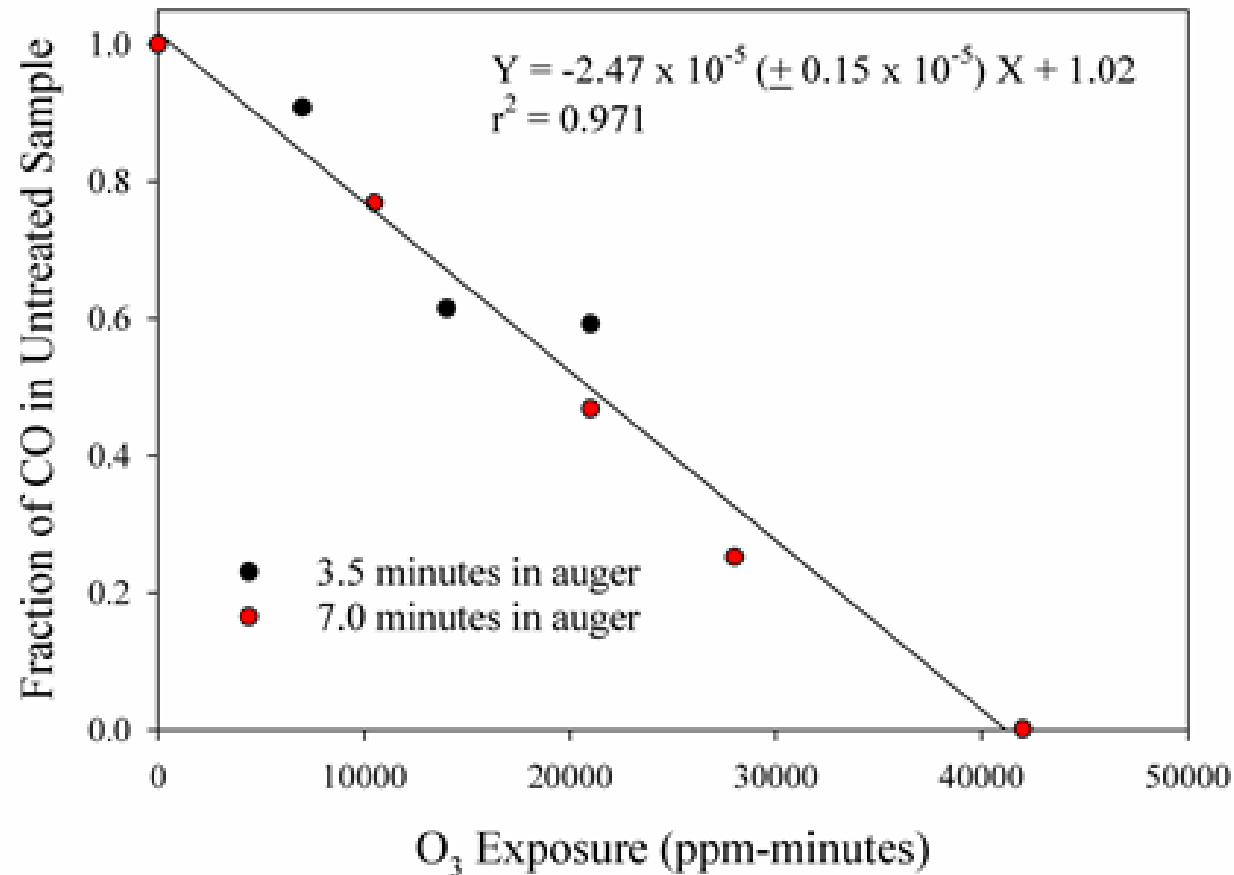


CO Offgassing after O₃ Exposure

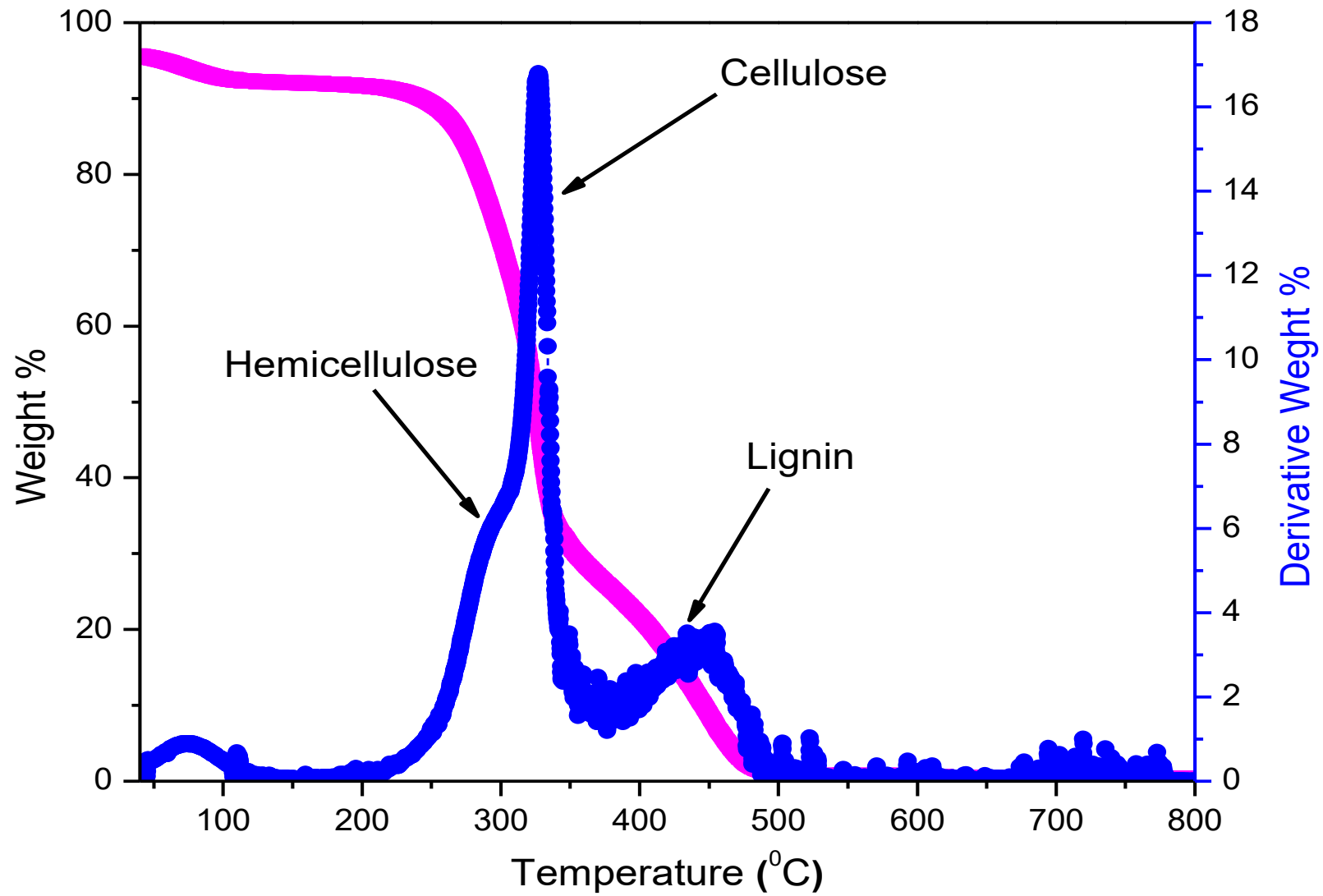


O₃ exposure time: 7 min, Flow rate: 1L/min, Length of the Auger: 6 feet, Mass of wood fiber: 57 g/min

CO Offgassing after O₃ Exposure



Modification of the Wood



TGA of O_3 exposed (6000 ppm) wood fiber (No CO off-gassed by the fiber)

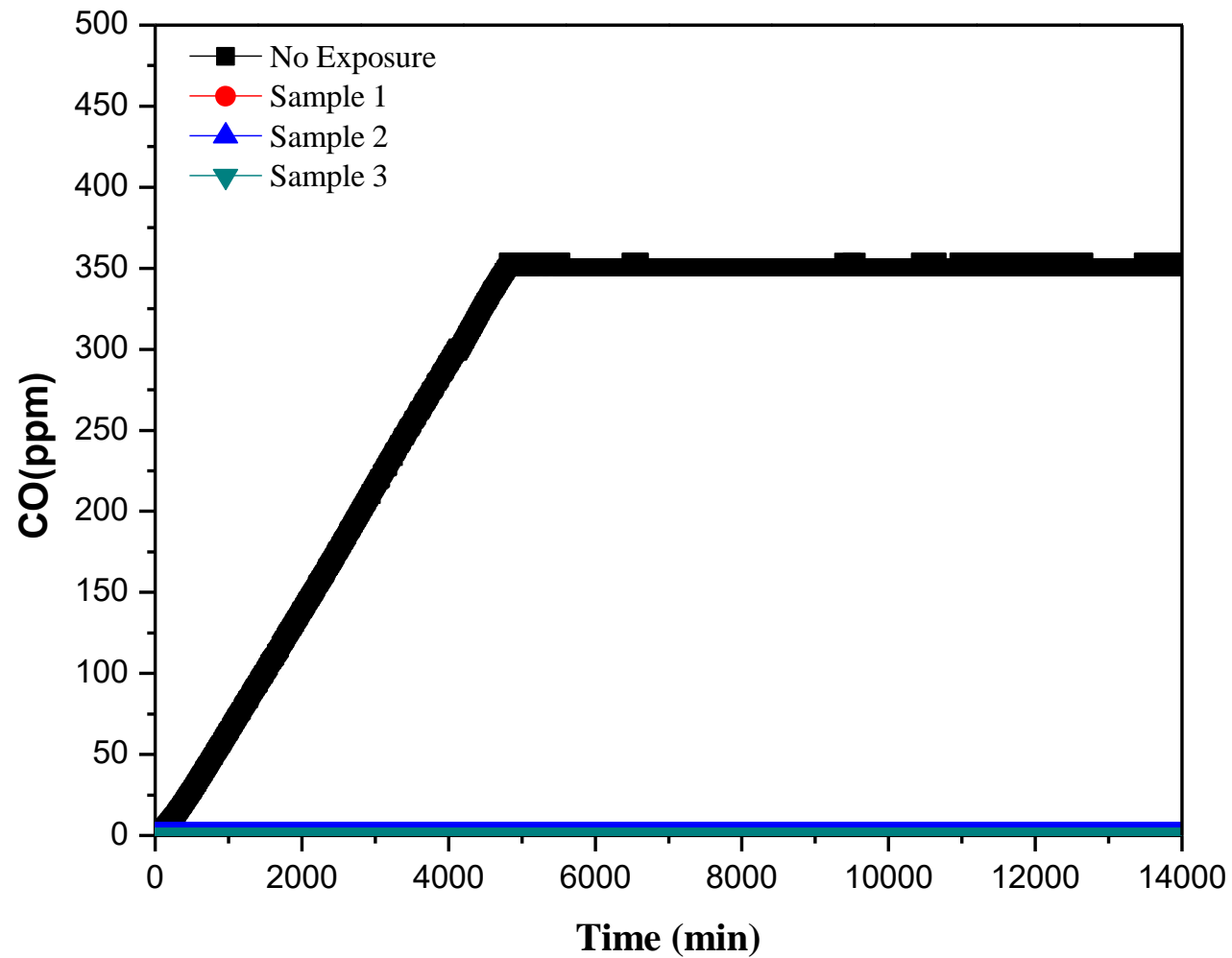
Final Test

- 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



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.



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Kelli Ramsey

**In support of the Alliance for Green Heat's 4th
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Elimination of CO Off-Gassing from Stored Wood Pellets

Kelli Curran Ramsey, Marketing Manager

Curran Renewable Energy

Massena, NY



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ENERGY FROM THE FOREST TO YOU™

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!



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ROCHESTER

Institute for a Sustainable Environment



at Clarkson University



Questions? Please contact me at
kelli@curranpellets.com



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Questions?

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