

# FORMALDEHYDE EMISSIONS FROM COMBUSTION SOURCES AND ITS CONTRIBUTIONS TOWARD VOLATIVE ORGANIC COMPOUNDS AND HAZARDOUS AIR POLLUTANTS

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**ENGINEERS**



# Formaldehyde Emissions from Combustion Sources

*What is Formaldehyde?*





# Formaldehyde Emissions from Combustion Sources

- Formaldehyde is a colorless pungent irritating gas  $\text{CH}_2\text{O}$  used chiefly as a disinfectant and preservative and in chemical synthesis.
- Formaldehyde is used in preserving dead animals in laboratories for studies to prevent decay.
- Formaldehyde is found in processed wood products and building materials.
- Formaldehyde vapor can cause respiratory effects and could have links to cancer. Therefore it is classified as a hazardous air pollutant according to USEPA.

# Formaldehyde Emissions from Combustion Sources

While there are many evaporative sources of Formaldehyde there is also another type of source which will be discussed.

They are Combustion Sources!

# Formaldehyde Emissions from Combustion Sources



# Formaldehyde Emissions from Combustion Sources



# Formaldehyde Emissions from Combustion Sources

## Mobile Sources

- Motor vehicles (cars, trucks, motorcycles, etc.)
- Boats
- Construction Equipment/Portable Generators
- Fuel fire lawn equipment including fuel fired snow blowers

## Stationary Sources

- Boilers
- Stationary Engine (Emergency Generators)
- Turbines



# Formaldehyde Emissions from Combustion Sources

Common Fuels that are Combusted

Liquid Fuels

- Gasoline
- Diesel/No. 2 Fuel Oil
- Kerosene/No. 1 Fuel Oil
- Jet Fuel
- Biodiesel

Gaseous Fuels

- Natural Gas
- Propane
- Acetylene
- Biogas (from landfills and anaerobic digesters)

# Formaldehyde Emissions from Combustion Sources

Reaction during fuel combustion:



This is the main reaction with Carbon Dioxide and Water as the products.

However, there are “mid products” that occur within the reaction which are known as products of incomplete combustion(PIC). The most common PIC is...

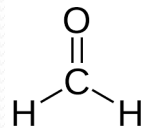
# Formaldehyde Emissions from Combustion Sources

- Carbon Monoxide!



- The second most common Product of Incomplete Combustion is:

- Formaldehyde!



- Other Products of Incomplete Combustion include Acetaldehyde, Acrolein and Methanol

# Formaldehyde Emissions from Combustion Sources

- As mentioned earlier, Formaldehyde is classified as a Hazardous Air Pollutant (HAP) (note that Carbon Monoxide is not a HAP).
- Subject to NESHAPS requirements for control of Hazardous Air Pollutants.
- If a facility has the potential to emit 10 tons per year of Formaldehyde or contributes to 25 tons per year of total HAPs it is a major source for HAPs and the facility is Subject to a Title V Operating Permit plus additional regulatory controls.



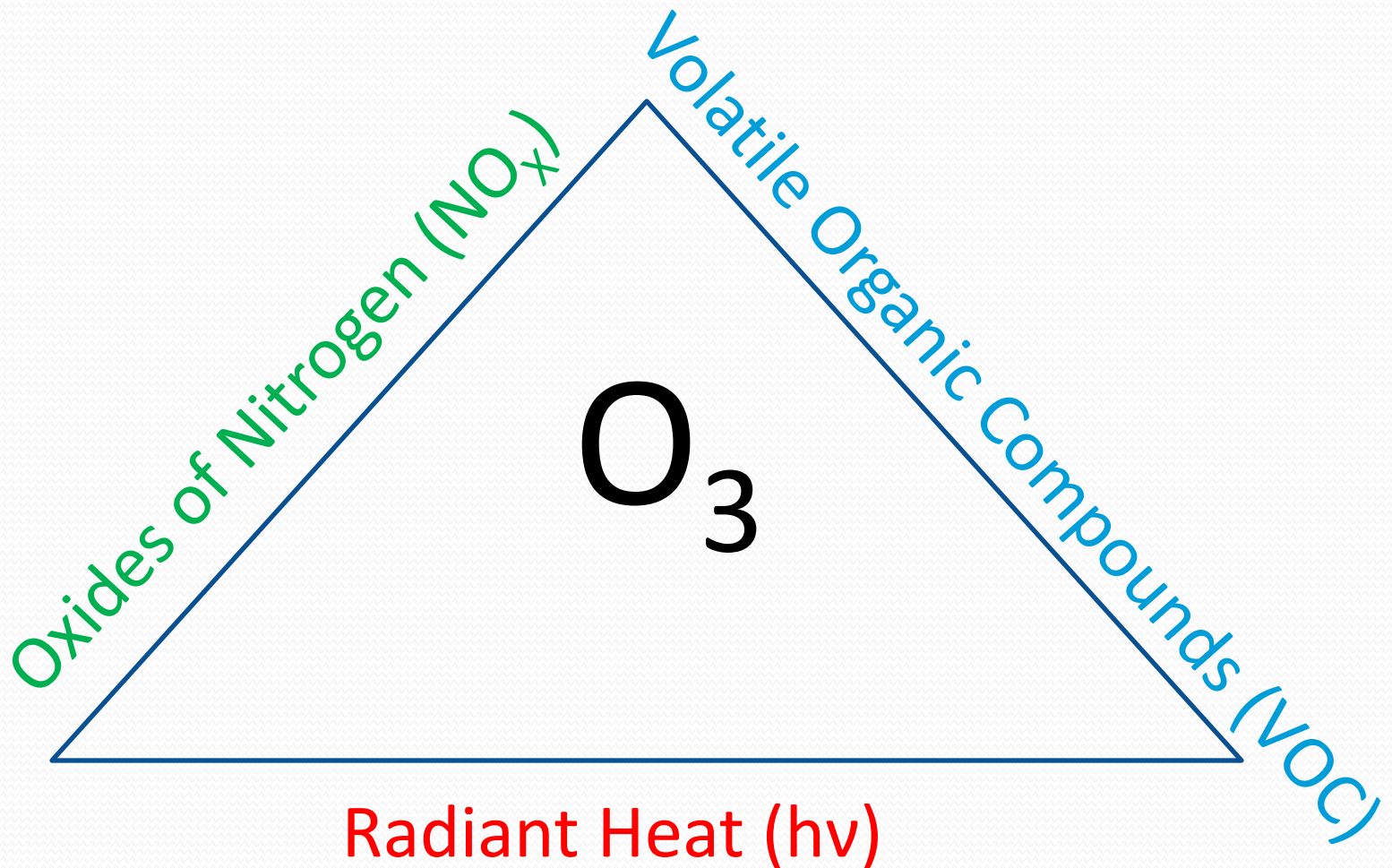
# Formaldehyde Emissions from Combustion Sources

However, there is another air pollution issue with formaldehyde.

What is this issue????

Formaldehyde is a volatile organic compound which can contribute to the formation of ozone

# The Ozone Triangle



# Volatile Organic Compounds

Definition as of 40 CFR 51.100(s)

Organic Compound

Any carbon compound that is not, elemental carbon, carbon dioxide, carbon monoxide, carbonic acid, metallic carbides and carbonates and ammonium carbonate.

Volatile Organic Compounds are Organic Compounds except for what is listed in 40 CFR 51.100(s) which are demonstrated not be Ozone precursors.

The vast majority of the organic compounds listed as non-ozone precursors are refrigerants (chloro-fluoro hydrocarbons).

# Volatile Organic Compounds

Here are other compounds that are listed:

- Methane
- Ethane
- Acetone
- Methyl Acetate
- Methyl Formate
- Methylene Chloride
- 1,1,1 Trichloroethane (Methyl Chloroform)
- Perchloroethylene (Tetrachloroethylene)

Note that while they are not VOCs, some are hazardous air pollutants while methane is a greenhouse gas.



# Formaldehyde Emissions from Combustion Sources

## How Volatile Organic Compounds Are Measured

- There is no direct method to measure Volatile Organic Compounds (VOC) that is approved by USEPA.
- The most accurate equivalent measurement is Non-Methane Hydrocarbons (NMHC). Methane is the most common product of incomplete combustion (PIC).
- Emissions samples must be measured using two approved EPA methods:
  - Method 25A – Total Hydrocarbons using Flame Ionization Detector
  - Method 18 – Methane using Gas Chromatography
- Subtract the Methane from THC should result in NMHC. However there is one problem.

# Formaldehyde Emissions from Combustion Sources

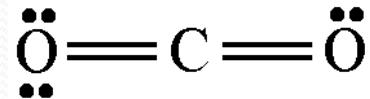
The Measurements ARE NOT PERFECT

- Difference could be a negative concentration. Agencies will accept this and assume that it is either “zero” or “below detectable limits”.
- Method 25A does not provide specifics on certain compounds.
- The Flame Ionization Detector measures alkanes, alkenes and alkynes and aromatic alkanes (like benzene and toluene).
- It is assumed that Non-Volatile Organic Compounds excluding methane measured in 25A offset VOCs not measured in 25A.

# Formaldehyde Emissions from Combustion Sources

For Combustion Emissions Method 25A using a Flame Ionization Detector will not measure the two most common carbon compounds that are emitted (Hint they are both inorganic). They are:

Carbon Dioxide



Carbon Monoxide

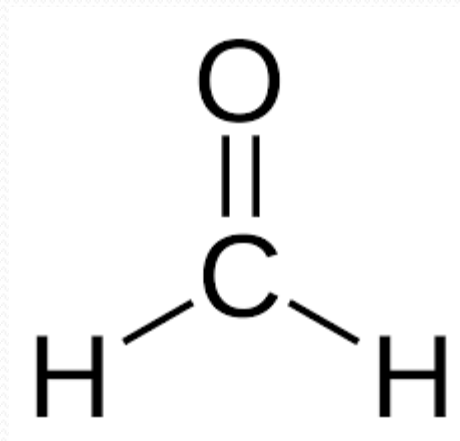


Both have one thing in common

Multiple bonds between Carbon and Oxygen.

What other compounds have this?

# Formaldehyde Emissions from Combustion Sources



FORMALDEHYDE!

But Formaldehyde is a VOC and should be measured as part of Total Hydrocarbons.



# Formaldehyde Emissions from Combustion Sources

Other Hydrocarbon Compound Groups that have the carbon oxygen double bond include aldehydes, ketones, carboxylic acids and esters. Many are products of incomplete combustion.

While some like acetone, methyl acetate and methyl formate are classified as not ozone contributors, most are classified as VOCs.

Well it looks like EPA and NJDEP have noticed this....

# Formaldehyde Emissions from Combustion Sources

Last December NJDEP has sent letters to facilities that operate reciprocating engines burning gaseous fuels including Natural Gas, Propane, Landfill Gas and Biogas generated from Anaerobic Digesters.

It mentions that formaldehyde may be under reported and permits will need to be modified to include formaldehyde emissions.

The letter specifically mentions that VOC test methods in particular Method 25A does not include Formaldehyde.

# Formaldehyde Emissions from Combustion Sources

This is noted in Table 1 of Subpart JJJJ of 40 CFR 60 which is New Source Performance Standards for Spark Ignited Reciprocating Engines

VOC limits in grams per brake horsepower hour and parts per million have a superscript “d” which states “For purposes of this subpart, when calculating emissions of volatile organic compounds, emissions of formaldehyde should not be included.”

This indicates the difference of method results of 25A and 18 are used to determine VOC emissions and that formaldehyde is not included.

# Formaldehyde Emissions from Combustion Sources

Note that this is focused on gas fired reciprocating engines which most commonly are

- Gas fired emergency generators
- Cogeneration Units burning natural gas and biogas

The latter will require stack testing and periodic testing for VOCs.

There are two types of spark ignited engines which are:

- Rich Burn – Higher fuel to air ratio (close to Upper Explosive Limit-UEL)
- Lean Burn – Lower fuel to air ratio (close to Lower Explosive Limit – LEL)



# Formaldehyde Emissions from Combustion Sources

Compression Ignition Engines (ones that burn liquid fuels like diesel) are subject to New Source Performance Standards of 40 CFR 60 Subpart IIII. This regulation has limits for non methane hydrocarbons (NHMC) and does not specify formaldehyde.

Note that there is also a Maximum Allowable Control Technology (MACT) standards for Stationary Source Reciprocating Engines which is 40 CFR 63 Part ZZZZ. It sets additional standards for carbon monoxide and formaldehyde emissions. This also covers compression ignition engines.

# Formaldehyde Emissions from Combustion Sources

## **Determination of Formaldehyde Potential to Emit.**

Because Formaldehyde is a Hazardous Air Pollutant it should be reported separately if the potential to emit exceeds reporting thresholds in accordance with New Jersey Regulations.

In accordance with N.J.A.C 7:27-17.9, the reporting threshold for Formaldehyde is 3.5 pounds per year.

# Formaldehyde Emissions from Combustion Sources

## **To determine emission Formaldehyde emission rate:**

- Obtain from manufacturer (most likely in grams per brake horsepower-hour).
- If you get VOC emissions from manufacturer ask whether it is formaldehyde inclusive.
- Use AP-42 – Section 3.2. Note there are different factors for 2 stroke lean burn, 4 stroke lean burn and 4 stroke rich burn all given in grams per brake horsepower-hour.
- AP-42 does not indicate inclusiveness of formaldehyde for VOC emissions.

# Formaldehyde Emissions from Combustion Sources

## **Stack Testing**

Now that it is established that VOC testing does not include Formaldehyde, a third method will be needed for Formaldehyde determination.

That method is Method 323 which is specifically for formaldehyde emissions for natural gas combustion.

To determine VOC emissions you should add concentration results of Total Hydrocarbons (Method 25A), and Formaldehyde (Method 323) and subtract Methane (Method 18)

# Formaldehyde Emissions from Combustion Sources

How To Prevent Generation of Formaldehyde in Combustion – Two Types

- Increase Temperature
- Increase Excess Air

But there is a consequence to that

**Increased NO<sub>x</sub>**

# Formaldehyde Emissions from Combustion Sources

An optimal temperature and excess air is needed to minimize both PIC (including carbon monoxide and formaldehyde) and NO<sub>x</sub>.

Pollution control may be necessary to remove formaldehyde just like carbon monoxide.

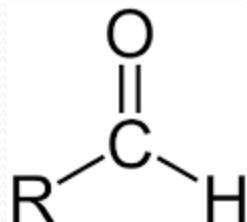
- Lean burn engines
- Afterburners
- Catalytic Oxidizers



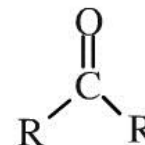
# Formaldehyde Emissions from Combustion Sources

At this time USEPA and NJDEP are focused on engines burning gaseous fuels. However, other combustion sources may be addressed as well as other pollutants.

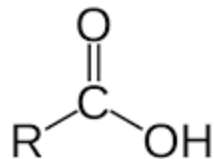
Aldehydes



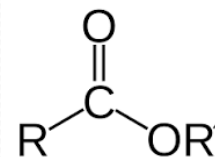
Ketones



Carboxylic Acids



Esters



# Formaldehyde Emissions from Combustion Sources

## Conclusions:

- If NJDEP requests including Formaldehyde emissions addressed in permit or stack test, first determine if Formaldehyde Potential to Emit is of reporting thresholds. If so permit will be modified.
- VOC testing should include Methods 25A, Method 18 for methane and Method 323 for Formaldehyde.
- Review pollution control devices to ensure it can remove Formaldehyde if necessary.

# Formaldehyde Emissions from Combustion Sources



# Thank You!



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