NOx and Nitrous Oxide Generation from Digester Gas Combustion Engines and Reduction of These Gases to Prevent Ozone and Greenhouse Gas Effects

May 7, 2024

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For New Jersey Water Environment Association Conference

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Biogas generated from anaerobic digesters are now burned in boilers for heat and engines and turbines to generate heat and electricity.

It is beneficial because it reduces methane (a greenhouse gas) from the atmosphere and saves money for the facility in place purchasing heat and electricity. Also it prevents emissions being generated for purchased electricity (unless generated from non combustion sources).

Biogas has methane content ranging from 50 to 67.5 percent methane with a balance of carbon dioxide and other impurities like sulfides and siloxanes.

Biogas burned in engines is usually pretreated in carbon absorption units to remove sulfides and siloxanes so the engine operates cleaner without any clogging of the pistons caused by silicon dioxide.

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The focus of this presentation is emissions of nitrogen/oxygen compounds.

There are three types of compounds with nitrogen and oxygen:

- Nitric Oxide (NO)
- Nitrogen Dioxide (NO_2)
- Nitrous Oxide (N_2O)

NO and NO_2 are classified as NO_X which can contribute to ozone (O_3) generation. NO and NO_2 can convert to nitrous (HNO_2) and nitric acids (HNO_3). Note that Ozone and NO_X are monitored as criteria pollutants under Title 1 of the Clean Air Act Amendments of 1990.

N_2O is classified as a greenhouse gas under federal regulations 40 CFR 98.

True or False – All nitrogen/oxygen compounds generated through combustion are dependent on nitrogen containing fuels only.

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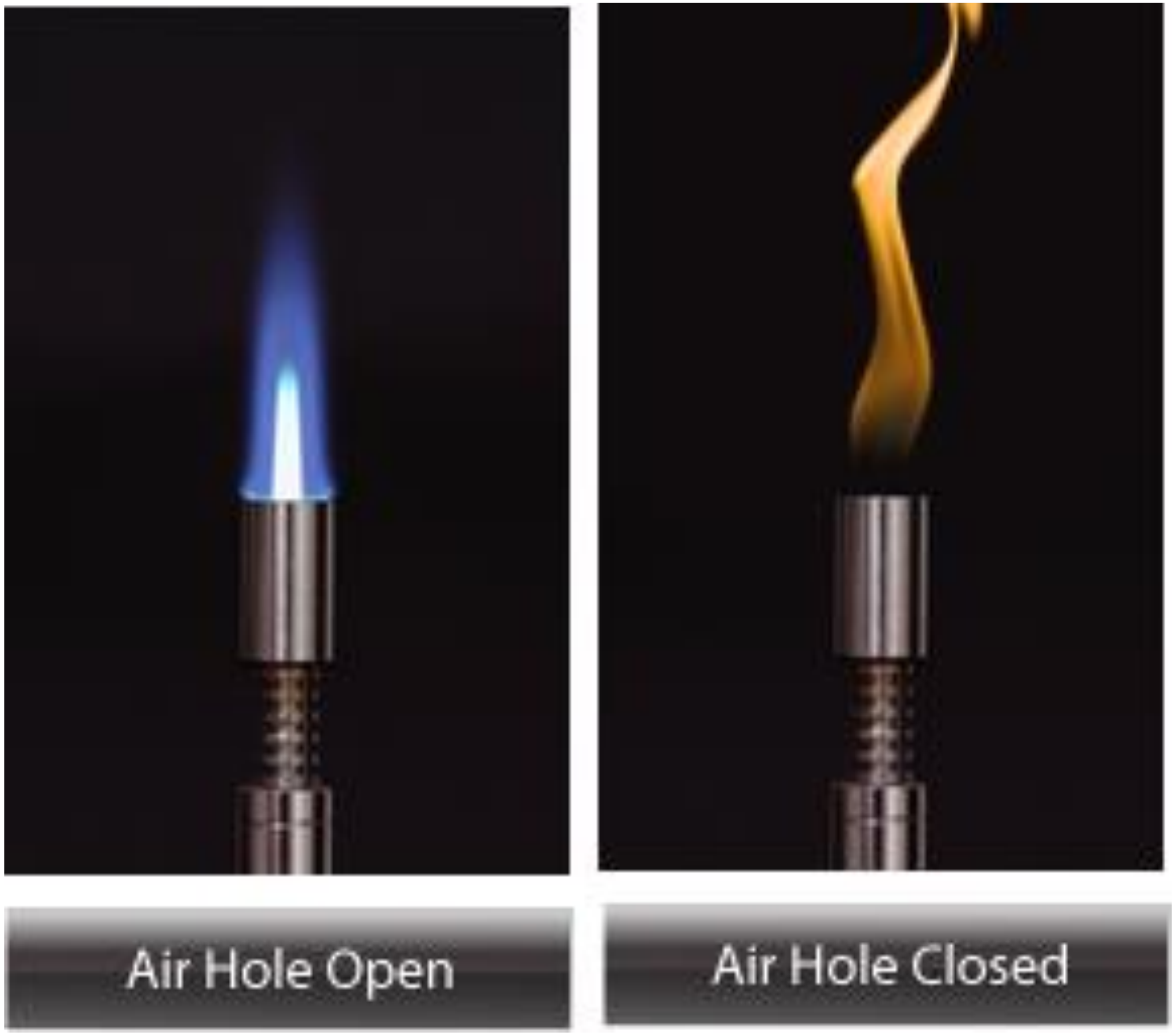
FALSE - Most nitrogen oxygen compounds are generated by reaction of a very small percentage of the nitrogen and oxygen in combustion air.


Air Hole Open
Air Hole Closed

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Nitrogen/Oxygen Compounds will increase with higher temperatures and increased combustion air.

While lower combustion temperatures and less excess air prevents nitrogen/oxygen compound generation. However, this increases products of incomplete combustion (PIC) and unburned fuel which contains methane.

Products of incomplete combustion include carbon monoxide (CO) and volatile organic compounds (VOC) which may include formaldehyde.

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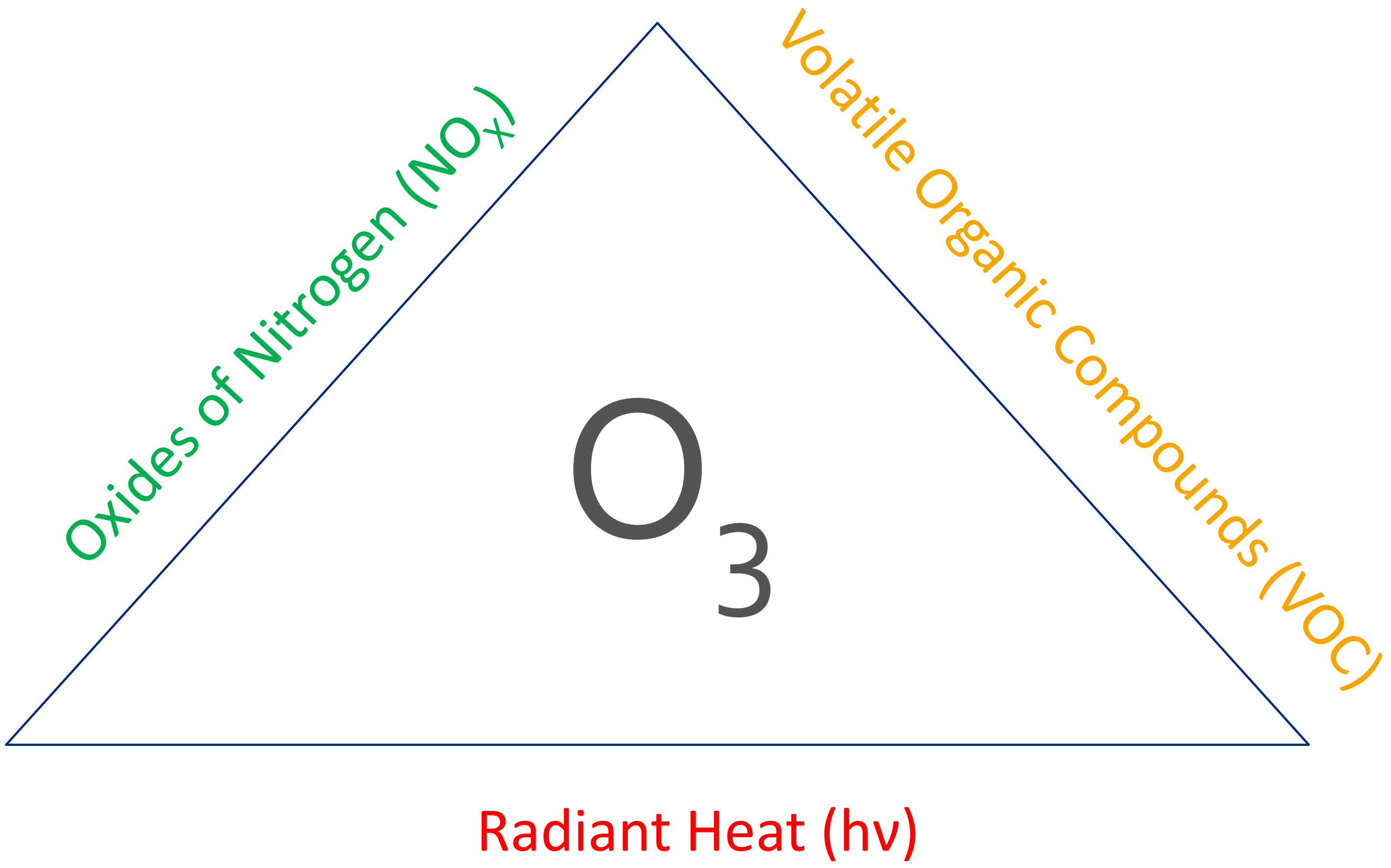

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- The Nitrogen Cycle
  - $NO_2 + h\nu = NO + O$
  - $O + O_2 + M = O_3 + M$
  - $O_3 + NO = NO_2 + O_2$
- The VOC Oxidation Cycle
  - $OH + HCHO = H2O + HCO$
  - $HCO + O_2 = HO_2 + CO$
  - $HO_2 + NO = NO_2 + OH$

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- Ozone (O_3) is a molecule with three oxygen atoms and can be used as a very strong oxidizer. However, unlike oxygen gas (O_2) it can cause health problems.
- The health effects of ozone include*:
    - Breathing difficulties
    - Coughing and sore scratchy throat
    - Aggravation of breathing conditions like emphysema, asthma and chronic bronchitis
    - Makes lungs susceptible to infection
    - Cause inflammation and damage to airways
- Source - EPA Website on Ozone Health Effects

What's the difference between Tropospheric and Stratospheric Ozone?

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- Tropospheric (Ground Level) Ozone (O_3) is generated when radiant heat (hv) causes Nitrogen Dioxide (NO_2) to break down to Nitric Oxide (NO) and an oxygen free radical (O) which in turn reacts with oxygen gas (O_2) to form ozone with the presence of particulates.
- However NO can immediately react with ozone to form NO_2 and O_2 completing the nitrogen cycle.
- VOCs and Oxygen with the aid of free radicals can deplete available NO which cannot react with O_3. Thus O_3 accumulates.
- Stratospheric Ozone is the Ozone Layer that protects earth from ultraviolet rays from coming to the earth's surface.

Why can't tropospheric ozone rise in the atmosphere to be stratospheric?

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- Volatile Organic Compounds
- Definition as of 40 CFR 51.100(s)
- An Organic Compound is 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 (chlorofluoro hydrocarbons).

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Other compounds listed:

Methane	Ethane
Acetone	Methyl Acetate
Methyl Formate	Methylene Chloride
1,1,1 Trichloroethane (Methyl Chloroform)	Perchloroethylene (Tetrachloroethylene)
2-Amino – 2- Methyl – 1- Propanol	Propylene Carbonate
T- Butyl Acetate	Dimethyl Carbonate

Cyclic, Branched or Completely Linear Methylated Siloxanes

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

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Based on actual measurements the ratio of NO and NO2 emissions from combustion sources is on average 3 to 1. Under AP-42 for a typical boiler burning natural gas. The emission factors in pounds per million cubic foot burned are as follows:

NO_X	100
VOC	5.5

Based on the above the emission factors for NO and NO2 are as follows:

NO	75
NO2	25

Also assuming total VOC is formaldehyde (HCHO) which has the same molecular weight as NO (30). The ratio of NO to VOC is about 15 to 1.

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The Nitrogen Cycle

$NO_2 + h\nu = NO + O$

$O + O_2 + M = O_3 + M$

$O_3 + NO = NO_2 + O_2$

The VOC Oxidation Cycle

OH + HCHO = H2O + HCO

$HCO + O_2 = HO_2 + CO$

$HO_2 + NO = NO_2 + OH$

With the higher rate of NO emissions versus VOC, O3 would not generate. What then causes ozone accumulation?

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Emissions don’t “stay in their lane” once they enter the atmosphere.

VOC emissions can also come from evaporative sources not just products of incomplete combustion.

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Digester Gas/Biogas vs. Natural Gas

Biogas from anaerobic digesters are on average consist of 60 percent methane and 40 percent carbon dioxide.

Therefore, emission factors for biogas need to be multiplied by 0.6 (or actual methane content) to get specific emissions.

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- Decrease Radiant Heat—Weather and greenhouse gas dependent. The higher the temperature and longer days the more radiant heat. During the winter radiant heat is low with overall colder temperatures and shorter days where VOC and CO run at higher rates. Meanwhile during warmer weather months where days are longer, radiant heat is much higher and NOx increases along with the generation of ozone.
- Decrease NO_X—Combustion at lower temperature and decrease excess air with less reaction of Nitrogen and Oxygen in combustion air. Use low NO_X burners and fuel recirculation methods.
- Decrease VOC—Combustion at higher temperature for less generation of products of incomplete combustion which also includes CO.
- The challenge is reaching an optimal temperature and excess air to minimize both Products of Incomplete Combustion which is VOCs and CO and NOx.
- Greenhouse gases also factor into this.

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For large engines burning either natural gas or biogas to generate heat and electricity may require periodic testing of NO_X and CO (as well as O_2). It may also require formal stack testing from a state agency which issues the air permit.

Combustion adjustment may be necessary to balance the emissions which include before and after measurements at different loadings (low, 25%, 50% 75% and 100%).

Period monitoring is conducted in accordance with ICAC Method CTM-034.

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For periodic testing, CTM-035 requires NO_X and CO to be measured in dry parts per million volumetric. Oxygen (O_2) needs to be measured in dry volumetric percentage.

CTM-034 measures NO and NO_2 separately this plays into the calculations of emissions in pounds per hour for NO_X.

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For facilities that have permits that require reporting emissions for either periodic monitoring or combustion adjustment. The conversion formula to use for converting CO and NOX concentrations into emissions in pounds per hour are as follows:

Lb/hr = MMBTU/hr X F Dry Factor X O2 Correction Factor X MW

/387,000,000

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MMBTU/hr – heat input which can be converted from fuel rate (natural gas is 1,020 BTU/cf. Digester gas is percent methane (measured or assumed).

F Dry Factor – estimated volumetric stack gas flow rate minus moisture in standard cubic feet per MMBTU. For natural gas it is 8,710. For digester gas it varies based on methane amount.

O_2 Correction Factor = 20.9%/(20.9%-percent O_2 measured). 20.9 is the atmospheric percentage of oxygen.

MW is molecular weight in pounds per pound-mole. Molecular weights are as follows:

- NO – 30
- NO_2 – 46
- CO - 28

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However, for required stack testing EPA Method 7E is required and assumes all NO_X as measured as NO_2.

This could be a problem if Method 7E measures NOX above permit conditions but in actuality they are not.

Stack Testing May Not be Required if the Engine has an EPA Certificate of Conformity.

If an engine (including emergency generator) does not have a Certificate of Conformity provided by the manufacturer, then stack testing for VOC, NO_X and CO is required once every three years even for emergency generators in accordance with 40 CFR 60 Subpart JJJJ.

	UNITED STATES ENVIRONMENTAL PROTECTION AGENCY 2018 MODEL YEAR CERTIFICATE OF CONFORMITY WITH THE CLEAN AIR ACT	OFFICE OF TRANSPORTATION AND AIR QUALITY ANN ARBOR, MICHIGAN 48105

Certificate Issued To: Power Solutions International, Inc. (U.S. Manufacturer or Importer) Certificate Number: JPSIB5.70EMT-006	Effective Date: 07/19/2017 Expiration Date: 12/31/2018	Byron J. Bunker, Division Director Compliance Division	Issue Date: 07/19/2017 Revision Date: N/A

Manufacturer: Power Solutions International, Inc.
Engine Family: JPSIB5.70EMT
Mobile/Stationary Certification Type: Stationary
Fuel : LPG/Propane
Natural Gas (CNG/LNG)
Emission Standards :
Stationary Part 1048
NMHC + NOx (g/kW-hr) : 2.7
CO (g/kW-hr) : 4.4
HC + NOx (g/kW-hr) : 2.7
Part 60 Subpart JJJJ Table 1
NOx (g/Hp-hr) : 2.0
CO (g/Hp-hr) : 4.0
VOC (g/Hp-hr) : 1.0
Emergency Use Only : Y

Pursuant to Section 213 of the Clean Air Act (42 U.S.C. section 7547) and 40 CFR Part 60, 1065, 1068, and 60 (stationary only and combined stationary and mobile) and subject to the terms and conditions prescribed in those provisions, this certificate of conformity is hereby issued with respect to the test engines which have been found to conform to applicable requirements and which represent the following nonroad engines, by engine family, more fully described in the documentation required by 40 CFR Part 60 and produced in the stated model year.

This certificate of conformity covers only those new nonroad spark-ignition engines which conform in all material respects to the design specifications that applied to those engines described in the documentation required by 40 CFR Part 60 and which are produced during the model year stated on this certificate of the said manufacturer, as defined in 40 CFR Part 60. This certificate of conformity does not cover nonroad engines imported prior to the effective date of the certificate.

It is a term of this certificate that the manufacturer shall consent to all inspections described in 40 CFR 1068.20 and authorized in a warrant or court order. Failure to comply with the requirements of such a warrant or court order may lead to revocation or suspension of this certificate for reasons specified in 40 CFR Part 60. It is also a term of this certificate that this certificate may be revoked or suspended or rendered void *ab initio* for other reasons specified in 40 CFR Part 60.

This certificate does not cover large nonroad engines sold, offered for sale, or introduced, or delivered for introduction, into commerce in the U.S. prior to the effective date of the certificate.

NOx and Nitrous Oxide Generation from Digester Gas Combustion Engines and Reduction of These Gases to Prevent Ozone and Greenhouse Gas Effects

- A **greenhouse gas** is any gaseous compound in the atmosphere that is capable of absorbing infrared radiation, thereby trapping and holding heat in the atmosphere. By increasing the heat in the atmosphere, **greenhouse gases** are responsible for the **greenhouse** effect, which ultimately leads to global warming.

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- The most common greenhouse gas is…

Carbon Dioxide

- Carbon Dioxide (CO_2) has the ability to retain infrared heat and naturally occurs in the atmosphere.
- Carbon Dioxide is the main product of combustion for all carbon materials that burn or react with oxygen.
- $C_XH_X + O_2 \Rightarrow CO_2 + H_2O$
- Note that Carbon Dioxide is a product of combustion and not just a combustion by product.

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- Carbon Dioxide (CO_2) can be consumed by plants via photosynthesis. However, the CO2 generation has outweighed the consumption especially in recent years.

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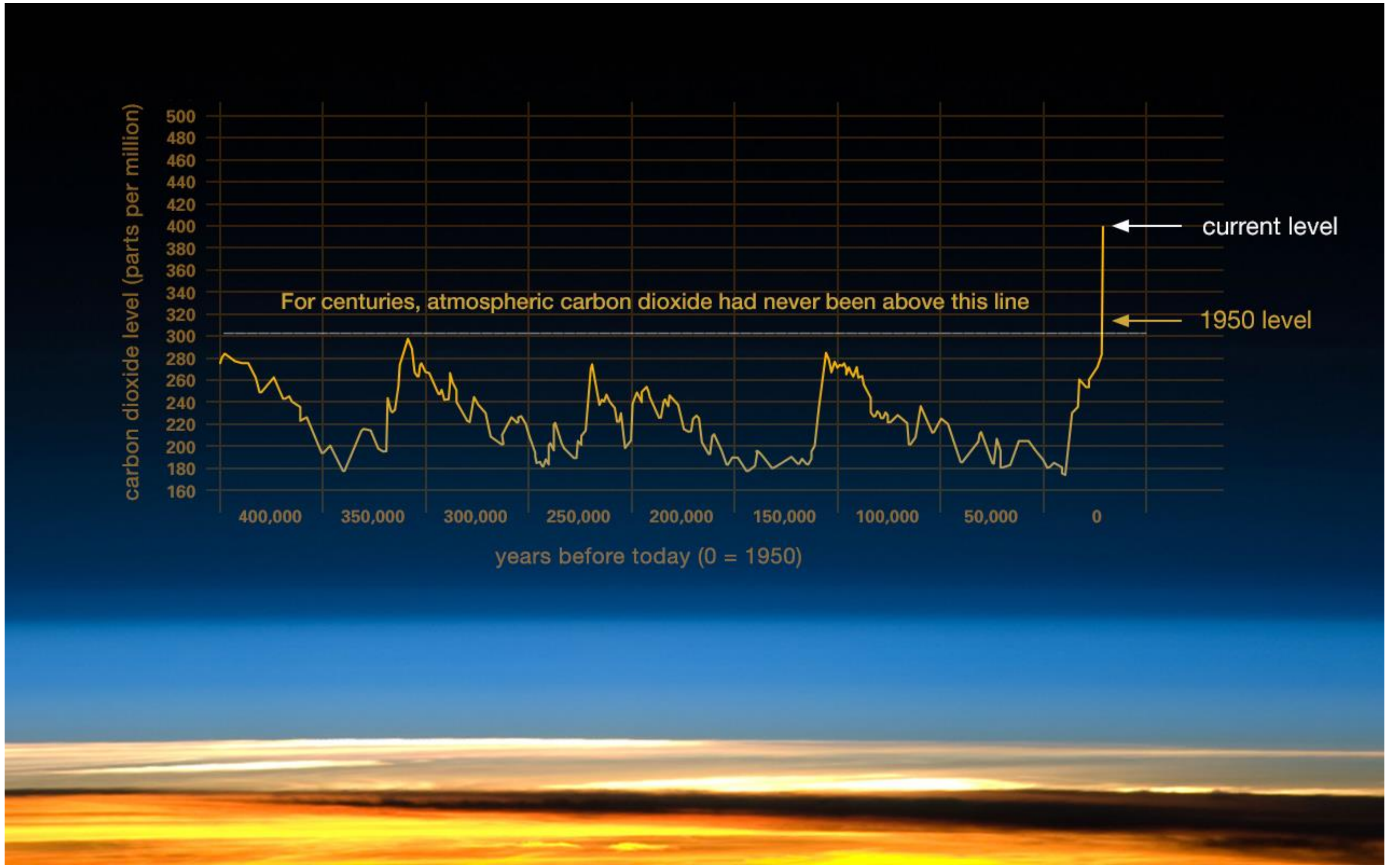

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- While Carbon Dioxide is the most common greenhouse gas, other gases have similar if not greater capability of holding infrared rays and thus contribute to global warming.
- The 100-year global warming effect is measured for each greenhouse gas compared to CO_2 or is classified as CO_2 equivalents (CO_2(e)).

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- The following is a list of greenhouse gases and their CO_2 Equivalents:

Carbon Dioxide	1
Methane	25
Nitrous Oxide	298

- Source: IPCC Fourth Assessment Report (2007).
- Note: other gases with higher CO_2(e) include sulfur hexafluoride and several chlorofluoro hydrocarbons.
- All greenhouse gases are now regulated by 40 CFR 98 for monitoring purposes only.

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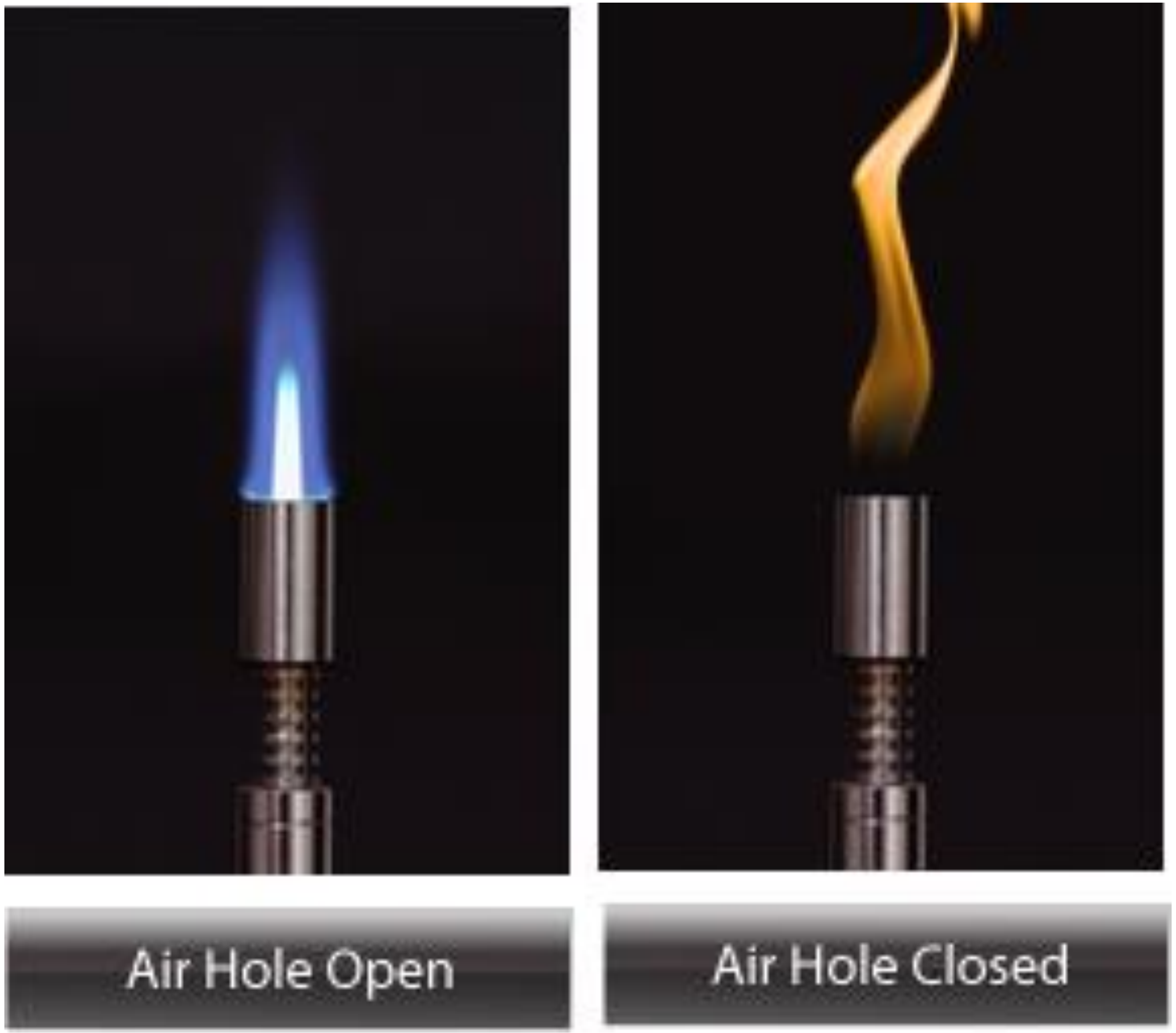
- Under AP-42 for a typical boiler burning natural gas. The emission factors in pounds per million cubic foot burned are as follows:

CO_2	120,000
Methane (CH_4)	2.3
N_2O	2.2
CO_2(e)	120,713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Methane is 2.3 lb/MMCF, CO_2(e) is 25 times the amount or 57.5 lb/MMCF.

N_2O is 2.2 lb/MMCF, CO_2(e) is 298 times the amount or 655.6 lb/MMCF.

Higher temperature combustion will generate more greenhouse gas while unburned methane while N_2O will increase CO_2(e) and more CO_2 will be generated due to PICs and CO decrease burning till full combustion.

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The best way to reduce Nitrogen/Oxygen emissions is to invest in low NOX combustion or fuel recirculation.

For engines Selective Catalytic Reduction (SCR) may be needed to reduce Nitrogen/Oxygen emissions using Urea injection in the flue gas to react with the Nitrogen/Oxygen compounds to generate Nitrogen Gas.

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In the future it is possible that hydrogen gas fuel will replace carbon based fuels with water as the only product of combustion.

Will NO_X and N_2O be still generated?

Can greenhouse gases and ground level (tropospheric) ozone be generated?

Can CO_2 generate (not necessarily from this reaction)?

Thank you

Questions?

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