

APTI Course 427

Combustion Source Evaluation

Chapter 5: Air Pollution Formation

Chapter Overview (outline)

- Introduction
- Acid Gases
- Particulate Matter
- Metals
- Nitrogen Oxides
- Smoke, Carbon Monoxide & Organic Compounds
- Opacity

Introduction (outline)

- Types of Pollutants
- Actual Emission Rates
- Potential Emission Rates
- Clean Fuels

Types of Pollutants

- Products of Incomplete Combustion (PIC)
- Pollutants resulting from inorganic contaminants in the fuel
- No_x
- Ozone, $\text{PM}_{2.5}$

Actual Emission Rates

- Measurements
- Mass balances
 - Gives an upper limit
- AP-42
 - Generic, not specific

Potential Emission Rates

Table 5-1. Emissions Originating in the Fuel

| <i>Fuel Constituent</i> | <i>Fuel Concentration</i> | | <i>Pollutant Concentration</i> | | <i>Primary Method of Control</i> |
|-------------------------------|---------------------------|-------------|--------------------------------|-------------------|----------------------------------|
| | <i>No. 6 Oil</i> | <i>Coal</i> | <i>Species</i> | <i>Conversion</i> | |
| Sulfur ⁽¹⁾ | 0.5 – 2% | 1 – 4% | SO ₂ | 99% | Low sulfur fuel |
| | | | H ₂ SO ₄ | 1% | Very low excess air |
| Ash | <0.05% | 10% | Particulate | 20 – 98% | Dust collector |
| | | | PM-10, 2.5 | 20 – 80% | Dust collector |
| Nitrogen ⁽²⁾ | <0.5% | 1% | NO _x | 10 – 50% | Combustion mod |
| Chloride | (low) | (low) | HCl | 100% | Fuel specs |
| C _n H _m | 98% | 85% | C, CO, HC | 0 – small | Combustion tuning |

Notes: [1] SO₄ in the fuel does not convert to SO₂ or sulfuric acid.
 [2] Only organic nitrogen contributes to NO_x formation.

Potential Emission Rates (cont.)

If 100% of contaminant converts to pollutant – eqn 5-1

$$\frac{\text{lb}}{\text{mmBTU}} = \frac{\% \text{ contaminant}/100}{\text{HHV} \left(\frac{\text{BTU}}{\text{lb}} \right) / 10^6} \times \frac{\text{lb pollutant}}{\text{lb contaminant}}$$

Example 5-1. Potential emissions

- Determine the potential SO₂ emission rate for 3% sulfur coal with HHV = 12,000 BTU/lb.

$$\frac{0.03 \left(\frac{\text{lb S}}{\text{lb coal}} \right)}{0.012 \left(\frac{\text{mmBTU}}{\text{lb coal}} \right)} \times \frac{64}{32} = 5 \left(\frac{\text{lb of SO}_2}{\text{mmBTU}} \right)$$

Clean Fuels

- Natural gas
 - Clean burning
 - Benefits catalysts
 - Significant pollutants
- Distillate oil
 - Some sulfur content
 - No premixed combustion

Acid Gases (outline)

- Sulfur Oxides
- Hydrochloric Acid

Sulfur Oxides

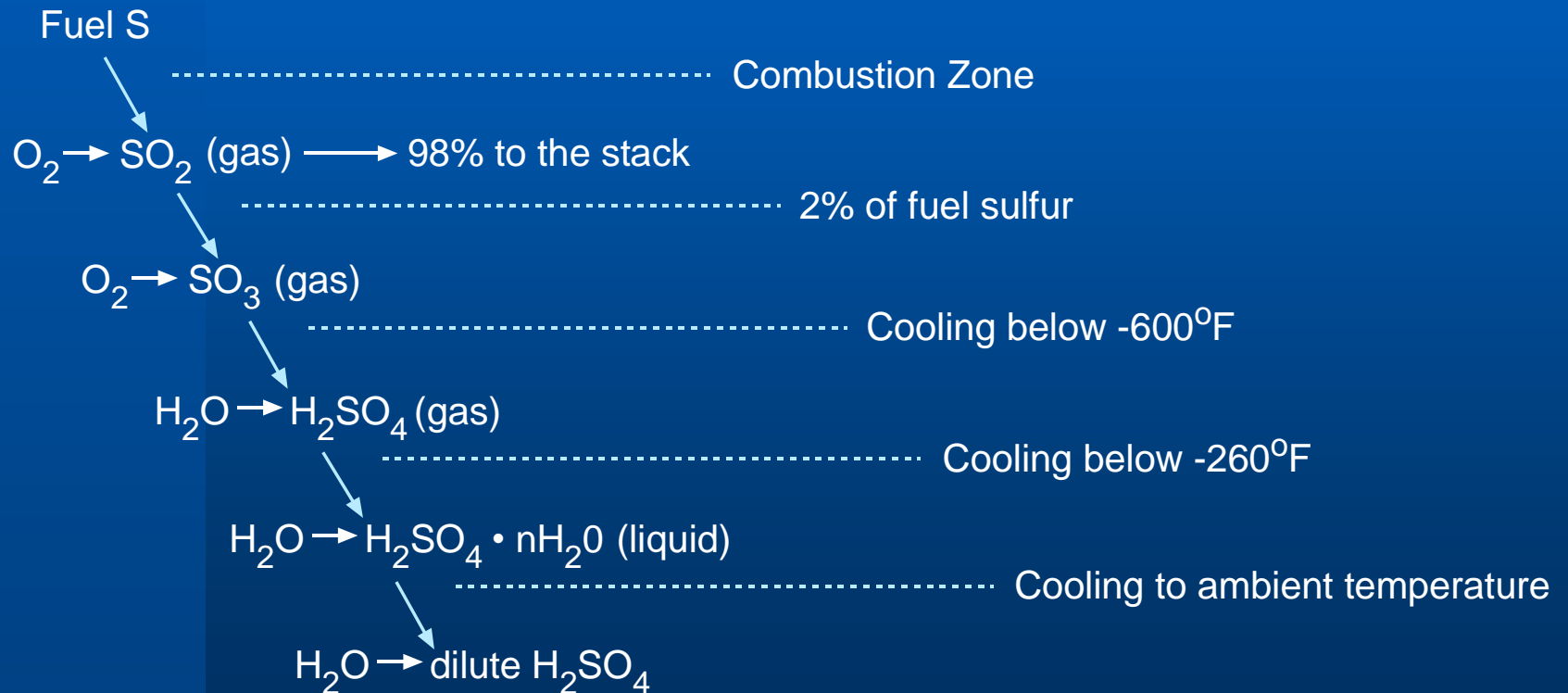
- SO_2
 - Emissions control by fuel S limits
 - Oxidizes slowly in the atmosphere

- SO_3 and Sulfuric Acid



Fuel Sulfur Conversion

Sulfur Oxidation



Example 5-2.

If 2% of the sulfur in oil with 1.5% S is converted to SO_3 , what is the flue gas concentration?

Solution: (a) Determine emission rate (lb/mmBTU)

$$\frac{0.015 \left(\frac{\text{lb S}}{\text{lb oil}} \right)}{0.0185 \left(\frac{\text{mmBTU}}{\text{lb oil}} \right)} \times \frac{80}{32} \left(\frac{\text{lb SO}_3}{\text{lb S}} \right) \times 2\% = 0.0405 \left(\frac{\text{lb SO}_3}{\text{mmBTU}} \right)$$

Example 5-2. (cont'd)

Convert this to ppm by volume

$$\frac{0.0405 \left(\frac{\text{lb SO}_3}{\text{mmBTU}} \right)}{10,500 \left(\frac{\text{ft}^3 \text{ fluegas}}{\text{mmBTU}} \right)} \times \frac{385}{80} \left(\frac{\text{ft}^3 \text{ SO}_3}{\text{lb SO}_3} \right) = 18.6 (10^{-6}) = 18.6 \text{ ppm SO}_3$$

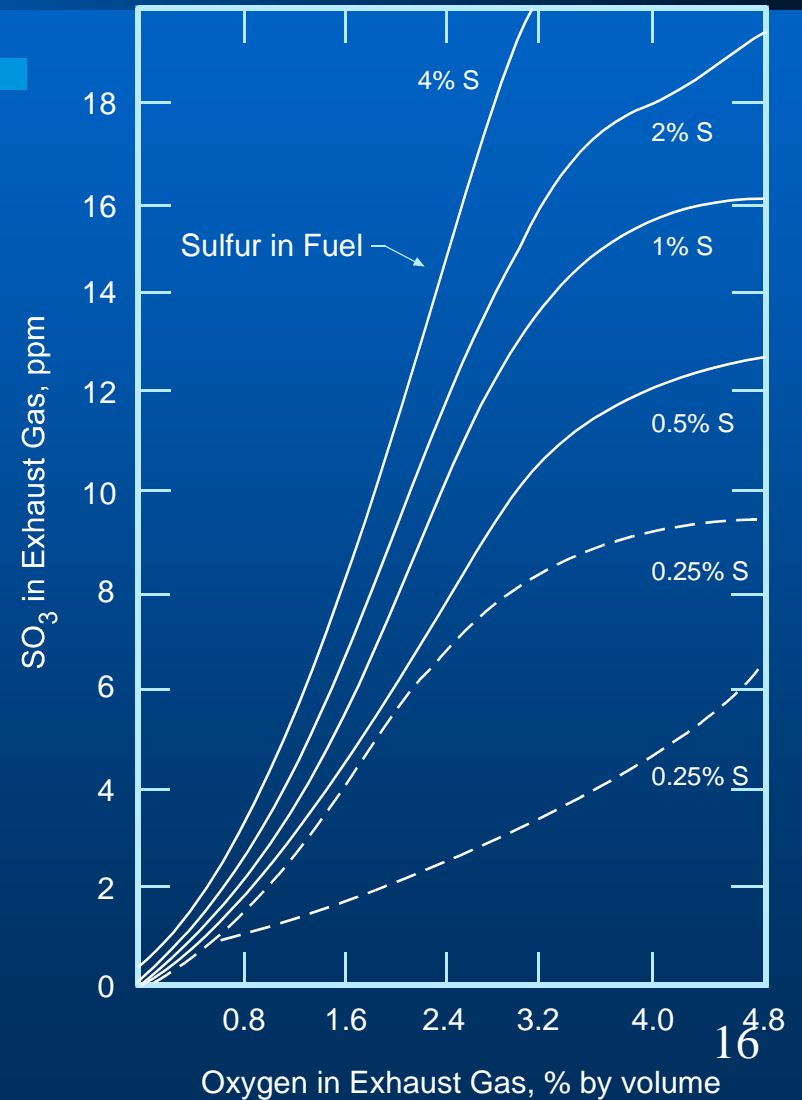
Correct this to a standard dilution level (3% O₂)

$$18.6 \text{ ppm} \times \frac{20.9\% - 3\%}{20.9\%} = 15.8 \text{ ppm SO}_3 @ 3\% \text{ O}_2$$

Conversion of Fuel Sulfur to SO_3

- Small but uncertain
- Vanadium influence
- Ash quantity and pH

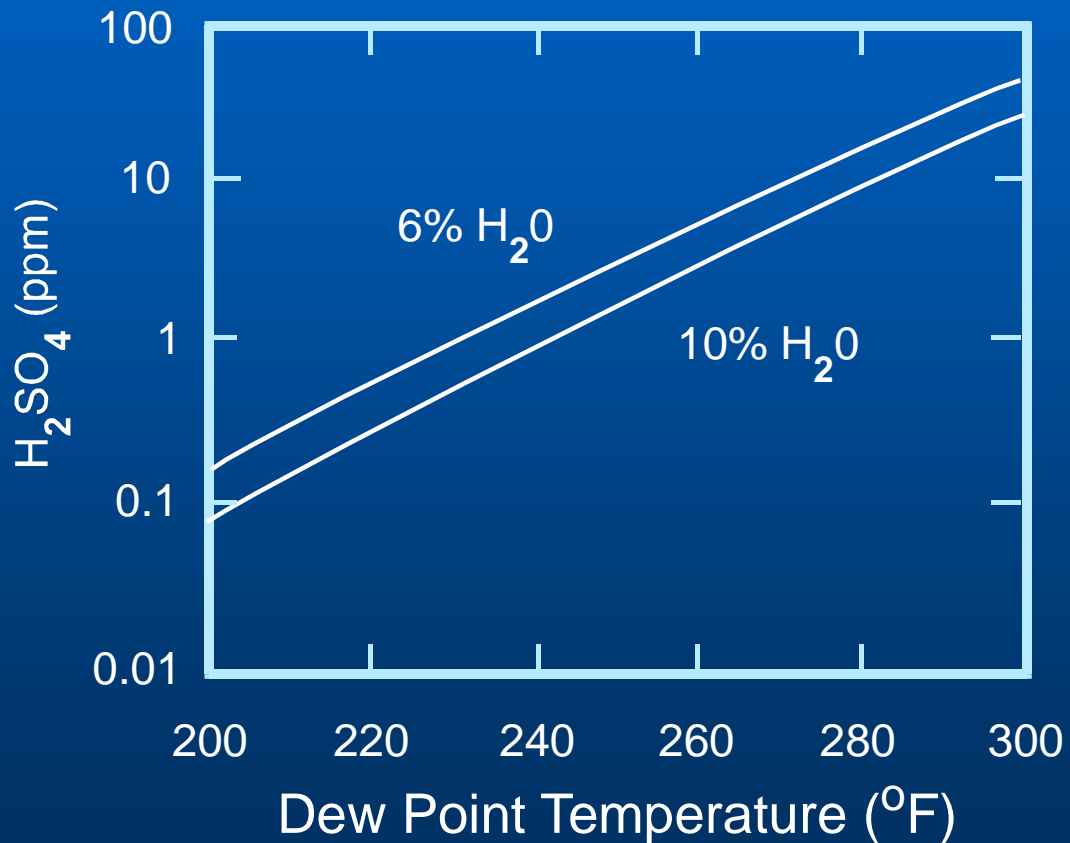
Conversion of Fuel Sulfur to SO_3 (cont.)



Sulfuric Acid Effects

- Plume impacts
 - Regional visibility
 - Plume behavior
 - Downwash
- Corrosion
 - Damage
 - Fallout

Sulfuric Acid Dew Point



Ash Interaction with Sulfur Oxides

- Coal ash
 - Acid interaction
 - Amount of scrubber solids
- #6 Oil ash
- Additives

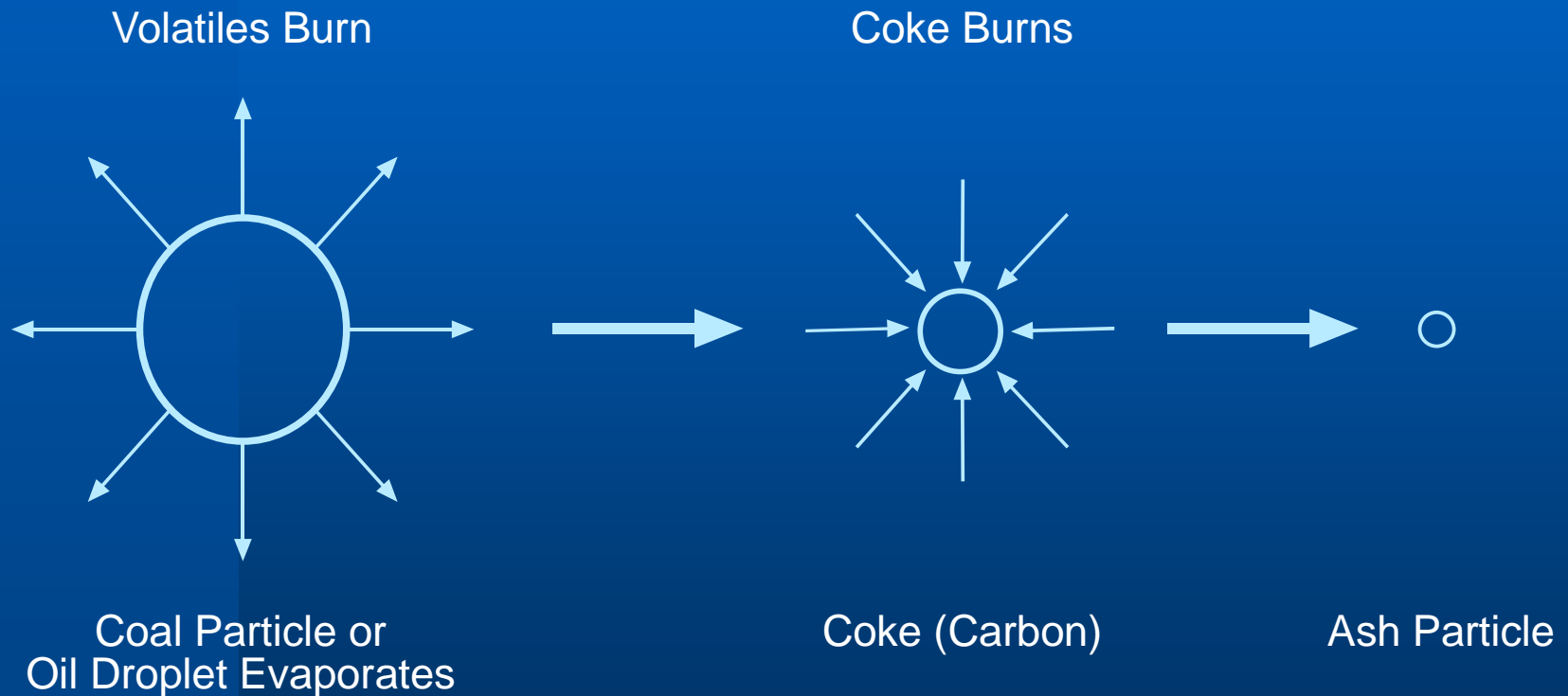
Hydrochloric Acid

- Organic vs Inorganic conversion Cl → HCl
- Cl₂ versus HCl
- Cl contribution to dioxins

Particulate Matter (outline)

- Particle Formation – two groups
 - Large Particles (mass)
 - Fine Particles (visibility)
- Enrichment of Some Chemicals in Fine Particles
- Mass Emission Transients from Soot Blowing

Particle Formation - Large Particles



Formation of Coke and Ash Particulate

Particle Formation - Fine Particles

- Formation mechanism
- 0.5 micron “limit”
- Species & particle surface area

Pulverized Coal Particulate

- Size
- Process
- Combustion time vs residence time

Example 5-3.

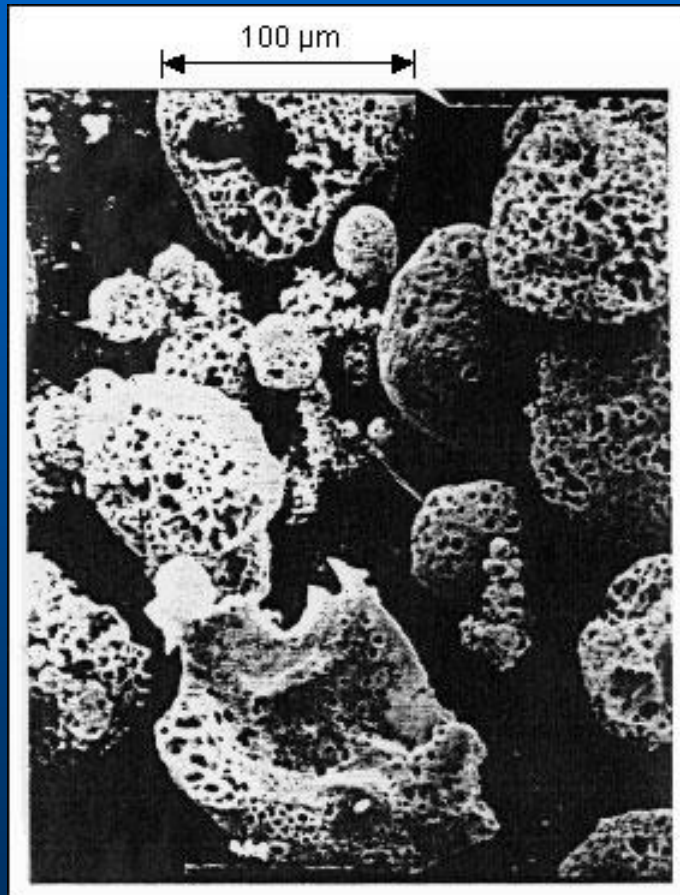
- Determine potential emissions for a PC furnace with coal properties are 9% ash and 12,500 BTU/lb. Assume 10% ash retention and no control.
- Solution:

$$0.09 \left(\frac{\text{lb ash}}{\text{lb coal}} \right) \div 0.0125 \left(\frac{\text{mmBTU}}{\text{lb coal}} \right) \times 90\% = 6.48 \left(\frac{\text{lb particulate}}{\text{mmBTU}} \right)$$

#6 Oil Emissions

- Particulate from
 - Ash
 - Sulfate
- Carbon
 - Coke
 - Soot (smoke)

Particulate from No. 6 Oil



Black Smoke

- Formation
- Combustion conditions required
 - Fuel rich area
 - Flame quenching
- Natural gas flames

Sulfuric Acid and Sulfate Particulate

- Acid or particulate or measurement method
- Coal-fired sulfate
- Oil-fired sulfate
- Formation factors
 - Fuel sulfur content
 - Vanadium
 - Excess air
 - Boiler ash deposits & temperatures

Example 5-4

A boiler fires #6 oil containing 1.4% sulfur and HHV = 18,500 BTU/lb. How much particulate is formed if 2% of the sulfur is oxidized to sulfate?

Solution:

$$0.014 \left(\frac{\text{lb S}}{\text{lb oil}} \right) \div 0.0185 \left(\frac{\text{mmBTU}}{\text{lb oil}} \right) \times \frac{96}{32} \left(\frac{\text{lb SO}_4}{\text{lb S}} \right) \times 2\% = 0.045 \left(\frac{\text{lb particulate}}{\text{mmBTU}} \right)$$

Enrichment of Some Chemicals in Fine Particles

Table 5-2. Some Elements Enriched in Fine Coal Fly Ash

| | | |
|-----------|------------|----------|
| Antimony | Gallium | Sodium |
| Arsenic | Lead | Thallium |
| Beryllium | Molybdenum | Uranium |
| Cadmium | Nickel | Vanadium |
| Chromium | Potassium | Zinc |
| Copper | Selenium | |

Mass Emission Transients from Soot Blowing

- Most emissions are emitted directly
- Ash accumulation
- Soot blowers
 - Purpose
 - Typical operation
 - Air pollution impacts

Metals (outline)

- Volatility of Metals and Compounds
 - Determines fine or course particle size
 - Affects health risk

- Mercury

Volatility of Metals and Compounds

- Examples – Table 5-3
- Vapor species vs vapor pressure
- Chloride compounds

Mercury

- Combustion emissions – vapor phase
- Emission sources
 - Municipal waste
 - Coal fired utilities
- Chemical forms
- Environmental fate

Example 5-5. Mercury emissions

Determine daily mercury emissions for an 800-megawatt power plant. Plant heat rate is 9900 BTU/kw-hr with a 60% utilization factor. It burns coal with 0.13 ppm mercury and HHV = 11,900 BTU/lb.

Solution:

(a) Determine emissions rate

$$0.13 (10^{-6}) \left(\frac{\text{lb Hg}}{\text{lb coal}} \right) \div 0.0119 \left(\frac{\text{mmBTU}}{\text{lb coal}} \right) = 10.9 (10^{-6}) \left(\frac{\text{lb Hg}}{\text{mmBTU}} \right)$$

Example 5-5 (cont'd)

(b) Determine daily energy use:

$$800,000(\text{kw}) \times 9900 \left(\frac{\text{BTU}}{\text{kw} - \text{hr}} \right) \times 60\% \times 24 \left(\frac{\text{hr}}{\text{day}} \right) = 114,048 \left(\frac{\text{mmBTU}}{\text{day}} \right)$$

(c) Multiply energy use x emissions rate:

$$10.9 (10^{-6}) \times 114,048 = 1.24 \text{ lb/day Hg emissions}$$

Nitrogen Oxides (outline)

- Overview of NO_x
- Thermal NO_x Formation
- NO_x Formation from Fuel Nitrogen
- Premixed and Diffusion Combustion
- NO_x from Typical Combustion Systems
- Control covered in Chapter 6

Overview of NO_x

- $\text{NO}_x = \text{NO}_2 + \text{NO}$
- NO_2 used for weight
- Ambient concentrations
- Ozone formation
- Other oxides
- All combustion makes NO_x : $\text{N}_2 + \text{O}_2 \leftrightarrow 2\text{NO}$

Control Approaches

- Two approaches
 - Combustion strategies
 - Back-end controls

Formation Mechanisms

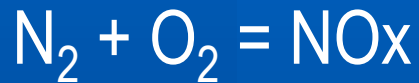
- Thermal NO_x
- Fuel NO_x
- Prompt NO_x

Typical Emission Rates

Table 5-4. AP-42 data for Uncontrolled NO_x Emissions

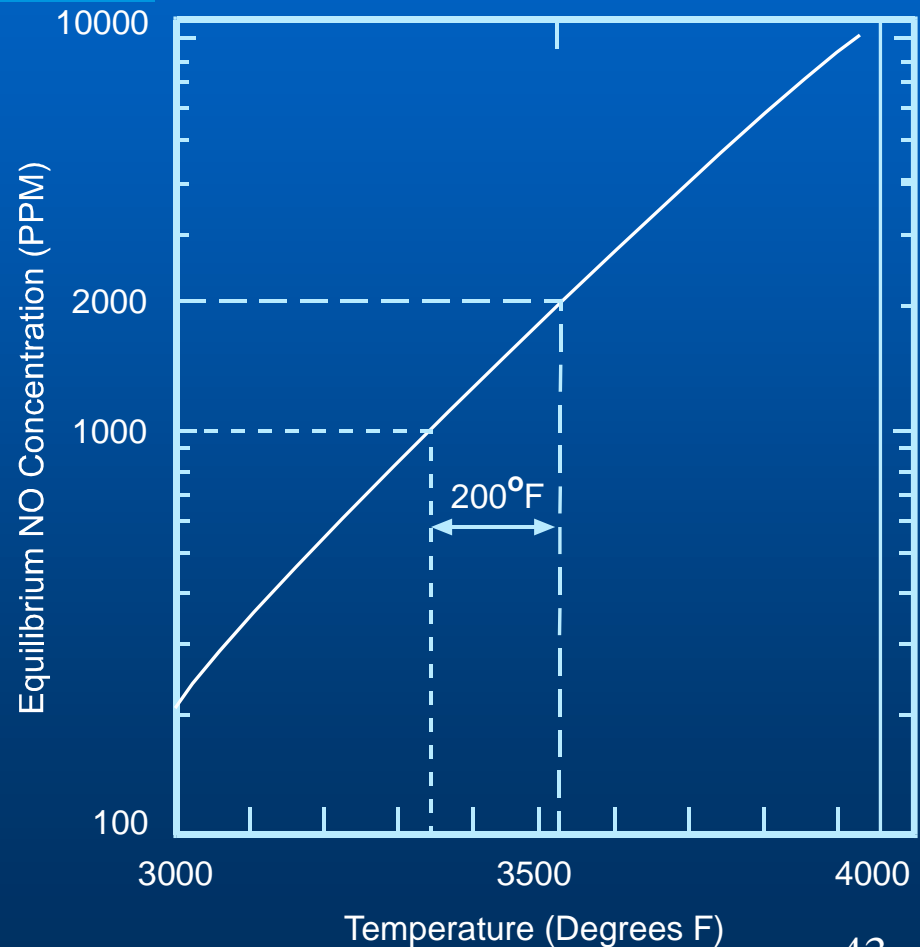
| <i>Combustion Source</i> | <i>AP-42 Units</i> | <i>Heat Input Units</i> |
|------------------------------------|------------------------|-------------------------|
| Combustion Turbine | 67.8 lb/1000 gal. fuel | 0.5 lb/mmBTU |
| Diesel Engine | 500 lb/1000 gal. fuel | 3.7 lb/mmBTU |
| Utility Boiler Firing No. 6 Oil | 67.8 lb/1000 gal. fuel | 0.46 lb/mmBTU |
| Commercial Boiler Firing No. 2 Oil | 20 lb/1000 gal fuel | 0.15 lb/mmBTU |
| Pulverized Coal Boiler | 21 lb/ton coal | 0.81 lb/mmBTU |
| Wood Fireplace | 1.8 lb/ton wood | 0.15 lb/mmBTU |

Thermal NO_x Formation



Modeling in real flames is complex

No significant decomposition



NO_x Formation

- Fuel impacts on NO_x
 - Amount formed
 - Control techniques
- Analytical approaches to predicting NO_x?

NO_x Formation from Fuel Nitrogen

- Fuel nitrogen can:
 - react with oxygen to form NO, or
 - react with another N atom to form N₂
- Affects boilers, not engines

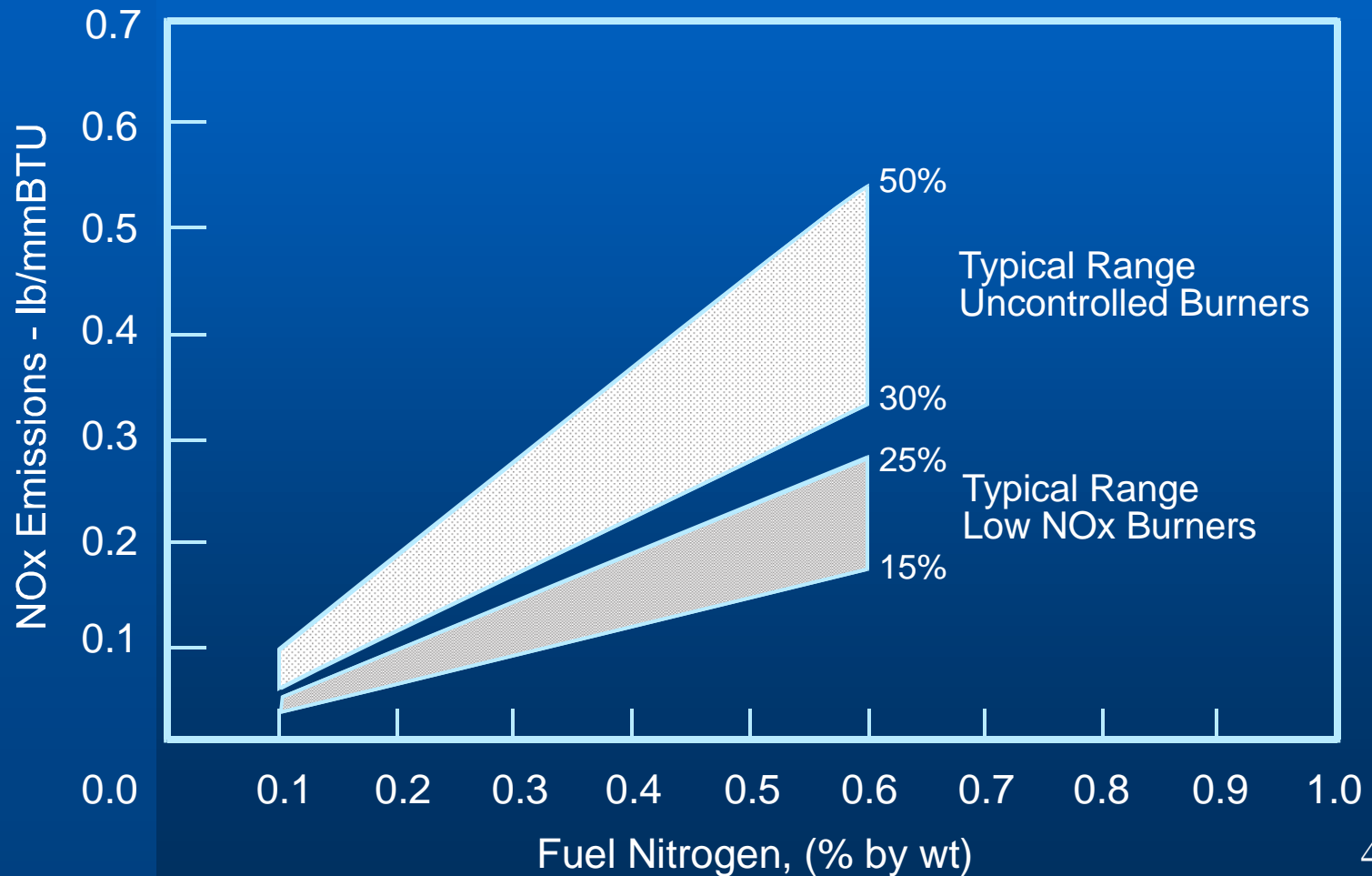
Example 5-6. Fuel NO_x

A utility fires coal with 1.3% N and HHV = 13,200 BTU/lb.
Find the potential NO_x emissions from fuel N.

Solution:

$$0.013 \left(\frac{\text{lb N}}{\text{lb coal}} \right) \div 0.0132 \left(\frac{\text{mmBTU}}{\text{lb coal}} \right) \times \frac{46}{14} \left(\frac{\text{NO}_2}{\text{N}} \right) = 3.2 \left(\frac{\text{lb NO}_x}{\text{mmBTU}} \right)$$

NOx Emissions vs. Fuel Nitrogen

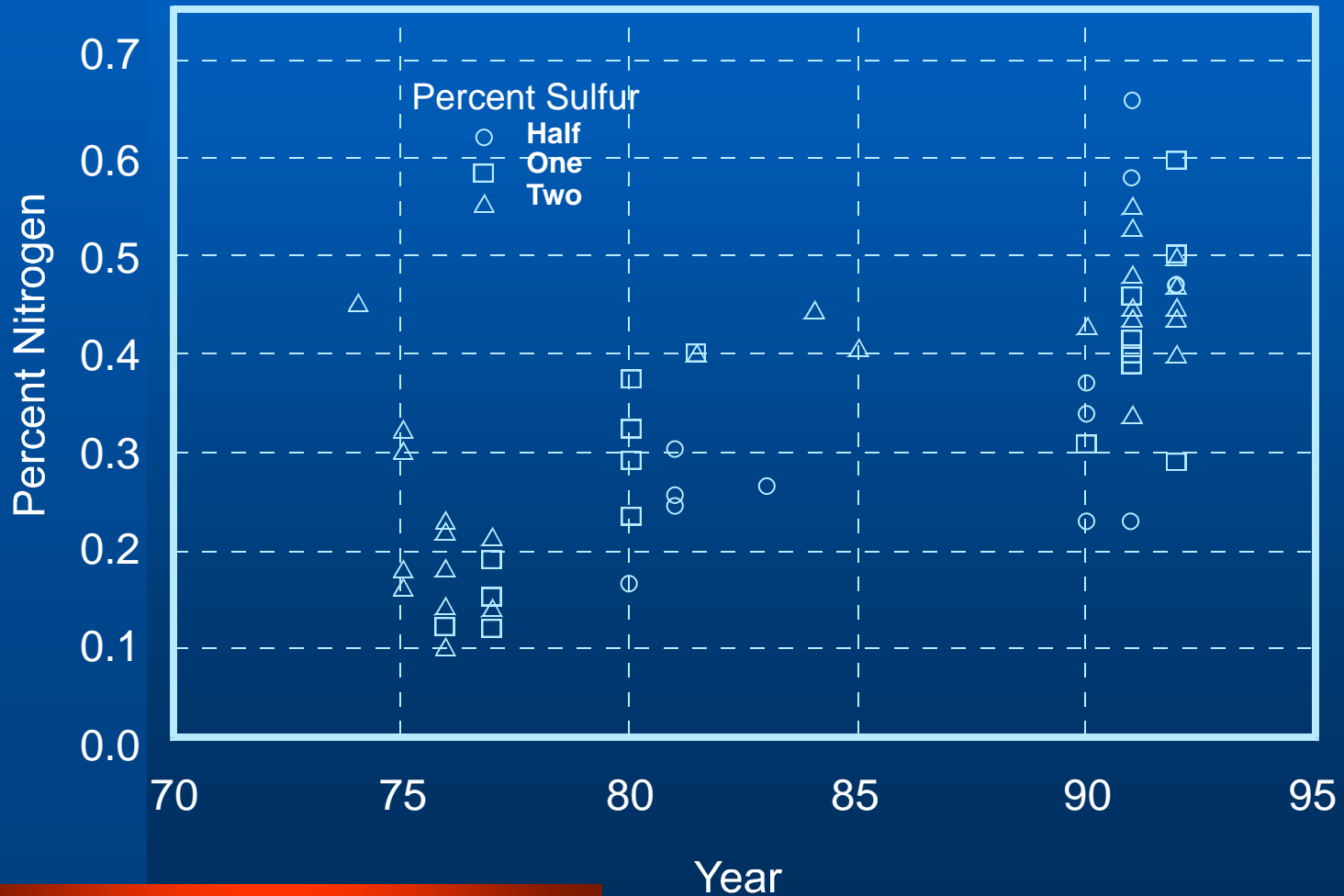


Typical Fuel N

Table 5-5. Typical Fuel Nitrogen Content

| <u><i>Fuel</i></u> | <u><i>Nitrogen (% by wt.)</i></u> |
|--------------------|-----------------------------------|
| Coal | 0.5 - 2 |
| Residual Oil | 0.3 - 0.6 |
| No. 2 Oil | < 0.1 |

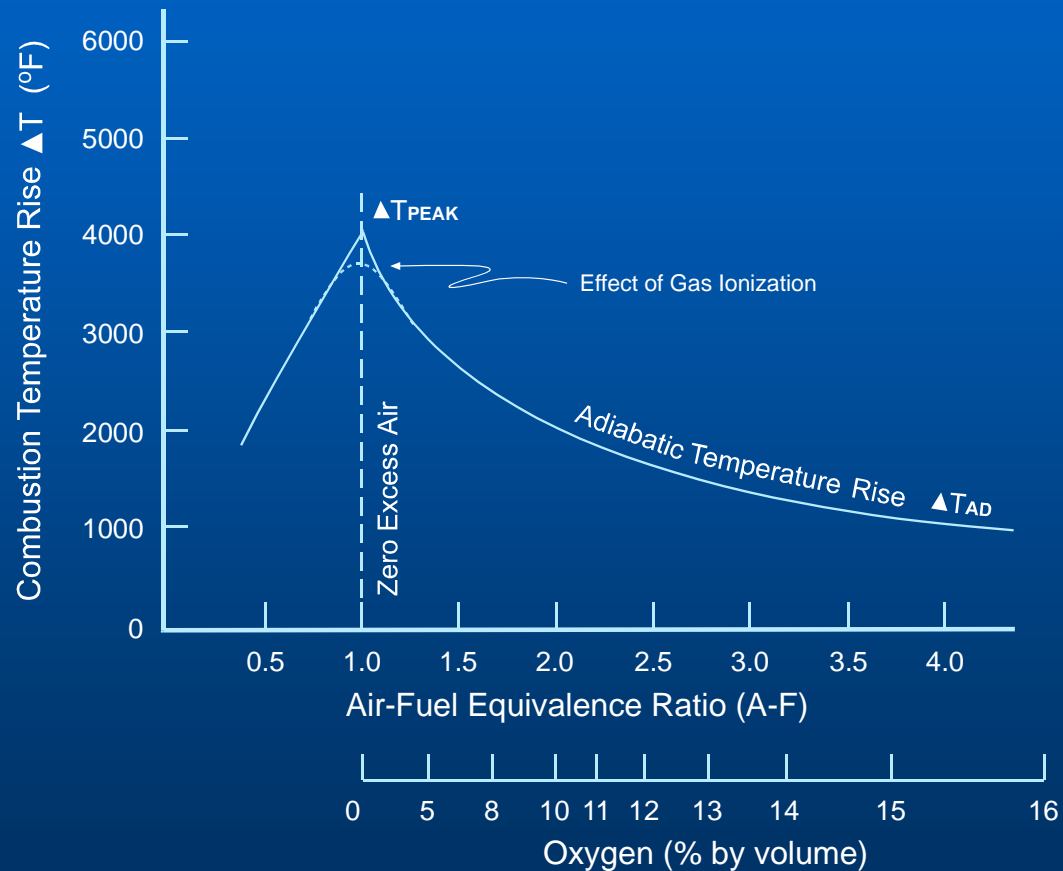
Residual Oil Nitrogen vs. Time



Premixed and Diffusion Combustion

- Diffusion
 - Typical of most combustors
- Premixed
 - Gas & gasoline reciprocating engines
 - Some low NOx combustors
- Temperatures of premixed & diffusion flames (Fig. 4-5)
- O₂ concentrations

Premixed and Diffusion Combustion (cont.)



NO_x from Typical Combustion Systems (outline)

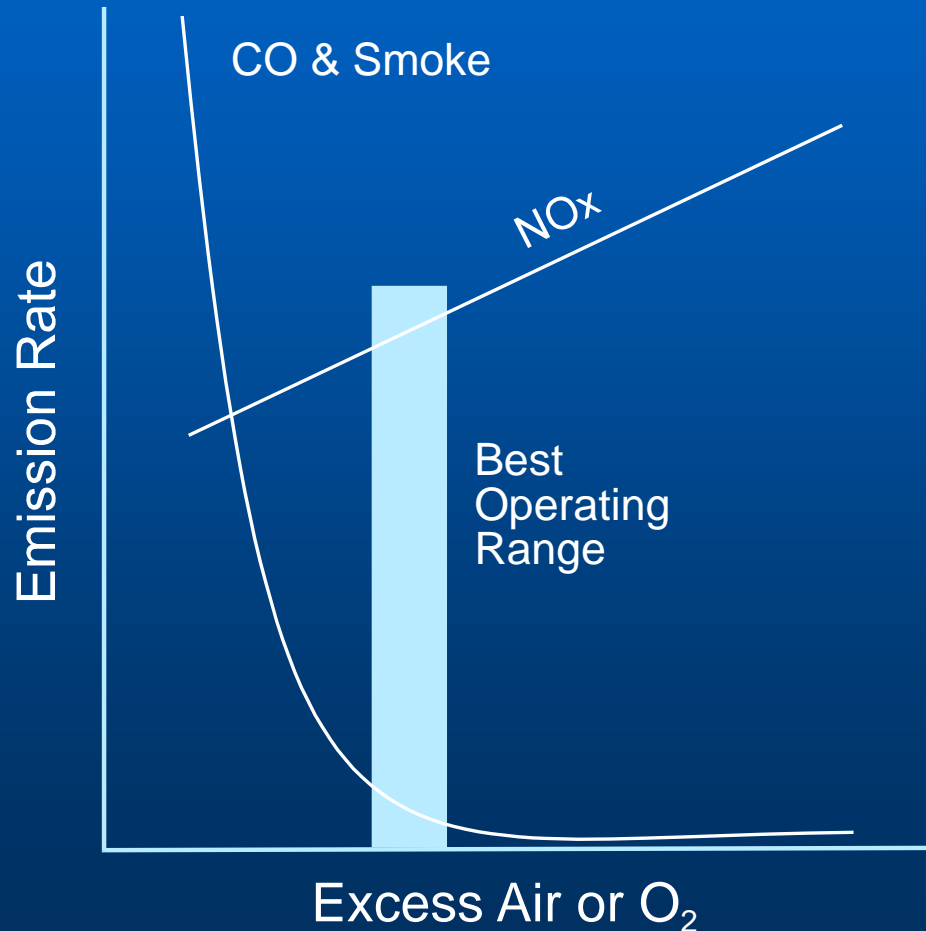
- History of NO_x control
 - Combustion versus back end
- Combustor categories
 - Boilers and Furnaces
 - Reciprocating Engines
 - Combustion Turbines
- Load range impacts

NO_x from Boilers and Furnaces

- Wide range of sizes & fuels
- Temperatures
- Air & fuel flow control
 - Matching air to fuel
 - Trade off of PIC & NO_x (Fig. 5-9)

NO_x from Boilers and Furnaces (cont.)

Typical NO_x and CO vs. Excess Air



Fuel Effects on Boiler Emissions

- Three fuel categories:
 - (1) Clean fuels
 - (2) Residual oil, pulverized coal sander dust
 - (3) Solid fuels

Fuel Effects on Boiler Emissions (cont.)

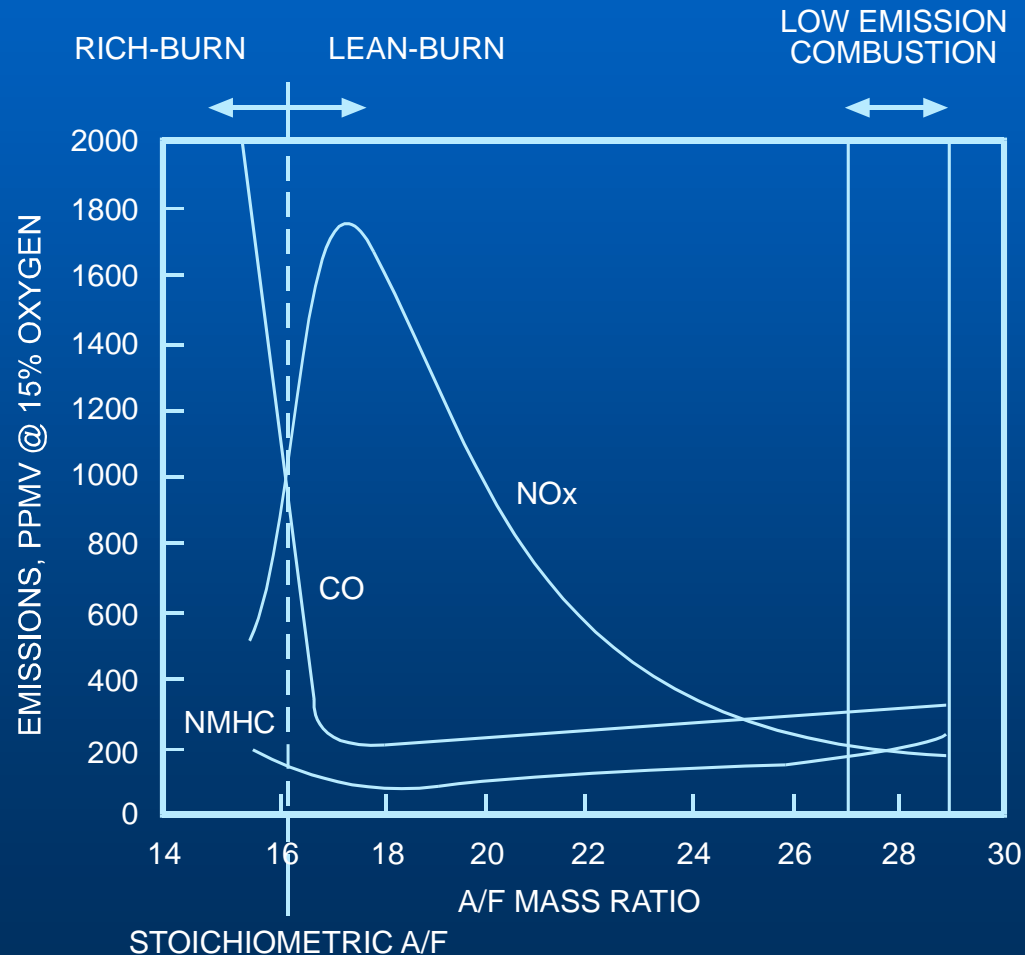
- Suspension versus grate burning
- Size implications
 - Small boilers =?? Clean fuel
 - Multiple burner implications

NO_x from Reciprocating Engines

- Fuels
- Operating temperature & pressure
- NO_x emission levels (Fig 5-10)
- Diesel versus gas engines
 - Diffusion vs premix
 - Rich burn & lean burn
- Emission predictability

NO_x from Reciprocating Engines (cont.)

Emissions vs.
Excess Air for Gas
Fired Engines



Combustion Turbines

- Overview
 - Aircraft derivative
 - Steady state combustion
 - Traditional versus new “low NOx” combustors
- Fuel flexibility
- NOx emissions
 - Use of water injection
- Predictability
 - Integration of engine & emission controls
 - Ambient conditions

Smoke, Carbon Monoxide & Organic Compounds (outline)

- Complete Combustion and Fuel-Air Mixing
- Burner Geometry
- Excess Air
- Incinerator Temperatures
- Dioxin-Furan Formation

Complete Combustion and Fuel-Air Mixing

- PIC
 - Organics (VOC)
 - Smoke (carbon) & CO
 - Startup & transient operation
- CO
 - Surrogate for organics
 - Typical levels

Elements of Complete Combustion

- Effective fuel air mixing
- Sufficient O₂
- No quenching

3 T's of Combustion

- Time
- Temperature
- Turbulence

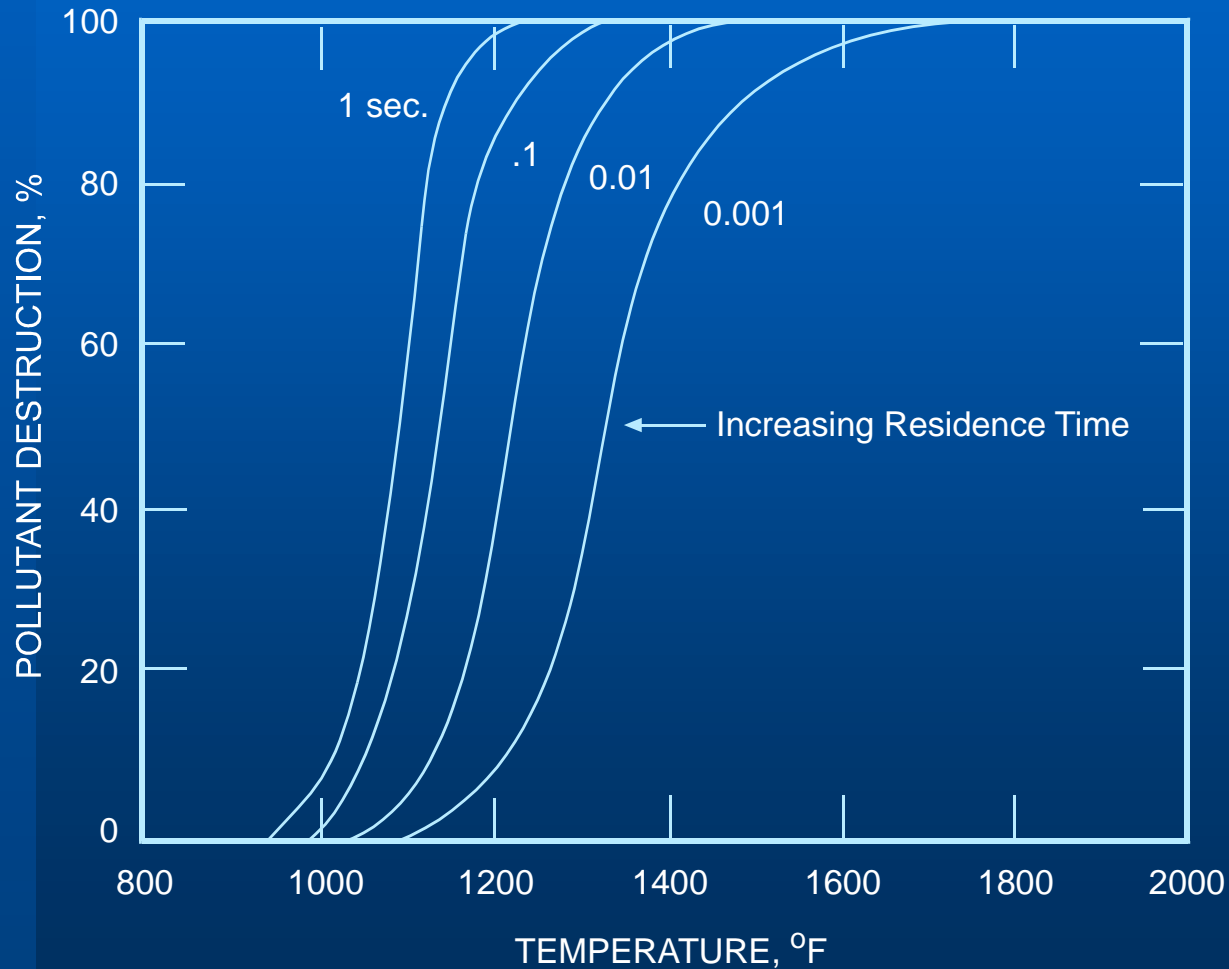
Burner Geometry

- Objective: complete, fast fuel-air mixing
- Geometry (design) governs mixing
 - Air flow pattern
 - Fuel injection pattern
- Good mixing → low PIC emissions
- Low NO_x combustion is different

Excess Air (review)

- A basic requirement
- Burner performance characterized by LEA
- Minimum (& maximum) excess air levels
- Operating for no smoke versus low NO_x

Incinerator Temperatures



Solid Waste Incinerators

- Basic design is important
 - Nonuniform combustion is a given
- High temperatures typically necessary
- Good excess air control

Dioxin-Furan Formation

- PCDD and PCDF
 - Stable & persistent
 - Combustion generated
- Toxicity
 - Very low levels are of concern
- PIC formation
 - Mostly from Cl aromatics, but . . .
 - Some organic fragments required
- Sources
 - Transformer fires, bad incinerators, forest fires
- Elimination

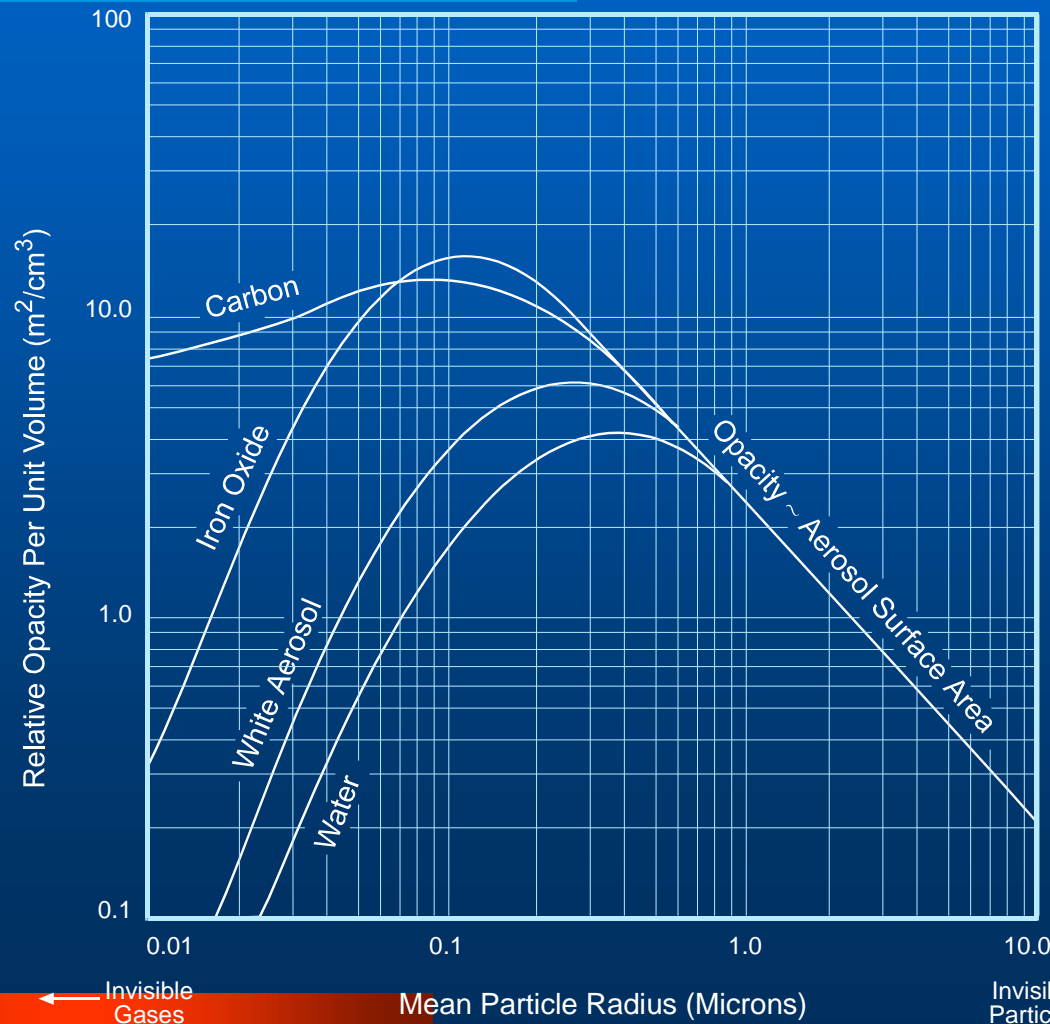
Dioxin-Furan Formation (cont.)

- Back end formation
 - 500°F
 - Cl₂ & organic PIC
- Avoidance

Opacity

- Regulatory background
- Method 9 versus Method 5
- Opacity vs. Particle Size

Dust Opacity vs. Particle Size



Opacity vs. Emission Rate

- Coal fired particulate emissions
- Residual oil-fired particulate
 - Mass emissions
 - Black plumes
 - White, brown, misc. plumes
- Sulfuric acid mist opacity

Conclusions

- Emission generating mechanisms
- Pollutant quantity – conservation of mass
- Combustion influence on PIC and NOx
- Particulate emissions
 - Large particles
 - Fine particles

Chapter Summary

- Introduction
- Acid Gases
- Particulate Matter
- Metals
- Nitrogen Oxides
- Smoke, Carbon Monoxide & Organic Compounds
- Opacity