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APTI 427: *Combustion Source Evaluation* is a four-day, resident instructional course designed to introduce combustion-related pollution problems such as estimating the actual and potential air pollution emissions from combustion sources; reviewing applications for permits to construct combustion facilities; and developing recommendations to improve the performance of malfunctioning combustion equipment. The course is intended primarily for those with an engineering and/or scientific degree, or completion of course RE100 and OL 2000, or six months of equivalent work experience. Major topics discussed include:

- Combustion sources burning liquid and solid wastes
- Combustion sources burning fossil fuel
- Combustion engines (diesel engines, gas turbines, etc.)
- Pollution control devices
- Combustion principles
- Design and operational parameters
- Selected fundamental calculations
- Fuels

How to Use This Workbook

This workbook is to be used during classroom instruction, telecourse sessions, and individual study. The workbook contains instructional objectives and materials for each of the seven chapters.

Each chapter provides a lesson goal, instructional objectives, subject narrative, and reference materials that may guide your study. Each chapter also contains a reproduction of selected lecture slides intended to guide your notetaking. The slides are presented to generally follow the course outline; however, the instructor may on occasion vary the order of presentation or present material not included in the workbook. Each student, therefore, should take thorough notes of the lecture content throughout the course, but not rely solely upon graphic reproductions for the course content.

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LIST OF TERMS AND ACRONYMS

TERM	DEFINITION
ACFM	Actual cubic feet per minute
BACT	Best Available Control Technology
BIF	Boilers and Industrial Furnaces - refers to federal waste fuel use regulations
CAAA	Clean Air Act Amendments
CEM	Continuous Emission Monitors
CFC	Chlorofluorocarbon
CT	Combustion Turbine
DAS	Data Acquisition System
DP	Differential Pressure or Delta P
DSCFM	Dry standard cubic feet per minute
engine	Either a combustion turbine or a reciprocating engine
EPA	Environmental Protection Agency
ESP	Electrostatic Precipitator
F_c-factor	Standard cubic feet of CO_2 generated when 10^6 BTU of energy is released by combustion. Value varies from 1000 to 2000 depending on the fuel.
F_d-factor	Standard cubic feet of dry flue gas with zero excess air generate when 10^6 BTU of energy is released by combustion. Value is between 8700 and 9900 depending on the fuel.
F_w-factor	Similar to F_d except water vapor is included. Value is about 10,500 for most fuels; somewhat higher for high moisture fuel.
FGC	Flue gas conditioning – adding something such as SO_3 to the flue gas to improve performance of a control device such as a dust collector.
FGD	Flue gas desulfurization
FGR	Flue gas recirculation - technology used to reduce the formation of NOx emissions by recirculating flue gas into the combustion.
FID	Flame ionization detector

FRM	Federal Reference Method – all the test methods in 40CFR60 Appendix A.
HAP	Hazardous Air Pollutants
Heat input rate	Usually the same as fuel firing rate – normal units: mmBTU/hr
HHV	Higher Heating Value (of a fuel) - a number obtained by a lab analysis that includes the energy from condensing all moisture in the flue gas; usually reported as BTU per pound. This number is always higher than the LHV.
incineration	Combustion for purposes of destruction/disposal; usually implies there is no energy recovery. A politically incorrect term in some circles.
LEL	Lower Explosive Level – the volume concentration of a gas in air at which it can be ignited (e.g. explode) - in air this typically requires an energy content of about 50 BTU/ft^3 of mixture.
LHV	Lower Heating Value (of a fuel) – a number in BTU/lb obtained by a lab analysis that excludes the energy from condensing moisture in the flue gas; usually reported as BTU per pound. This number is always lower than HHV.
LNB	Low NOx Burner – federal and local definitions of what this means are absent or vague.
MACT	Maximum Achievable Control Technology
MW	Molecular weight
NAAQS	National Ambient Air Quality Standards
NDIR	Non-dispensive infrared
NESHAP	National Emission Standards for Hazardous Air Pollutants
NSCR	Non Selective Catalytic Reduction – NOx destruction by reaction with CO and hydrocarbons – typically used in automobile exhaust systems.
NSPS	New Source Performance Standards
OFA	Over-fire air
PC	Pulverized coal
PIC	Products of Incomplete Combustion – e.g. carbon, CO and organic compounds
ppm	Parts per million. When referring to gas concentration ppm is on a volume basis. Otherwise it is usually on a weight basis.

ppmd	Parts per million by volume, dry basis – all water removed from the gas.
ppmw	Parts per million by volume, wet basis – all water vapor remains in the gas during analysis.
psi	Pounds per square inch
RM	Reference Method (test) – see 40CFR60 Appendix A.
SCA	Specific collection area
scf	Standard cubic feet – gas volume at 68°F and 29.92 inches mercury atmospheric pressure.
scfm	Standard cubic feet per minute
SCR	Selective Catalytic Reduction – NOx destruction (control) method similar to SNCR, but at much lower temperature by using a catalyst.
SIP	State Implementation Plan
SMD	Sauter Mean Diameter – a definition of droplet diameter that yields a number proportional to the surface area of the drops in a liquid fuel spray.
SNCR	Selective Noncalytic Reduction System
Standard pressure	Atmospheric pressure at sea level = 29.92 inches = 760 mm Hg = 14.7 psia
Standard temperature	68°F = 528°R = 20°C = 293°K
Stoichiometric ratio	The air/fuel (or fuel/air) ratio compared to the ratio at which the amount of oxygen is exactly sufficient to completely burn all the fuel (1.0 means perfectly matched).
STP	Standard Temperature and Pressure
Thermal loading	Heat release per unit furnace volume, usually BTU/hr per ft^3
TRS	Total Reduced Sulfur – gaseous sulfur compounds not including sulfur oxides.
UEL	Upper Explosive Limit
VOC	Volatile Organic Compound
W.C. or w.g.	Water column or water gage – a measurement (usually in inches) of gas pressure using a manometer.
WtE	Waste to Energy – usually refers to municipal garbage fueled boilers that generate electric power.

USEFUL DATA

ENERGY DIMENSIONS

1 BTU = Energy to heat 1 lb H_2O x 1°F
(10^6 BTU = 1 mmBTU)
1000 Joules = 0.948 BTU (a Joule is a Newton-Meter)
(Approximately 1000 BTU is required to evaporate 1 lb water into steam)

ENERGY RATE vs POWER

1 BTU/hour = 0.293 WATTS
3410 BTU = 1 Kilowatt-hour
1000 BTU/hr = 0.393 Horsepower
(10^6 BTU/hr . 30 "Boiler HP"; 100 Boiler HP = 3450 lb/hr Sat. Steam)
1 hp = 0.746 kw

CONVERSION FACTORS

Atmospheric Conditions at sea level (standard conditions)

Pressure	14.7 psia 1013 millibars 29.92 inches Hg 760 mm Hg
Air Density	0.0764 lb/ft^3 @ 60F 0.075lb/ft^3 @ 68F (or 385 ft^3 per lb-mole) (EPA Standard)

Flue Gas Density: usually similar to air - for high moisture levels use a weighted average -
0.046xB + 0.075x(1 - B)
where B is the weight fraction of water.

Absolute Temp (ERankine) = 460 + EFahrenheit
Absolute Temp (EKelvin) = 273 + ECentigrade
°R = 1.8 x °K
Standard Temp = 68°F = 528°R = 293°K

Molecular Weight (MW):	Air	28.97
	Typ. combustion flue gas	28.5 - 30

AIR EMISSION CONVERSIONS

Multiply	by	To obtain
grains/ft^3	2.29	gm/m^3
ppm	41.4 x mol. wt.	µg/m^3
lb/mmbtu	$\frac{387(10^6)}{Fd \times MW} \times \frac{20.9 - y}{20.9}$	ppm @ y%O_2
	(where Fd = dry F factor)	
lb	7000	grains
lb	453	grams

FORWARD

Course Purpose

This course is directed toward the community of individuals responsible for regulating sources of air pollution – inspectors, permit writers, enforcement agents and those who write the rules. The overall intent is to provide an understanding of how various combustion systems work so that regulation of the resulting air pollution is viable, but no more burdensome than necessary. APTI 427 is an advanced course that requires students to have some experience or exposure to air emissions measurements and at least passing familiarity with stationary combustion sources such as boilers, power plants or stationary engines. That being said, each section of this book attempts to provide an introduction for those unfamiliar with stationary source air pollution. This text will serve as the primary document for students taking this course, and is intended to serve as a useful reference once the course is complete.

Organization of this text follows the intended course sequence. This required some compromises between the best course sequence and the organization that would be optimum for a reference book. For example, the discussion of fuels in Chapter 4 overlaps the information on combustion systems presented in Chapter 2, and it is unnatural to separate NOx formation in Chapter 5 from NOx control in Chapter 6. In particular, Chapter 7 is a review, which includes material that may fit well in several preceding chapters.

References are included at the end of each chapter. References in each list are intended as sources of additional information rather than to identify the origin of any material in the body of each chapter.

Relationship to Other APTI Courses

The course content of several other APTI overlaps the material in this course. These courses include:

1. APTI Course 413, "Control of Particulate Matter Emissions"
2. APTI Course 415, "Control of Gaseous Emissions"
3. APTI Course 418, "Control of Nitrogen Oxide Emissions"
4. APTI Courses 474, "Continuous Emission Monitoring"
5. APTI Course OL2000, "Basic Concepts in Environmental Science"

Most of our largest combustion sources are fired with coal and they all have dust collectors to control particulate emissions. This course provides an abbreviated

coverage of dust collectors commonly used on combustion sources in Chapter 6. Similarly many of our larger combustion sources emit SO_2 and they increasingly are using scrubbers to control emissions. Most stationary sources have negligible VOC emissions, but combustion devices are one way to control VOC emissions from other types of sources. This course provides a substantial discussion of thermal oxidizers and incinerators. Since one of the primary methods of controlling NOx emissions is by combustion system design, NOx emissions are discussed here in considerable detail. Monitoring methods are not covered in this course, but there is considerable discussion of how to interpret and use monitoring data.

Chapter 1: Overview

LESSON GOAL

Demonstrate a general understanding of the significance and types of combustion sources and the variety of pollutants they emit through successful completion of the chapter review exercises.

STUDENT OBJECTIVES

When you have mastered the material in this chapter, you should be able to:

1. Provide examples of some common types of combustion sources.
2. Describe how carbon and energy are related in the global carbon cycle.
3. Provide a general perspective on the fuel/energy sources and their uses in the U.S.
4. Describe generally the major types of combustion sources and their potential air pollutants.
5. Describe the most common ways or dimensions of reporting air pollutant emissions.
6. List, in general terms, three principal categories of air pollution from combustion sources.
7. List at least one significant pollutant associated with each of the major types of fuel or combustion source.
8. Describe briefly the two types of engines used in mobile and stationary sources of combustion and the principal air pollutant(s).
9. Describe a steam-electric power system and draw a simple schematic of its operation.
10. Discuss other combustion sources such as cement kilns, solid waste incinerators, hazardous waste incinerators, and thermal oxidizers.

Chapter 1: Overview

1.1 SIGNIFICANCE OF COMBUSTION SOURCES

Combustion sources are everywhere in the industrial world. Combustion is arguably more vital to our society than fire was to early man. As one can see from the list of common combustion sources in Table 1-1, combustible fuel sources touch our lives almost continuously in one form or another. Electric power can be generated from non-combustion sources, such as wind, solar and hydroelectric energy, but the vast majority of the U.S. power comes from the combustion of fossil fuels, such as coal, oil, and natural gas.

Table 1-1. Examples of Sources and Fuels

Source Type	*Principal Fuels*
Steam-electric power plant	Bituminous coal, subbituminous coal, residual oil, natural gas (fossil fuels)
Waste-to-energy steam power plant	Wood, municipal solid waste, misc.
Factory boiler	Gas, No. 2 oil, No. 6 oil, site specific waste
Combustion turbine power plant	Natural gas or distillate oil
Cement kiln	Fossil fuels, tires, used oil, hazardous waste
Residential or commercial furnace	Natural gas or No. 2 oil
Trucks, cars & railroad engines	Gasoline or diesel fuel
Incinerators	Natural gas fumes, organic liquid and solids

This chapter provides a general overview of the significance and variety of each of these fuels used during the combustion process. The major sources of combustion, such as engines, boiler systems, and others, will be discussed in later sections of this chapter. However, the emphasis in this brief overview is to discuss the sources of combustion that are most relevant to air pollution control and emission-oriented projects.

1.2 CARBON AND ENERGY

All the common fuels are hydrocarbons. Most include a large number of compounds that may include oxygen and various contaminants. But their energy, and therefore their fuel value, derives almost entirely from the oxidation of carbon and hydrogen. Since all fuels are, or were, formed with the help of solar energy, fuels represent stored solar energy, which we release at our convenience in combustion devices. Figure 1-1 illustrates the cycle in which carbon dioxide is converted to hydrocarbons by photosynthesis with solar energy, followed by oxidation back to CO_2. Although the actual pathways are complex, the total energy released during oxidation is the same as the energy absorbed during photosynthesis. Hydrocarbon fuels are an efficient and practical way to store a large amount of energy.

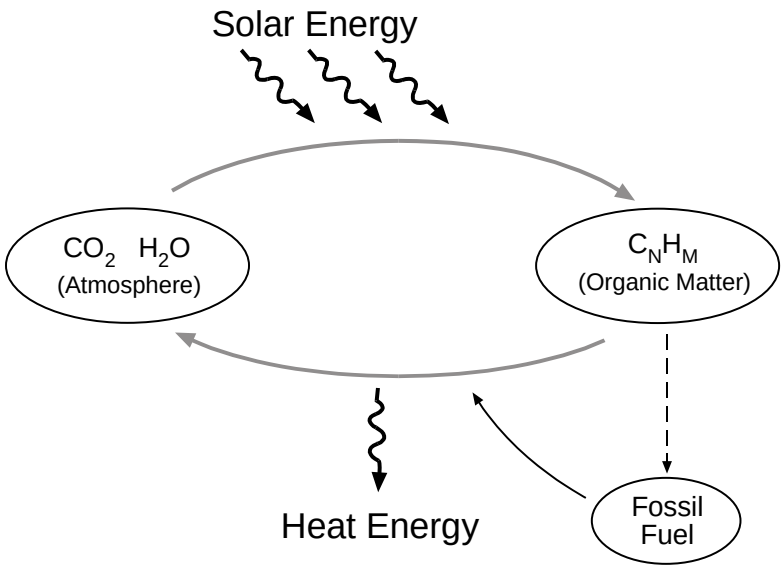

Figure 1-1. Energy and Carbon Cycle

In Figure 1-1, hydrocarbons are divided into two groups according to the timescale in which they participate in the cycle. The "organic matter" hydrocarbons are all living matter, wood and other biologic material on the surface of the planet. Most of this material will oxidize and return to the atmosphere within a few months or years either by combustion, natural decay or conversion in the bodies of living animals. Fossil fuels, on the other hand, were created originally from green hydrocarbons. However, they have been sequestered for hundreds of millions of years, so the cycle time for fossil carbon is on a scale that is hard to comprehend.

The combustion required to power our society takes carbon, which was sequestered long ago, and returns it to the atmosphere. Atmospheric carbon dioxide levels have, over the past century, increased from about 270 ppm to about 360 ppm indicating that the emissions rate to the atmosphere exceeds the rate that natural systems can sequester or convert carbon dioxide to green hydrocarbons. Figure 1-2 represents

data compiled by the Department of Energy showing recent annual energy production and consumption in the U.S. (2000). Note that fossil fuels account for about 82% of the total energy used in the U.S.

Energy Flow 2010, Quadrillion Btu

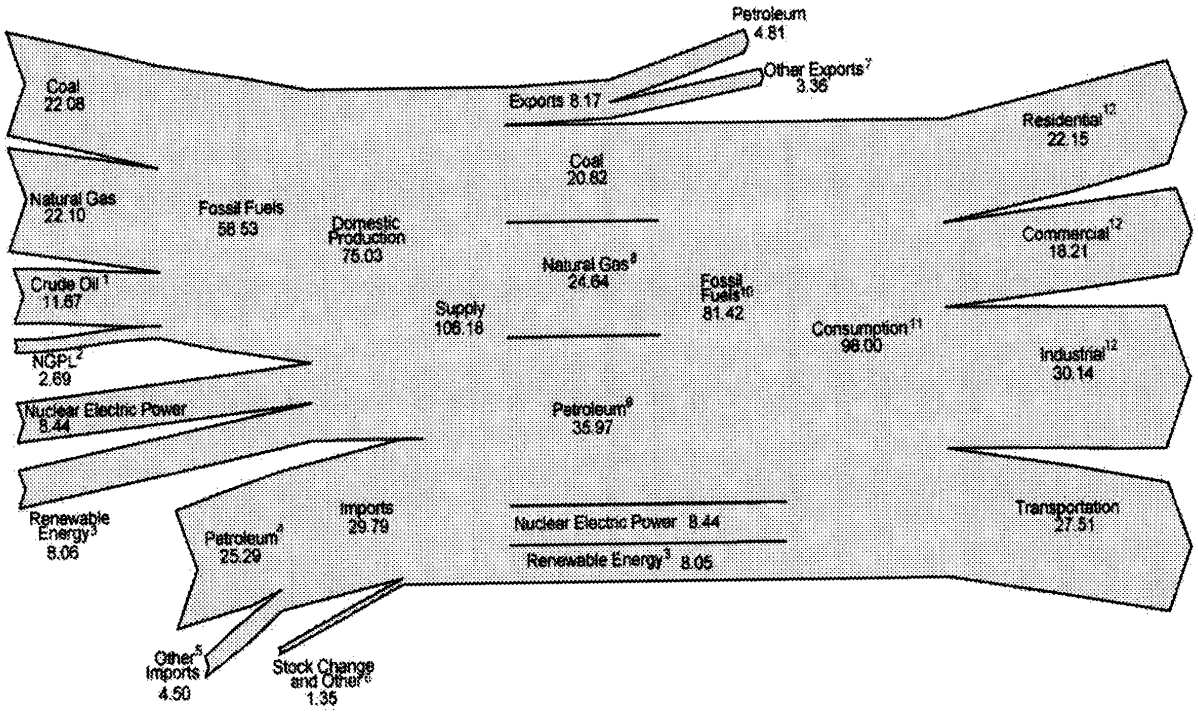

Figure 1-2. Annual U.S. Energy Production and Consumption

U.S. Department of Energy, Energy Information Administration, Annual Energy Review 2010, available at www.eia.doe.gov/oiaf/aeo/index.html.

Thus far, there has been much less public concern with the part of the combustion cycle where solar energy is stored in living matter than with the use of that stored energy. Although we have developed ever more effective ways to use hydrocarbon fuels, combustion systems and their resulting air pollution continue to be a major source of concern.

1.3 FUELS

Combustion systems and emissions controls are developed around specific fuels. For example, an automobile engine and its exhaust catalyst will only function properly using gasoline with specific characteristics; the engine will not run if the tank is filled with No.2 oil. Some sources are built to run on several different fuels. Boilers are a good example; most coal-fired boilers can also fire either oil or gas. In addition, any oil-fired boiler can be retrofitted to fire gas. The fuel limitations of a combustion device go beyond the fuel handling hardware for a number of reasons – usually

related to the amount of ash in the fuel or the corrosive character of the resulting flue gas. Table 1-2 summarizes a number of fuels and the dominant characteristics that relate to air pollution or combustion system design.

Table 1-2. Fuel Characteristics

Fuel	*Chief Characteristic*
Natural Gas	Mostly CH_4 (methane) - usually burns clean
LPG	Mostly C_3H_8 (propane) - higher density than CH_4
Light Oil (No. 2, Diesel)	Few contaminants - a mixture averaging CH_2
Heavy Oil (No. 4, No. 6, residual)	Black (close kin to tar), not readily pumped or burned when cold, sulfur and other contaminants
Coal (bituminous, anthracite, lignite)	Contaminated with sulfur, ash, rock & water. Composition - C to CH
Wood	Moderate ash, water content is high & variable. Typical composition - CH_2O
Waste Oil	Distillate oil with some contaminants
Refinery gas, producer gas, coke oven gas	Gas mixtures with inerts plus some contaminants
Landfill gas, sewage treatment gases	Mostly CH_4 & CO_2 with smelly contaminants
Solid wastes	Contaminated with almost anything

The owner of a combustion device will choose the least expensive fuel that is practical and permitted. Their decision is constrained by existing firing equipment (a gas-fired boiler cannot fire coal without major changes) and environmental restrictions (usually related to fuel sulfur content). Typically, the cleanest and simplest fuels, such as natural gas and light oil, are more expensive than the dirty, troublesome fuels, such as coal and residual oil. So the decision many stationary source operators must face is whether to pay rising fuel prices or incur the expense of installing, operating and maintaining expensive fuel handling and air pollution control equipment.

Several of the listings in Table 1-2 deserve comment.

- Distillate oil differs radically from residual oil. When a refinery processes crude oil, it begins by removing all the lighter constituents that are used to make gasoline, No. 2 oil, lubricating oil and all the “clean” petroleum products. What is left over is called “residual” or No. 6 oil. Most of the crude oil contaminants remain in the residual oil; therefore, No. 6 oil tends to have high concentrations of ash, nitrogen and sulfur – all of which contribute to air pollution. So distillate fuels are relatively clean burning, while residual oils generate much higher emission levels.

- Coal has a very high ash content which means that all coal-fired boilers must have dust collectors to control particulate emissions. Coal also tends to have high levels of both sulfur and nitrogen, which generate emissions of SO_2 and NOx.
- While wood is viewed as a natural, renewable fuel it is not always clean burning. When wood is wet it does not burn easily or well, which usually results in the emission of visible smoke, CO and other organic compounds. Ironically, waste wood such as demolition debris, railroad ties and telephone poles are viewed as "contaminated," even though as fuels they tend to have low emissions of CO and other organics. This is true because they are relatively dry. While organic preservatives like creosote burn cleanly, the CCA (copper-chrome-arsenic) found in pressure treated wood can generate hazardous particulate matter.
- Natural gas combustion, although considered clean, generates NOx the same as any other combustion process.

Another way to look at fuel consumption is in terms of the total amount of atmospheric carbon produced in the form of CO_2. Table 1-3 lists the amount of carbon (in the form of carbon dioxide) generated by various sectors of our society. Note that electric power generators are the largest emitters of carbon at 557 (sum of the right column) followed closely by transportation at 496. These two sectors are also the largest source of various air pollutants.

Table 1-3. Carbon Emissions (10^6 tons)

Sector	*Total Carbon*	*Electric**
Transportation	496	1
Industrial	481	180
Residential	290	193
Commercial	243	183
Totals	1,510	557

*Electric is part of the total.

U.S. Department of Energy, Energy Information Administration, Annual Energy Review 2000.

1.4 AIR POLLUTION

Ambient air pollution results directly and indirectly from terrestrial contaminants emitted into the air. Combustion sources commonly emit visible smoke (carbon) as well as nitrogen oxides (NOx), sulfur dioxide (SO_2), and other invisible gases. Some of these substances react chemically in the atmosphere to create smog, ozone and the ingredients of acid rain.

Although stack emissions are diluted by at least 1000 to 1 after leaving the stack, the sum total of emissions in some areas is sufficient to compromise ambient standards, either locally or regionally. Atmospheric dilution is not an acceptable approach to air pollution control locally and regionally it has little or no effect. So our approach to air pollution problems is to reduce emissions rather that manipulate the stack design.

1.4.1 Emission Rates

The amount of emissions produced by combustion sources is proportional to (1) the amount of fuel burned and (2) the type of contaminants in the fuel. Emissions also depend on the combustion process. EPA's *Compilation of Air Pollution Emission Factors (AP-42)* (ref. 6) is a useful reference which allows you to relate emission rates to fuel use. For example, in order to calculate combustion source emissions, simply identify the specific type of fuel source in AP-42 and then multiply the appropriate factor by fuel use to determine the amount of typical emissions. The reliability of these factors will vary depending on the size of the database, and is classified by EPA on a scale of A (high) thru E (low). However, regardless of the reliability of these results, EPA takes no responsibility for any of this data. Combustion source operators must use it at their own risk. For example, source operators have been penalized after discovering that their actual emissions were higher than they had assumed based on AP-42 data.

Emission rates can be expressed in several ways. Listed below are some common measurement units in English dimensions with a brief explanation.

lb/hour or tons/year	This form supports a regional air pollution inventory and/or a cap on total emissions from one or a group of sources.
ppm or lb/ft^3 corrected	Nearly all instruments measure pollutant concentration. Concentration measurements are always expressed in corrected form (e.g., ppm corrected to 3% O_2) to eliminate the effects of varying amounts of air dilution.
lb/mmBTU	Referencing the emissions to the combustion-firing rate allows regulation of different size sources with a single limit. The emission in lb/mmBTU can be calculated from measured stack values of pollutant concentration and O_2 or CO_2 concentrations if the fuel type is known (F-factor method).
lb/ton of product	By referencing emissions to production rates (tons, kw-hr, etc.) a combustion source is rewarded for efficient production.

The most common unit used to express combustion source emissions is "lb/mmBTU." This is generally viewed as the simplest way to express such emissions; therefore, this convention will be used throughout the remainder of this text.

1.4.2 Types of Pollutants

Emission formation and control is discussed in Chapters 5 and 6. However, for the purpose of this discussion, emissions from combustion sources can be broken into three groups:

1. Products of incomplete combustion or PIC (CO, carbon, organic species)
2. Emissions formed from fuel contaminants (SOx, particulates, etc.)
3. Nitrogen oxides (NOx)

As a general rule, PIC emissions are small to negligible from stationary sources, so in many cases they are not specifically regulated. One of the reasons PIC emissions are rarely significant is that, for most sources, they are accompanied by black smoke. Visible smoke was the first air pollutant ever to be regulated and it is still the most common form of pollution today. Most sources that are not smoking also do not emit PIC. However, there are exceptions - primarily those sources that burn very clean fuel. If a source has a low PIC emission rate, it is by definition burning the fuel completely. Generally, this means the source has 100% combustion efficiency. Chapter 7 will discuss in greater detail combustion source efficiency and the difference between combustion and thermal efficiency.

Fuel contaminants, such as inorganic substances, are any chemical in the fuel other than carbon, hydrogen, or oxygen. Common examples are sulfur, nitrogen and ash that pass through the combustion zone to form sulfur oxides (SOx), nitrogen oxides (NOx) and particulate matter (PM). The amount of air pollution formed may depend on the combustion system as well as how much of the contaminant is in the fuel. For example, 100% of fuel sulfur will burn to SO_2 and will be emitted unless it is collected or scrubbed out. On the other hand, the amount of fuel nitrogen converted to NOx is highly dependent on the design and operation of the combustion system. Fine particulate matter, particularly $PM_{2.5}$ (particulate smaller than 2.5μm), can be formed from fuel sulfur as well as from ash, which shows that the emissions may be interrelated.

Nitrogen oxides are a distinct category of combustion pollution because NOx is emitted by all combustion sources regardless of the amount of fuel nitrogen present. Atmospheric N_2 and O_2 are normally very stable, but they can react with each other in a combustion zone. The amount formed is strongly dependent on combustion temperature, so some sources generate a lot, while others generate very little. Thus a major element of NOx control efforts has been to modify combustion system design to develop "low NOx" burners. One of the ironies of combustion NOx control is that any adjustment that lowers NOx emissions tends to increase PIC emissions; with a few notable exceptions. The reason for this is further described in Chapter 5.

Emission control before 1970 generally referred to visible smoke that could usually be limited by combustion system adjustment or maintenance. Emission control efforts have broadened and intensified since. Emissions formed in the combustion zone (uncontrolled emissions) depend on fuel composition, but combustion system hardware and emissions control devices determine how much ultimately goes up the stack (controlled emissions). Table 1-4 presents the emission rates for a variety of fuels and sources both with and without emission controls.

Table 1-4. Typical Emission Rates (lb/mmBTU)

Source	*Pollutant*	*Uncontrolled*	*Controlled*
Natural gas furnace	NOx	0.1 to 0.5	.02 to .02
No. 6 oil fired boiler	NOx Particulates SO_2	0.45 0.10± 2.50	0.25 0.05± <1.00
Pulverized coal boiler	NOx Particulates SO_2	0.80 10.00 4.50	0.40 <0.05 <1.50
Wood fired boiler	Particulates	2.50	0.1 to 0.6
Diesel Engine	NOx Particulate – PM10 CO	3.2 0.05 – 1.0 0.85	1.9
Combustion Turbine	NOx	0.50	0.035

Any combustion source can emit CO, particularly during an upset, but many emit very little. Most boiler sources emit very little carbon monoxide or hydrocarbons except possibly during a cold start up. Reciprocating engines emit CO and VOC at predictable low levels. In many cases any operating event that generates significant CO will flag the problem with a cloud of dark smoke, which prompts corrective action. Much of the current effort in emissions control is focused on combustion tuning to reduce NOx emissions. While this may increase CO, it should not lead to excess CO emissions.

1.5 OVERVIEW OF COMBUSTION SOURCES

This course deals with stationary sources, specifically those large enough to be individually regulated. Table 1-3 shows that stationary sources generate roughly one third of the carbon dioxide emissions to the atmosphere. Regulating large sources of air pollution has no effect on smaller sources such as automobiles, homes and businesses that may contribute half or more of the pollution in any given area. This is particularly true in urban areas, many of which are identified as non-attainment for ozone.

Stationary sources come in all sizes from home furnaces to utility boilers. By way of comparison, the home furnace flue can be as small as two inches in diameter while an electric utility can have a stack with a 30-foot diameter flue. Emissions from most small sources are controlled by certification. For example, all units manufactured to a certain standard are presumed to meet certain emission criteria. This course is only concerned with those sources large enough to be individually regulated; meaning that each source has an operating permit and must certify that its emissions meet the criteria specified in the permit. Certification can be a one-time requirement for some smaller sources. An annual source test and/or continuous monitoring are generally required for larger sources.

1.5.1 Internal Combustion Engines

The term "engine" in this course includes two types of power source: (1) reciprocating engines and (2) combustion turbines (CT), also called gas turbines. Both are internal combustion (IC) devices in which the exhaust gases directly drive the power production hardware. The two types share a number of characteristics and are used interchangeably in some applications. But they differ considerably in their emission characteristics.

Stationary engines serve a number of common purposes including: emergency (stand-by) power generation, pipeline pumping and, increasingly, electric utility generators. Nearly all stationary engines burn clean fuels such as natural gas, or distillate oil, such as diesel or No. 2 oil. Therefore, the emission species of primary concern is NOx. PIC including VOC and particulate emissions are also a potential issue, primarily because of the potential health impacts. Although reciprocating engines can operate on heavy oil, which will generate emissions in addition to NOx, most of these are marine diesels rather land based stationary sources. Combustion turbines cannot operate on dirty fuel for long without the need for significant maintenance or repair. So most turbines and reciprocating engines are installed with a connection to natural gas, while No. 2 oil is used as a backup – if it is used at all.

The basic configuration of an engine is that it has a fuel supply line on one end and a power output shaft on the other. A single manufacturer ships a package that converts fuel to mechanical power. This is in contrast to steam power plants that are assembled on site with components from multiple manufacturers. The fact that turbines and

engine sources are "factory built" means the emission rates are very predictable based on load and ambient conditions.

There are two types of engines: reciprocating and gas turbine. Stationary reciprocating engines are simply larger versions of ordinary automobile or truck engines. They can be as large as several thousand horsepower (several megawatts) and the physical dimensions approach the limits of rail or highway transport. NOx emissions from reciprocating engines with no emission controls are among the highest of all sources. But emissions controls have been evolving for about 30 years and reciprocating engines can now be installed with relatively low emission rates.

Combustion turbines, (as opposed to steam turbines), are aircraft engines adapted for ground operation, where high altitude operation is not a concern. Until recently they were not built smaller than about 500 horsepower (0.4 megawatt), while the upper end ranges to about 200 megawatts (270,000 HP). Given these power levels, the physical dimensions are surprisingly small and well within U.S. highway transport limits. Nearly all of the large electric utility facilities built in the U.S. since the mid 1980s used a combustion turbine as the primary component. NOx emissions have evolved from moderately high levels in the late 1970s to extremely low levels today.

1.5.2 Boiler Systems

A boiler is nothing more than an extensively developed tea kettle. Fire heats water until it boils and the steam is piped off for various uses. Boilers are built as part of a system, so the steam is piped into a factory process that requires heat, or it is piped to a turbine that drives a pump or an electric power generator. Boilers are the most common stationary combustion source. They are present in most factories and are at the heart of the nation's electric supply system. Figure 1-3 is a schematic showing a boiler that feeds steam to a turbine connected to an electric generator. The boiler is an "external" combustion device because the exhaust gases do not contact the turbine that produces mechanical power.

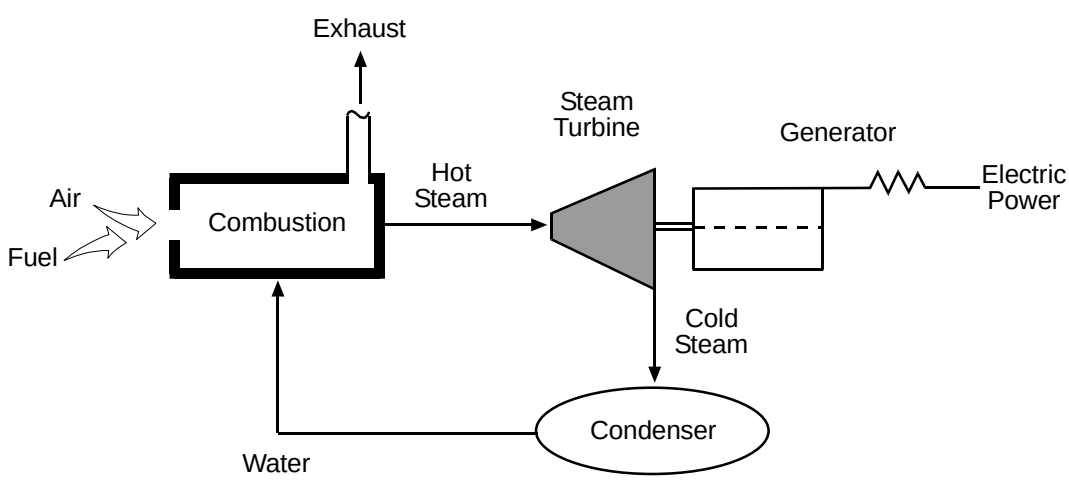

Figure 1-3. Schematic – Boiler, Turbine and Generator

Boilers are the oldest mechanical devices to use the heat from fire indirectly or to produce mechanical power. Unlike engines, boilers can and do burn any fuel that is combustible. Therefore, they emit a wide range of potential pollutants, depending on the fuel. Boilers come in all sizes from home furnaces to utility boilers where the firebox can be "big as a barn" and 200 feet high. Medium size industrial boilers with steam generating capacities less than about 200,000 lb/hr are usually factory built, prefabricated "package boilers." Above that size boilers are erected on site resulting in a custom-made, "one-of-a-kind" boiler, although it may have similar siblings. Steam conditions in such large boilers can have steam pressures up to 3600 psi at temperatures of 1000°F and higher, figures far removed from a teakettle. Boiler systems have a lot of supplemental components such as a water supply system, fuel supply system, various heat exchangers, and fans to move combustion air or flue gas. Overall, these are relatively complex systems and each one is unique.

1.5.3 Other Combustion Sources

In addition to engines and boilers there are a number of other types of combustors that, though less common, can still be significant local sources of air pollution.

Cement Kilns. These are large combustors used to manufacture Portland cement – the key ingredient of concrete. There are less than 200 active kilns in the U.S. They are well adapted to burn a wide range of fuels and generally burn the cheapest fuel available. Because they must operate at very high temperatures in order to make their product, a number of them are used to incinerate hazardous waste. There are also lime kilns that are similar to cement kilns, but they are usually smaller and operate at lower temperatures. Cement and lime kilns process limestone ($CaCO_3$) to generate lime (CaO), so they emit large amounts of CO_2 from the process in addition to the CO_2 from combustion.

Solid Waste Incinerators. Most municipal waste in this country goes to a landfill, but some of it is burned. In most cases, the combustor is a boiler where waste is the fuel and the facility is called a municipal waste-to-energy plant. This avoids the stigma associated with the word incinerator. The term incinerator is generally reserved for facilities where there is no energy recovery. Waste water treatment plants generate solid sludge, which, in many cases, is fed to a sludge incinerator. Recently designed units operate cleanly, but the older ones can be a significant source of air pollution.

Hazardous Waste Incinerators. Combustible waste that is legally defined as hazardous is required to go to a facility that is licensed to burn it. In addition to certain cement kilns, there are several facilities in this country specifically built and permitted to burn certain hazardous wastes. All facilities that burn waste must demonstrate their ability to safely manage the waste. There are extensive monitoring requirements designed to ensure compliance. However, the legal classification of a waste may have no relation to its combustion characteristics. Some hazardous substances, such as benzene, burn quite easily and cleanly, while other non-hazardous fuels, such as wet wood chips, can be a source of substantial air pollution and, sometimes, hazardous substances. During normal operation, all modern incinerators achieve nearly 100% destruction (complete combustion) of organic waste.

Thermal Oxidizers. This term is commonly used for combustors that consume organic vapors such as solvents, phenols, etc. emitted by industrial facilities. Thermal oxidizers are pollution control devices that consume fuel without making any steam or useful energy. When designed and operated properly, they consume essentially 100% of the target pollutants and their only significant emissions may be NOx.

Review Exercises

1. Bituminous and subbituminous coal are fossil fuels that can be used in which of the following combustion sources?
   a. Combustion turbines and reciprocating engines
   b. Steam-electric power plant
   c. Residential furnace
   d. Incinerators

2. Fossil fuels account for approximately what percentage of the total energy used in the U.S.?
   a. 100%
   b. 80%
   c. 60%
   d. 40%

3. The chief characteristic of natural gas is that it _____?
   a. has few contaminants and is composed of a mixture averaging CH_2.
   b. is contaminated with sulfur, ash, rock and water.
   c. is a gas mixture with considerable inert species plus some contaminants.
   d. usually burns clean and is composed mostly of CH_4 (methane).

4. _____ is an example of a common clean fuel for firing industrial equipment.
   a. Waste oil
   b. Wood chips
   c. Light oil
   d. Refinery gas

5. Typically stack emissions are diluted more than _____ after entering the atmosphere.
   a. 1:1
   b. 10:1
   c. 100:1
   d. 1000:1

6. Which category of combustion source emits the greatest amount of carbon dioxide?
   a. Natural gas furnaces
   b. Cement kilns
   c. Electric power generators
   d. Factory boilers

7. The common way(s) to express combustion source emissions is _____.
   a. lb/mmBTU
   b. lb/ton of product
   c. lb/hour or tons/year
   d. ppm or lb/ft^3 corrected
   e. all of the above.

8. Which of the following is an example of an emission from a combustion source?
   a. PIC
   b. Emissions formed from fuel contaminants
   c. Nitrogen oxides
   d. All of the above

9. Which of the following, when designed and operated properly, consume essentially 100% of the organic pollutants?
   a. Solid waste incinerator
   b. Hazardous waste incinerator
   c. Thermal oxidizer
   d. All of the above

10. Which of the following pollutants is usually formed primarily from inorganic fuel contaminants?
   a. Particulates
   b. Carbon dioxide
   c. PIC
   d. Organic species

Review Answers

1. b. Steam-electric power plants

2. b. 80%

3. d. usually burns clean and is composed of CH_4 (methane).

4. c. Light oil

5. d. 1000:1

6. b. Cement kilns emit the highest concentration of CO_2 (lb/mmBTU)
   c. Electric-power generators as a group emit the greatest total tonnage of CO_2.

7. e. All of the above.

8. d. All of the above

9. d. All of the above

10. a. Particulates

References

[1] Data on global carbon and CO_2 is available on numerous web sites including www.epa.gov www.noaa.gov http://cdiac.esd.ornl.gov/ http://globalchange.gov/.

[2] U.S. Department of Energy, Energy Information Administration, Annual Energy Review 2000, available at www.eia.doe.gov/oiaf/aeo/index.html.

[3] Handbook of Energy Systems Engineering, Leslie C. Wilbur, Editor, (John Wiley & Sons, New York, 1985). This is a hefty handbook that covers many areas including useful sections on producing and combusting gas, oil and coal.

[4] Seinfield, John H. and Pandis, Spyros N. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, (John Wiley & Sons, Inc., 1997). This book could be an academic text as well as a reference. The wealth of detail about the atmospheric behavior of carbon, sulfur and nitrogen compounds as well as aerosols (PM2.5) makes it relevant to the study of combustion air emissions.

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Chapter 2: General Types and Characteristics of Combustion

LESSON GOAL

Demonstrate a general understanding of the various types and characteristics of combustion systems, their methods of operation and their impact upon air pollution control through successful completion of the chapter review exercises.

STUDENT OBJECTIVES

When you have mastered the material in this chapter, the student should be able to:

1. Describe how fuel and air flows are controlled for combustion systems.
2. Describe generally how reciprocating engines and combustion (gas) turbines convert fuel into mechanical energy.
3. Define the terms *combined cycle* and *cogeneration* as they relate to the use of waste heat from engine power sources.
4. Describe the typical size range of engines, turbines and boilers.
5. Describe the difference between *suspension* and *grate* firing.
6. Explain the general operating concept of burners used in face-fired boilers.
7. Describe the most common burner configurations used in large boilers.
8. Explain how solid fuels are burned in stoker and fluidized bed combustors.
9. Describe the use of oxidizers and flare combustion to control air emissions.
10. Discuss the fuel storage, handling and processing requirements of natural gas, oil, coal, wood, and municipal waste.
11. Explain generally how air flow controls work.

12. Detail the overall operation of a steam electric power plant and be familiar with the primary steam system components.

13. Describe how fuel ash impacts the operation of a combustion facility.

Chapter 2: General Types and Characteristics of Combustion

2.1 COMBUSTION SYSTEMS

There are several types of combustion systems and a number of variations within each type. Each type of source has its own air emission characteristics and in some cases its own set of applicable regulations. Thus anyone working with air pollution controls from various sources needs to understand the source characteristics and know where that source fits in the world of air pollution regulations.

Fire is a familiar phenomenon, but the fire in a combustion system differs from an open campfire or the fire in a fireplace in several respects: (1) the fire is completely enclosed in a combustion chamber, (2) the flow of both fuel and air into the chamber is carefully controlled, and (3) the burner is designed to mix the fuel and air in a way that creates a stable flame and promotes clean combustion. Combustion systems are made up of a number of components, some of which are illustrated in Figure 2-1.

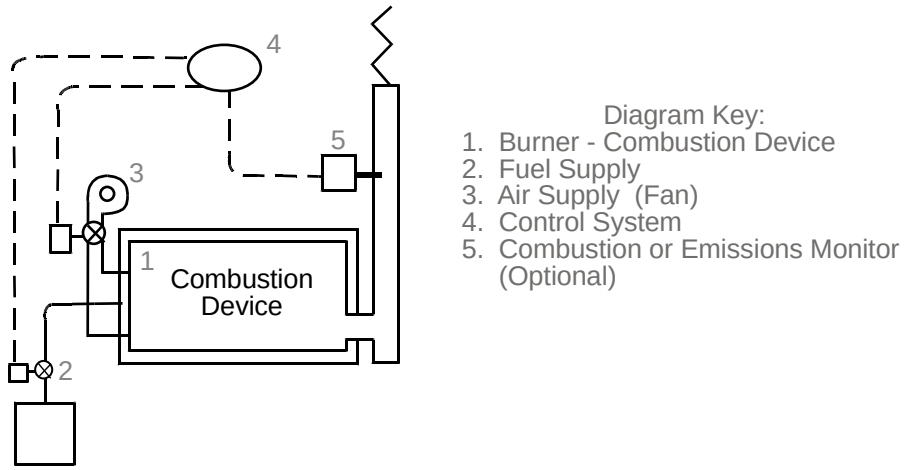

Figure 2-1. Combustion Source System Components

Major systems include:

- Burner device(s) and combustion chamber (controls combustion performance)
- Fuel storage and supply system
- Air supply system
- Heat transfer components to make use of the heat released by combustion
- Air pollution control systems
- Controls and data management to allow automatic operation

There may also be a number of auxiliary systems or components such as a water treatment system. Many of these components can affect combustion performance and air emission levels either directly or indirectly. For example, worn components in a steam turbine reduce its efficiency, which means the combustion system will fire more fuel in order to achieve normal full load. The steam turbine is remote from the combustion system, but its deterioration increases the fuel flow and that, for a variety of reasons, can substantially increase air emissions.

Whether or not any part of a facility has an apparent connection to potential air emissions, a person working with the facility should be aware of the various components in a combustion facility and the way that each interrelates with other parts of the system as a whole.

Therefore, this chapter provides a basic description of the most common types of combustion systems and their related components. The chapter begins with a general overview of the various types and characteristics of combustion systems, their methods of operation and their impact upon air pollution control. Specifically, this chapter will discuss major sources of combustion, such as engines, boiler systems, and others. The chapter concludes with a review of fuel storage and handling procedures, steam system components, and ash handling. The purpose of this chapter is to introduce the various types and characteristics of basic combustion systems and their operation.

2.2 TYPES OF COMBUSTION SYSTEMS

Engines of all sizes are becoming a much more common source of power and, from an air pollution perspective, they are the simplest group of combustion sources to manage. They only burn clean fuels like gas and distillate oil, so there is usually no concern over emissions of SO_2 and particulates. They are relatively simple in the sense that an engine is a package from one manufacturer, unlike the conglomeration of components from various manufacturers that is typical of most other types of sources. The fact that a turbine or engine is “factory built,” means the emissions should be quite predictable from one engine to the next; which is not necessarily true of sources built on-site.

2.2.1 Engines and Turbines

Internal combustion engines are used extensively in emergency power generation and pipeline pumping applications. By the end of the 20th century market forces such as the movement toward deregulated electric power and plentiful supplies of natural gas, have resulted in engines displacing steam turbines as the prime mover of choice for new electric power generators. Engine based plants can be erected quickly and the air emissions from gas fired facilities can be controlled to very low levels. Combustion turbines can only burn clean fuels – preferably natural gas with No. 2 distillate oil as a backup. As a result, a growing fraction of the nation's domestic electric power capacity cannot utilize solid fuel. But since few of the steam plants have been retired, coal is still the primary fuel used for electric power generation. While some reciprocating engines, notably marine diesels, have been built to fire heavy oil, most stationary engines burn clean fuels. In many cases, stationary engines and turbines are built to fire natural gas backed up with No. 2 oil fuel capability if the gas supply is interrupted.

Engines come in two varieties: (1) reciprocating engines similar to automobile and truck engines, and (2) combustion/gas turbines similar to "jet" aircraft engines. Reciprocating engines can be tiny or as large as about 10 MW (13,000 HP). Gas turbine sizes range from "microturbines" smaller than 75KW (100HP) to more than 200 MW (270,000 HP. Virtually all new power plants and most new combined cycle or cogeneration units use a gas turbine as the primary component.

2.2.1.1 Reciprocating Engines: Lean/Rich, Diesel/Gas

Reciprocating engines are the oldest type of internal combustion engine, with some obvious similarities to their predecessor – the reciprocating steam engine. An example of the early steam engine is the steam railroad locomotive. Reciprocating engines operate by igniting a fuel-air mixture in a closed chamber then using the force of the expanding gas to push a piston that is connected to a crankshaft. Figure 2-2 shows the sequence of events, common to most reciprocating engines.

- The piston moves down drawing a fuel-air mixture into the chamber through the intake valve.
- The piston then moves up and compresses the fuel-air mixture.
- The mixture is ignited and the piston is driven downward – the power stroke.
- The crank continues to rotate and the exhaust valve opens, discharging the gaseous products of combustion.

An engine will have a number of cylinders, all lined up along a crankshaft. The cylinders vary in diameter from a few inches (automobiles) to more than a foot (industrial engines). Operating speeds depend on size: small engines can run at several thousand RPM while big stationary engines spin at less than 1000 RPM.

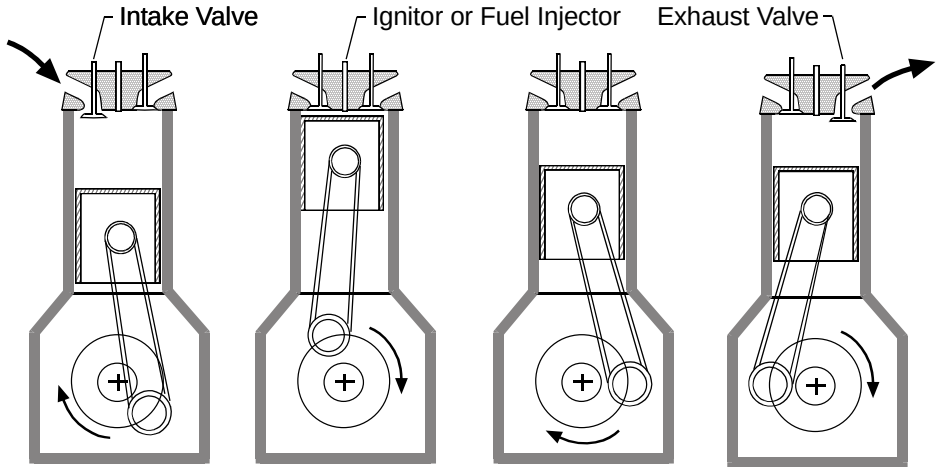

Figure 2-2. Operating Principle of a Reciprocating Engine

There is also a two-stroke version of the cycle in which the intake and exhaust functions occur during a short period when the piston is near the bottom of its stroke, the two-cycle engine. Environmentally, a two-cycle engine is somewhat dirtier than a four-stroke engine because some of the incoming fuel-air mixture invariably escapes with the exhaust gases, resulting in unburned fuel (VOC) in the exhaust.

Reciprocating engines can be further divided into several categories as summarized in Table 2-1. First there is a division according to how the fuel is ignited. When the fuel is natural gas (or gasoline) an ignitor (spark plug) is required to ignite the fuel. The spark is timed to occur just before the piston reaches top dead center, to achieve the most power. If the fuel is diesel oil, it can be injected (sprayed) into the chamber and the temperature of the compressed gases is sufficient to ignite the fuel. So a diesel injector replaces the spark plug. Diesel engines also have a higher compression ratio that gives higher compression temperatures than a gasoline engine. Diesel engines are somewhat more fuel efficient than spark ignition engines. Table 2-1 lists the major types of reciprocating engines and their characteristics.

Table 2-1. Types of Reciprocating Engines

Type	*Characteristics*
Natural gas fired	Gas mixed with the intake air, spark ignited
Diesel fired	Diesel oil auto-ignites and burns as it is injected, no spark required.
Dual fuel	Essentially a gas fired diesel engine. A small amount of diesel fuel is injected to ignite the gas with no spark plug.
Lean burn	Operates with more than 5% excess air
Rich burn	Operates with less than 5% excess air

The dual fuel engine is basically a diesel engine running on natural gas. Since there is no spark plug, a very small amount of diesel oil is injected to ignite the gas.

Lean and rich burn refer to the operating air-fuel ratio, a concept discussed further in Chapter 4. Rich burn means the engine operates with barely enough air for complete combustion. This gives maximum power, but also results in some degree of incomplete combustion causing increased PIC emissions. While increased PIC emissions are normally undesirable, these emissions are a necessary element for one type of catalytic air pollution control as discussed in Chapter 6. Modern automobile engines operate in a rich burn mode in order for the air pollution control catalyst to work. In general, rich burning is associated with more power and increased emissions while lean burning implies less power and lower emissions. These implications are discussed further in subsequent chapters.

Combustion in reciprocating engines is intermittent; whereas, it is continuous in all other combustion sources. Combustion is a transitory process with ignition and combustion being completed in roughly 10 milliseconds; combustion occurs many times each second in each cylinder. However, there is a fundamental difference in the combustion process between diesel oil and natural gas (or gasoline which evaporates before ignition occurs). Natural gas is mixed with the air before combustion starts. Diesel fuel is a liquid that mixes with the air and evaporates as it is burned. The difference between premixed and diffusion combustion is a key factor in the ability to control NOx emissions because premixed combustion allows engine designs that limit peak flame temperatures. Chapters 5 and 6 will discuss how NOx control efforts have been much more successful on gas-fired engines than on diesel fueled engines.

2.2.1.2 Combustion Turbines

Combustion turbines, also called gas turbines, were developed initially as aircraft engines in the middle of the 20th century. Compared with reciprocating engines, a combustion turbine can produce 10 to 100 times as much power from an engine of equivalent physical size. A combustion turbine has only a few (three at most) primary moving parts. The basic process is shown in Figure 2-3. Air is compressed by an axial or radial compressor (a turbine in reverse) to a pressure of anywhere from 8 – 20 atmospheres. Fuel is burned in a combustor raising the temperature and expanding the gas that is then expanded through a turbine. The turbine drives the compressor and there is power left over to turn a propeller, pump or electric generator. Design variations include two or three concentric shafts: one shaft may be used to drive the compressor while a second shaft may be used to turn the power turbine.

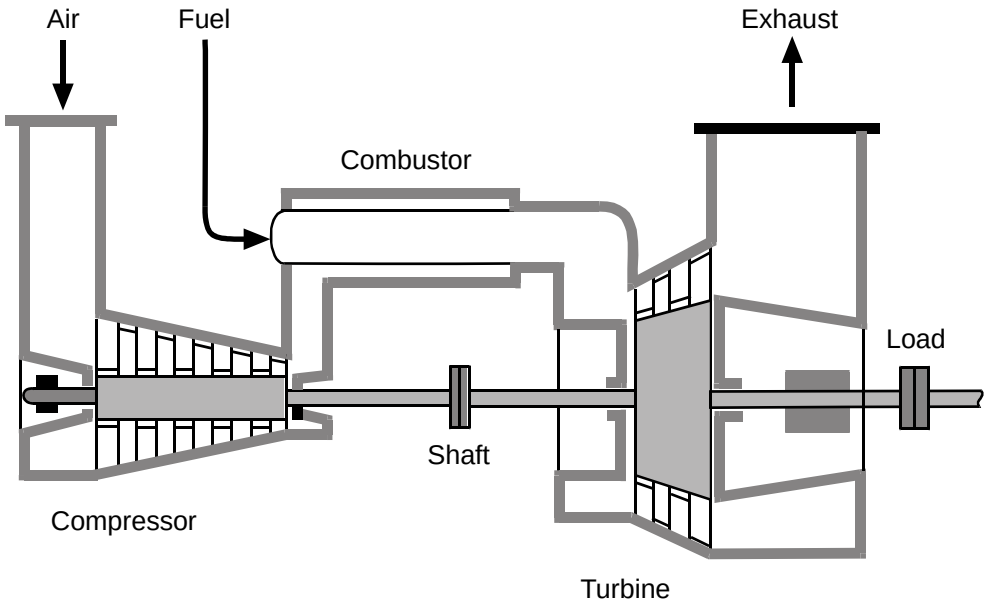

Figure 2-3. Components of a Combustion Turbine

Combustion turbines can only burn clean fuel, such as natural gas or distillate oil. Any contaminants ingested with the air or originating in the combustion zone can corrode, erode or deposit on the turbine blades, resulting in reduced performance. Without such damage, combustion turbines can operate thousands of hours without repair.

Combustion turbine efficiency is directly related to the temperature of the gas leaving the combustor and entering the turbine, usually called T5. That temperature (and hence engine thermal efficiency) is limited by the design of the turbine. If it is too high, the turbine blades are damaged. The current maximum temperature using internally cooled turbine blades is about 2400°F. Uncooled blades might be limited to 1200°F. Both of these temperatures are much lower than normal flame temperatures that are typically above 3000°F. So the combustor has a hot primary zone where the flame is stabilized and most of the combustion takes place. The hot gas from the primary zone is then diluted with additional air to achieve an acceptable turbine inlet temperature. Of course all the air comes through the compressor; the combustor simply divides it, supplying the right amount in the right place to give a stable primary zone and a uniform temperature around the turbine inlet nozzle. Since a lot of air is required for dilution, the total air flow through the engine is three to four times as much as is necessary to burn the fuel.

Recent developments in gas turbine designs are primarily related to NOx emissions control that is discussed in Chapters 5 and 6.

2.2.1.3 Combined Cycles and Cogeneration

Engines typically have thermal efficiencies of 30% to 40%; that is, the amount of fuel energy that is actually converted into shaft power. More than half of the energy is lost. Some of this loss is inevitable, as dictated by the second law of thermodynamics. But a major part of the loss is waste heat. Combustion turbines dump heat into the exhaust stack, while reciprocating engines lose heat to cooling water and up the stack. Steam turbines waste heat in the condenser downstream of the turbine. Chapter 7 provides a more detailed discussion of typical system efficiencies. If some of the waste heat can be utilized, the overall efficiency of the system is higher than that of the engine alone.

Combined cycle is a term used to describe a power system in which the waste heat from the primary engine is used to drive another power source. Figure 2-4 shows such an arrangement. Waste energy in the exhaust gas from an engine is used to heat a boiler that drives a steam turbine. The efficiency is increased from perhaps 35% for the engine alone to about 50% for the combined cycle system. Most of the large electric power plants built in the U.S. since the mid-1980s are combustion turbine combined cycle systems.

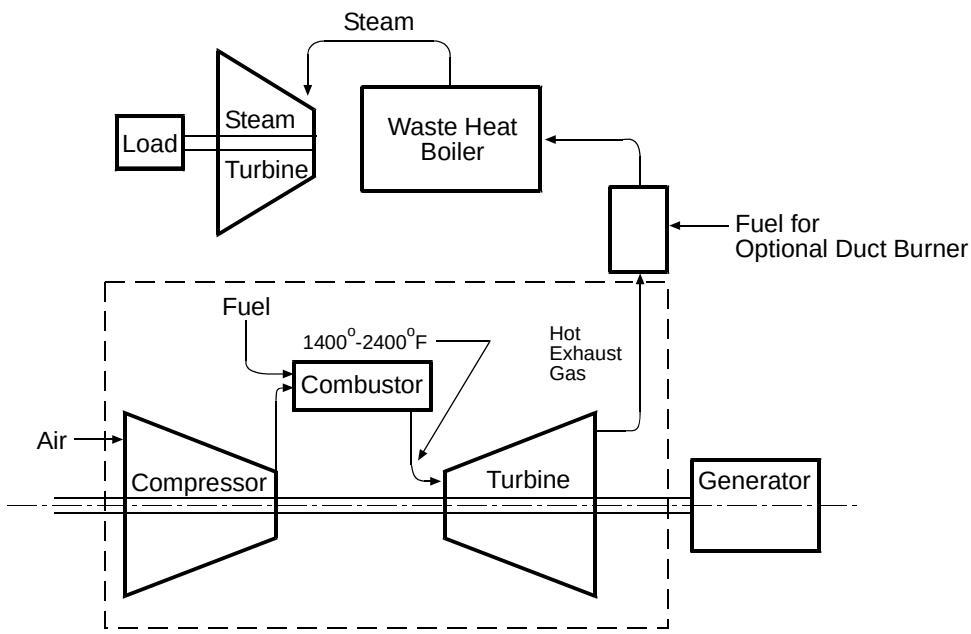

Figure 2-4. A Combined Cycle System

A closely related concept uses waste energy to heat a building or some manufacturing process instead of operating a steam turbine. When the waste heat from a turbine or engine is used directly for heating, the system is called *cogeneration*. Cogeneration was fairly common in the first half of the 20th century, but gradually disappeared with the evolution of huge electric generating plants. However, cogeneration has seen a resurgence in recent years at college campuses, factory complexes and some urban centers where there is a significant demand for heat.

2.2.2 Boilers

A boiler consists of a steel container with water on one side and fire on the other side of a steel wall. Fire heats water until it boils and the steam is piped off for various uses. Steam rises to the top and is piped off to drive a steam turbine, heat a building or support a manufacturing process. Figure 2-5 provides a schematic of a basic boiler. Boilers are ubiquitous, in that they are present in most factories and are at the heart of the nation's electric generating system. Steam heat from a boiler is the most common way to heat a building.

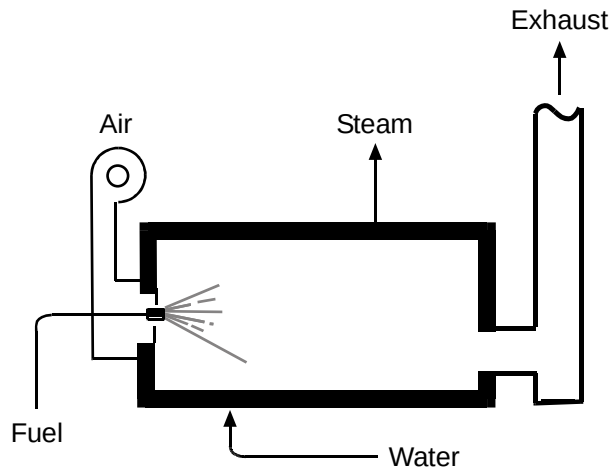

Figure 2-5. A Basic Boiler

Boilers were originally developed in the early 1800s to make steam for the first fuel powered engines, so they are found in some of the oldest mechanical devices used to produce mechanical power. Unlike engines, boilers can burn any fuel that is combustible. The original fuel was cordwood (logs). Coal, when it became available, was usually a more practical fuel and it displaced wood. In practice, boilers can be fired on virtually anything that burns; it comes down to building a combustor that will burn the fuel and sticking it in (or on) a boiler. This means that, unlike engines, boilers can be the source of a wide range of air pollutants derived from contaminants in the fuel.

The mechanical construction of boilers divides into two categories: (1) fire-tube, and (2) water-tube. The first boiler was probably a tank of water with fire under it. Then to increase the heat transfer surface, they put tubes through the tank and ducted the hot combustion gases through the tubes. This is the fire-tube configuration that was used for railroad locomotives and is still available for small to medium size commercial boilers. The physical size of the tank limits the size of fire-tube boilers to a maximum of about 50,000 lb/hr steam generation (65 mmBTU/hr).

Building the boiler with water inside the tubes and fire on the outside (a water-tube boiler) removes the size limitation of a single cylindrical pressure vessel. There is almost no limit on the number of tubes in a water-tube boiler, and thus no limit on the boiler size. [Some electric utility boiler firing rates exceed 10,000 mmBTU/hr.] The

tubes terminate in outlet and inlet manifolds – a steam drum at the top and a mud drum at the bottom. In between the tubes are welded to each other - side by side in sheets that form the walls of the firebox.

There is no apparent limit to the size of a boiler. Boilers come in all sizes from small home furnaces to utility boilers with a firebox that can be 50' x 60' x 200' high. Medium size industrial boilers with steam generating capacities less than about 200,000 lb/hr are usually factory-built, “package boilers” that fit on a highway truck or rail car. Above that size boilers are erected on site with the result that each is “one-of-a-kind”, although it may have similar siblings. Figure 2-6 is a graphic illustration of the size range of boilers.

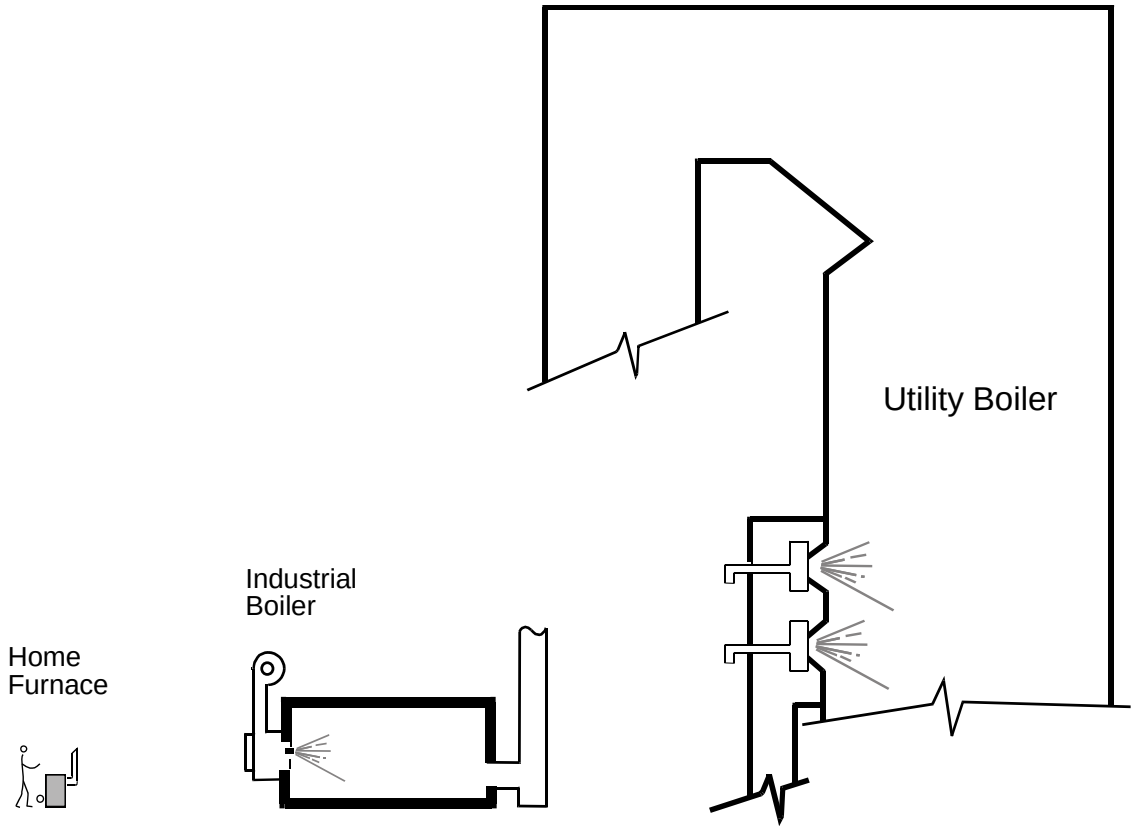

Figure 2-6. Comparative Sizes of Boilers

Boiler thermal capacities are referenced in different terms depending on their size and use. Table 2-2 lists some typical uses and measures of thermal capacity.

Table 2-2. Examples of Boiler Size		
Use	*Generic Size*	*mmBTU/hr*
Residential heat	50,000 BTU/hr	0.05
Commercial building heat	100 Horsepower	3.3
Factory - medium size	30,000 lb/hr steam flow	40
Manufacturing - large	200,000 lb/hr steam flow	250
Electric Utility	500 MW (electric)	5,000

2.2.2.1 Suspension Versus Grate Firing

Combustion in boilers or furnaces can be divided into two categories: *suspension fired* or *grate fired* depending on the physical form of the fuel. If the fuel is a gas, a liquid mist or a powdered solid, it can be burned in suspension, meaning that it takes less than about one second for combustion to be completed after the fuel is injected into the combustion zone. When the fuel is solid particles larger than about 1 mm (1/32 inch) it can only be burned over a period of time longer than several seconds. In this case the fuel is spread on a metal or refractory grate and air is blown up through the fuel bed. The process is called grate firing and is the principle behind all stoker type furnaces.

Suspension firing allows much better control of the combustion process than is possible with stoker firing. Suspension type burners use jets of fuel and of air that can be tailored for a specific fuel-air mixing pattern, thus controlling the flame. On a stoker, with air being blown up through the fuel bed, there is almost no control of fuel-air mixing, which severely limits control of combustion performance and the resulting emissions. However, some type of stoker (or its off-spring, the fluidized bed) is the only way to burn a solid fuel that cannot be pulverized to a fine powder.

Solid fuels contain significant amounts of ash and a stoker tends to keep much of this ash on the grate. By contrast, suspension firing of pulverized coal puts a large amount of ash in suspension. Some of it melts partially and the ash accumulates in various forms on all the boiler surfaces. As a result, a major aspect of operating a pulverized coal boiler is managing the ash and its impact on heat transfer.

Figure 2-7 shows a furnace with both grate and suspension fires. Within the two categories of grate and suspension fired combustors there are a number of variations in both the general configuration and the specific hardware design.

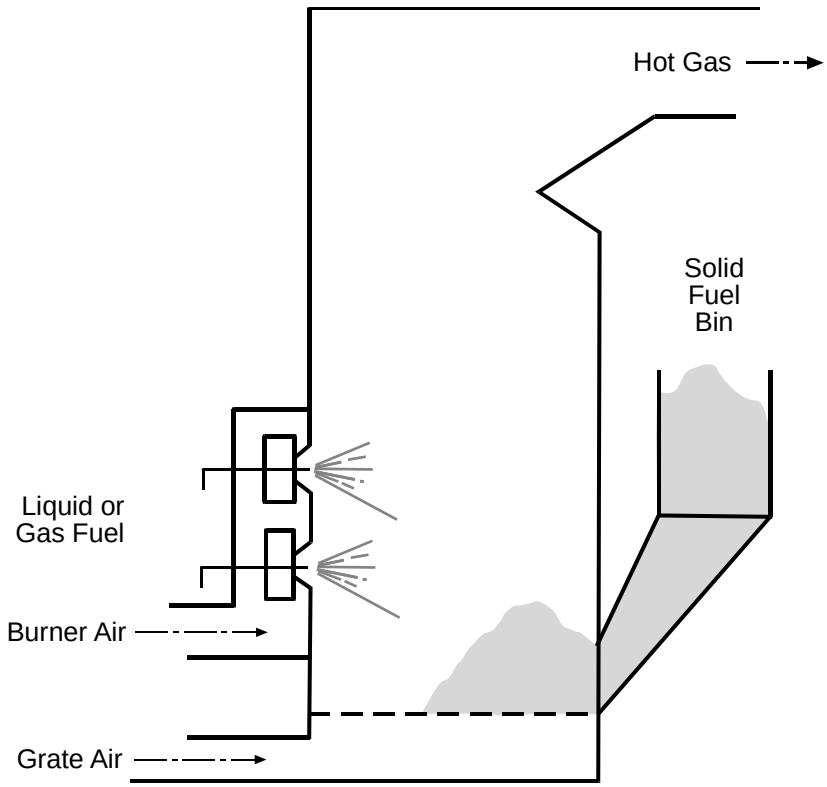

Figure 2-7. Suspension and Grate Firing

2.2.2.2 The Basic Burner Design

Suspension firing requires a burner that injects the fuel and air into the combustion zone. The burner design must achieve two critical goals:

(1) A stable flame that does not fluctuate wildly or blow out, and

(2) Complete mixing of fuel and air to minimize incomplete combustion and smoke.

The basic burner design may have secondary objectives such as limiting flame length or reducing NOx formation, and it does all these things by carefully tailoring the flow patterns of fuel and air as they enter the combustion zone.

Most suspension fired burners share a number of basic characteristics. Stable combustion is the most critical objective of a burner design. If the flame in a furnace should blow out and then be reignited a few seconds later, the accumulated fuel-air mixture in the furnace will ignite and the resulting explosion could be catastrophic. Stability is usually achieved by establishing a flow pattern that causes part of the flame to recirculate back on itself. Figure 2-8 illustrates a section of a circular burner that shows the elements common to most burners.
Air enters the burner through an adjustable register (dampers) and then flows through the throat into the furnace. The air register vanes are angled which causes the air to

rotate around the burner centerline. When the swirling air leaves the burner, centrifugal force causes it to spread away from the centerline leaving a low pressure region in the middle. This causes some of the flow in the center of the flame to come back toward the burner – a recirculation pattern that folds the flame back on itself. This recirculation assures that the fresh fuel and air are ignited as they enter the furnace. Thus the flow recirculation generated by air swirling as it leaves the burner is a key contributor to flame stability.

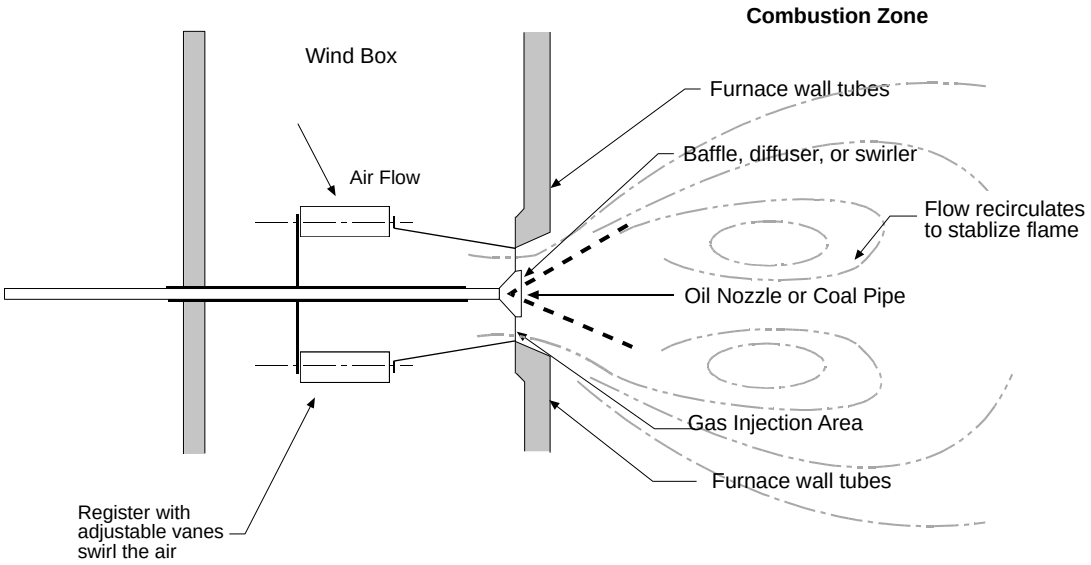

Figure 2-8. Basic Burner Design

A second component that contributes to flame stability is the baffle or diffuser positioned near the throat in the center of the burner. When there is no air swirl the baffle acts like a bluff body creating a flow eddy with some back flow. When the flow is swirling it tends to make the whole flow pattern more stable. In some burners this baffle alone is sufficient to serve as a flame stabilizer. In newer burner designs it takes the form of an axial swirler and becomes a primary element for flame stabilization.

Burners similar those in Figures 2-8 and 2-9 range in size from about 10 mmBTU/hr to more than 300 mmBTU/hr. The same basic design features appear in burners as small as those in a residential furnace.

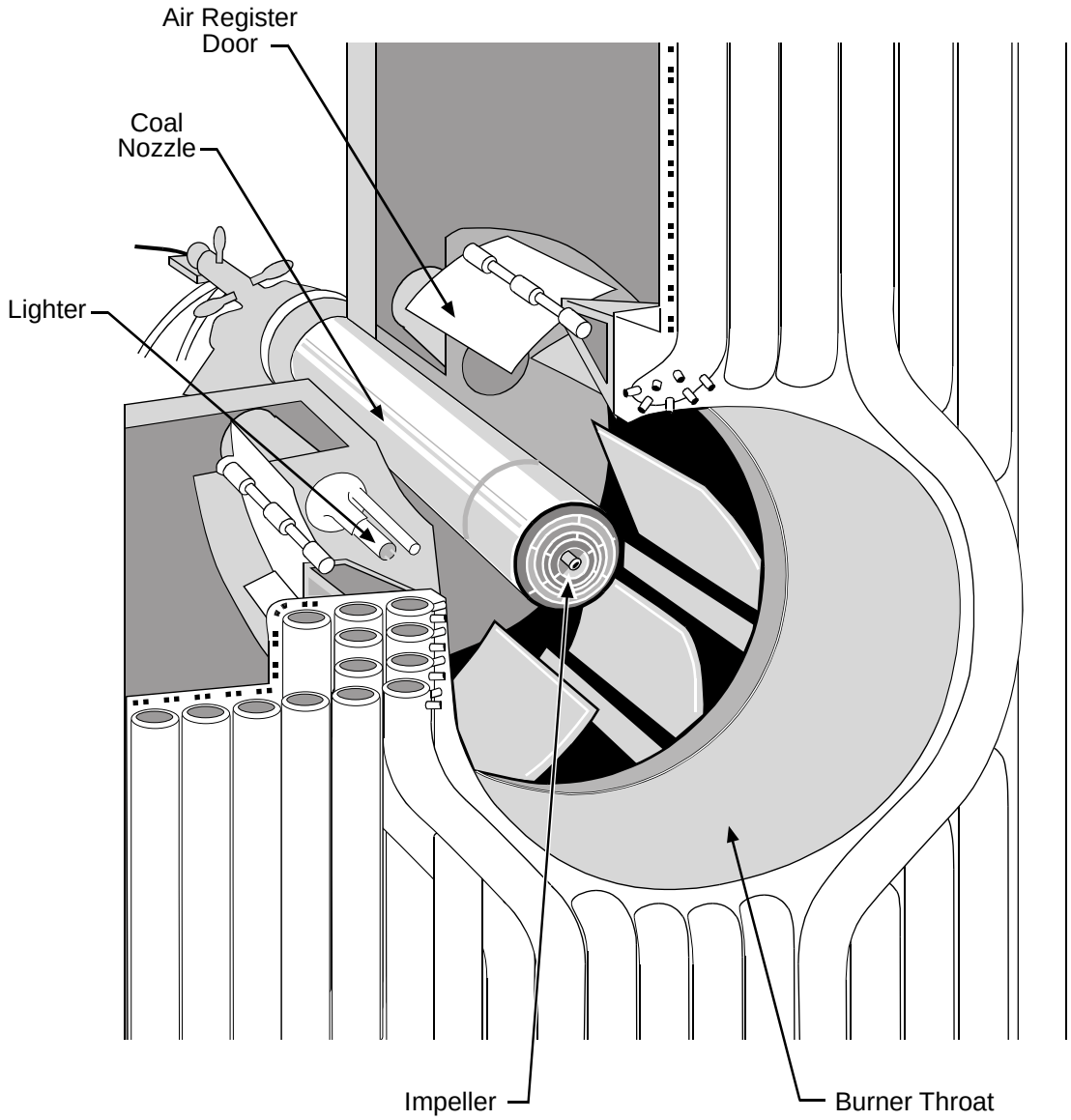

Figure 2-9. Typical Large Burner

Adapted from a drawing in Steam – 40th Edition by Babcock & Wilcox, 1992

In addition to stabilizing the flame, the burner design must assure complete mixing of the fuel with the air. Incomplete mixing means unburned fuel, which constitutes air pollution. Adjusting both the air flow direction and the fuel injection jets relative to the air flow controls mixing. A detailed discussion of this topic is beyond the scope of this text; however, a very general description of the key adjustments is described in the following paragraphs.

- Air flow is adjusted primarily by moving the air register that changes the amount of swirl (angular momentum); this changes the length of the flame and the strength of the recirculation zone.

- Gaseous fuel is usually injected through a large number of jets (several dozen) around the periphery of the throat. The number and orientation of these jets determines the distribution of the gas in the air stream, which is the beginning of the mixing process. A fairly uniform distribution is necessary for complete mixing and complete combustion.

- Liquid fuel is sprayed from a single nozzle in the center of the baffle with a conical spray or a series of steam atomized jets in a conical arrangement. The potential track of an oil spray is shown in Figure 2-8. The oil spray can penetrate as much as two or three feet before it loses momentum and the oil drops are carried by the air flow. The axial position of the oil nozzle can be adjusted, usually with the burner in operation. Both the conical spray angle and the number/size of the jets can be adjusted in the design of the atomizing nozzle. These variables determine how the oil is distributed in the air stream and, thus the uniformity of the fuel-air mixture in the flame.

- Pulverized (powdered) coal is blown into the flame through a pipe and a typical burner is shown in Figure 2-9. The end of the pipe can be fitted with a set of conical spreader vanes or a swirler to spread/direct the coal flow. The velocity of this coal/air flow is lower than the air velocity at the burner throat. The fuel-air distribution in the flame is determined by a combination of coal pipe exit conditions and the recirculation zone flow pattern.

2.2.2.3 Pulverized Fuel

Pulverized coal and wood sander dust can be fired in suspension - provided the particles are smaller than about 200 microns (micrometers). Sander dust is only available in quantity at a few wood products manufacturers, but the vast majority of coal burned in this country is by pulverized firing in large utility boilers. Figure 2-10 is a simple schematic of a portion of a pulverized coal firing system for a utility boiler. Crushed coal is fed to one of several coal grinding mills. About 20% of the boiler combustion air is supplied to the mill to transport the pulverized coal. The mill inlet air temperature is high enough to evaporate moisture from the coal and keep the powder dry as it is blown to the furnace. Each mill feeds a fixed set of burners - typically four to eight - with a flow that divides repeatedly after leaving the mill - ultimately ending with one pipe to each burner.

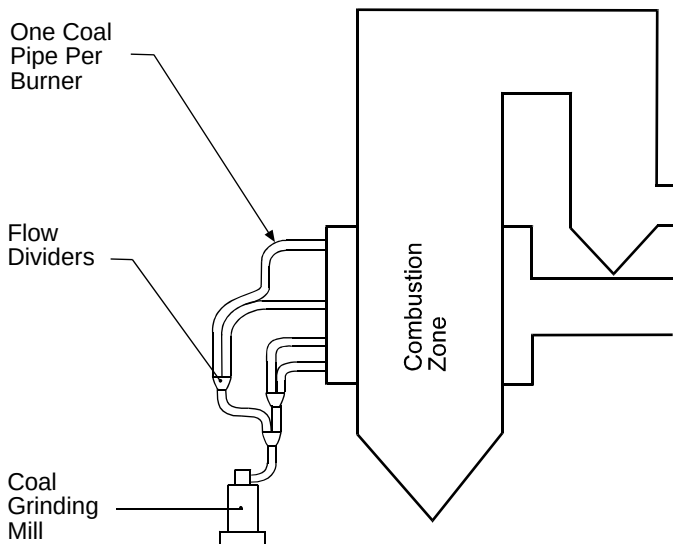

Figure 2-10 Elements of a Pulverized Coal System

Several aspects of pulverized coal firing deserve comment. First, pulverized coal, despite being a soft powder, is abrasive - particularly when it is blown through the system at velocities high enough to keep it fully suspended in the pipe. So the internal parts of the mills and all the coal pipes wear out in a matter of months or, at most, a couple of years. Worn components mean poorly ground coal or poorly distributed coal - both of which mean degraded combustion.

Second, it is challenging to design and maintain a system that evenly distributes a pneumatically suspended powder to all the burners. Fuel can be unevenly distributed between the burners and/or flow to individual burners can have a large density gradient across the coal pipe - causing most of the fuel to feed one side of the burner flame. Either of these fuel distribution problems causes rich/lean zones in the combustion chamber - which lead to higher excess air levels and higher NOx emissions . So both the design and the ongoing maintenance need to assure uniform distribution of fuel to all burners.

Third, coal typically contains about 10% ash, meaning that for every 100 tons fired, there are 10 tons of powdered ash passing through the furnace. This dust settles on all surfaces - which triggers the need for an extensive on-line cleaning system (soot-blowers) to maintain heat transfer rates. If the ash reaches its melting point in the combustion zone it can stick to surfaces - forming deposits that can grow very large and aren't easily removed. Ash melting point (and other characteristics) depend on the source of the coal, which means that each boiler has a list of mines that are known to supply acceptable coal. An integral part of operating a pulverized coal boiler is a constant effort to keep surfaces adequately clean and thereby control temperatures throughout the system.

Grinding mills such as that shown in Figure 2-11 generate pulverized coal. In this mill Crushed coal drops through the center feed tube into the grinding formed by a rotating bowl with rollers that ride against the sides. Hot air enters near the bottom, flows up around the bowl and out the top of the mill. Heat from the air dries the coal. The air flow picks up the coal dust and carries it through a classifier near the top of the mill. This is a cyclone (centrifugal) separator that drops the larger coal particles back into the grinding zone, while the fine dust is carried out of the mill to the burners.

Grind fineness depends on the settings of the classifier and on the amount of coal passing through the mill. In general, the higher the load on the mill, the coarser the grind. Another variable is coal hardness. Hard coal requires more energy to grind leading either to reduced mill capacity or to a coarser grind. Regular maintenance and overhaul are essential to keep coal mills operating properly.

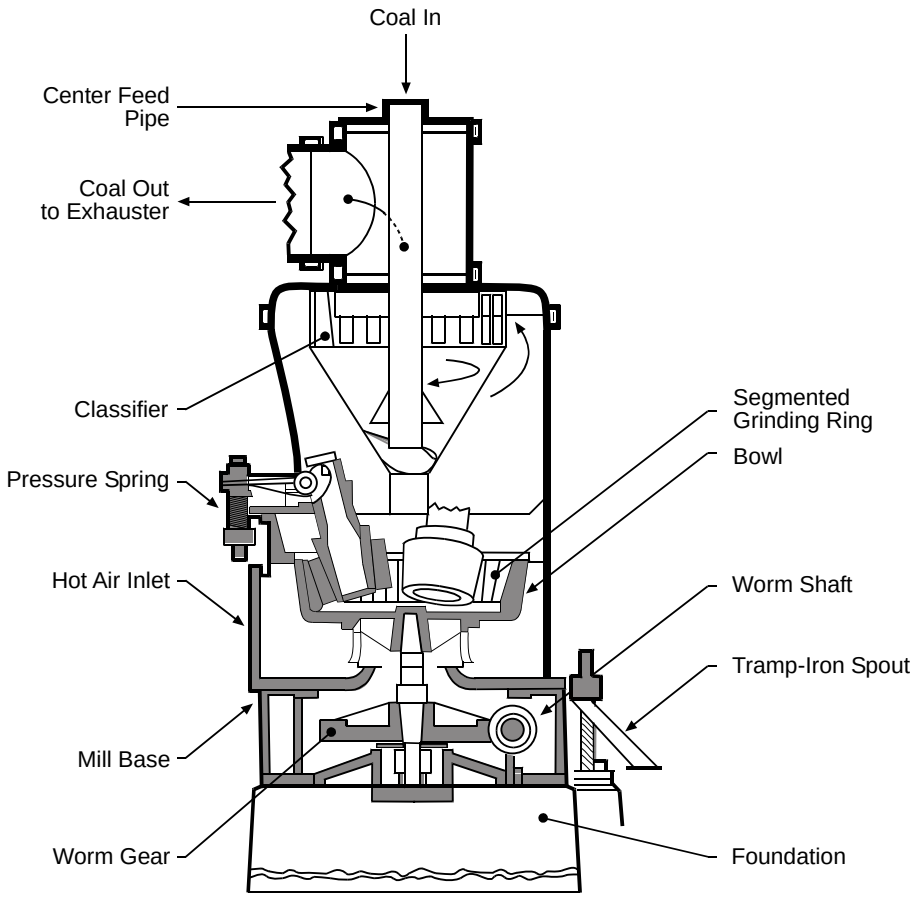

Figure 2-11. Coal Grinding Mill

2.2.2.4 Suspension Firing – Burner Arrangements

Furnaces and boilers, smaller than 100 mmBTU/hr, are usually fired with a single burner similar to that described in Figure 2-8 and depicted in Figure 2-9. Larger industrial and utility boilers use multiple burner arrangements. The most common arrangement, called *wall-fired* or *face-fired*, has rows of burners on one of the four walls of the firebox. A large utility boiler could have four or five rows of burners, each with as many as eight burners. A second, somewhat less common arrangement is *opposed wall-fired* in which matching rows of burners are mounted on opposite walls of the firebox. The top two sketches in Figure 2-12 are elevation (side) views of one row of wall-fired and opposed wall-fired configurations. About half of the large utility boilers in the U.S. are either wall-fired or opposed wall-fired.

Another burner arrangement common in utility boilers, called *tangential firing*, uses burners mounted in the corners of the firebox rather than in the walls. These burners differ from face fired burners in that they are rectangular rather than round and the only swirl is generated by a swirler in place of a baffle at the center of the burner. However, there is swirl for the furnace as a whole as shown in the lower right sketch of Figure 2-12 showing a plan view (looking from the top) of the furnace. Note that the burners are aimed not at the center of the furnace, but rather their aim is tangent to a theoretical circle in the center of the furnace, hence the term tangential firing. This arrangement does not create any recirculation patterns, but note that each flame impinges on its neighbor. The flame in the center of the furnace is stable because the burners light one another even though the individual burners might not be ignited. Tangentially-fired furnaces were built exclusively by the Combustion Engineering Company (CE was subsequently purchased by ABB) and account for roughly 40% of the large utility boilers in the U.S.

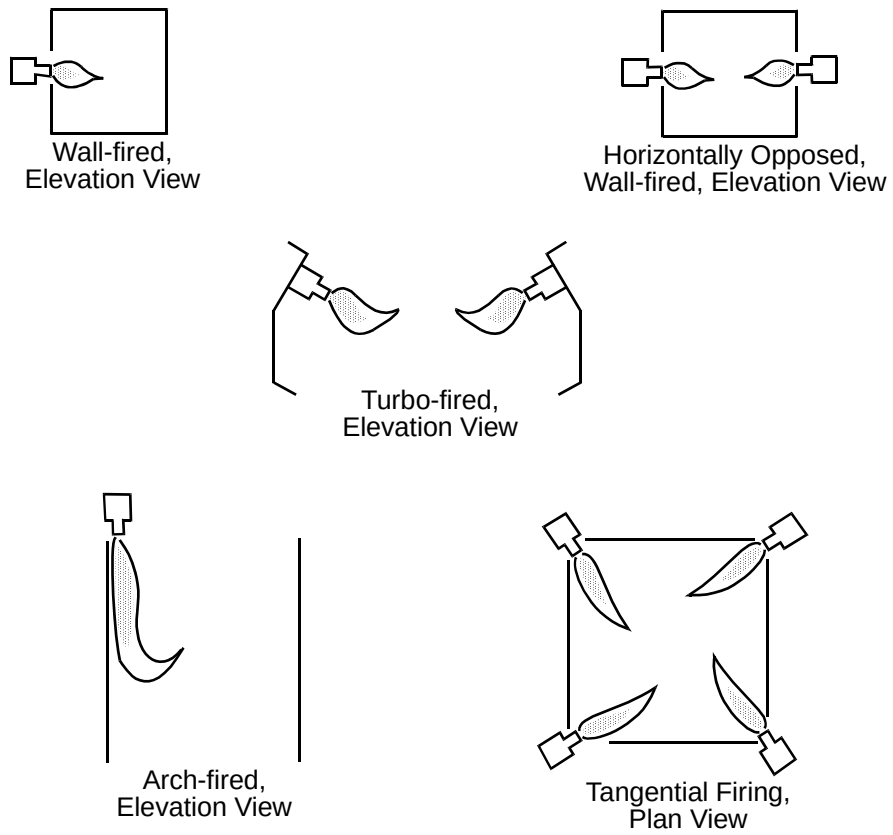

Figure 2-12. Large Boiler Configurations

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The two remaining sketches in Figure 2-12 are less common burner arrangements used in utility boilers. Each sketch shows one (or a pair of) burner in a line of burners across the furnace. These burners make little or no use of swirl and instead use the flame's buoyancy to recirculate the flow for flame stabilization. The population of these furnaces is small and there is little prospect that any more will be built.

Another burner with a limited population is the *cyclone burner*, which is designed to burn crushed, not pulverized, coal. Figure 2-13 is a cut-away view; the internal diameter of the burner is 6-8 feet. These burners, built primarily by B&W, eliminated the need to pulverize coal in order to burn it in a large boiler. Coal is crushed to less than 3/4" (like gravel), fed through the end of the barrel, and burned on the inside surface of the burner barrel, which is built of water tubes. Air is blown in through a tangential slot along the top of the barrel at hurricane velocity, about 300 ft/sec. This is high enough to distribute the coal around the circumference and burn it very intensely. Hot combustion gases and fine particulate depart through the burner throat into the main boiler firebox. Most of the coal ash melts to form a liquid slag that drains through a notch in the furnace wall. While this design overcomes the cost and complexity of a pulverized coal system, it suffers from a critical limitation: NOx emissions are high and difficult to control.

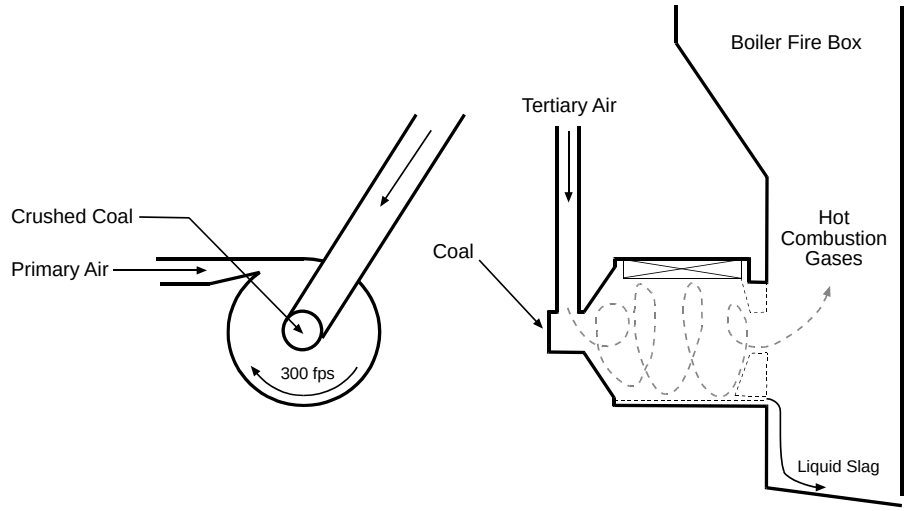

Figure 2-13. Cyclone Burner Concept

2.2.2.5 Stoker Fired – Coal, Wood, and Solid Waste

The stoker is the most primitive of current combustor designs, but it is capable of burning almost any solid fuel. Unless they are powdered, solid fuels can only be burned in a stoker or a fluidized bed combustor. Fuels fired in stokers cover the range from crushed coal to municipal solid waste. Stoker furnaces are used primarily in coal or wood-fired industrial boilers and to burn municipal solid waste. They range in size up to about 1000 mmBTU/hr. The physical dimensions of the grate set this upper limit; the maximum firing rate is about 1.0 mmBTU/ft^2 and dimensions larger than about 30 ft. are unmanageable. Stokers were used in utility boilers for the first half of the 20th century, but as the need developed for larger boilers, pulverized coal systems took over the market, where combustion uses the volume of the furnace not just the floor area. About 25 years after the transition from stoker to pulverized coal furnaces there began another transition, from coal to oil, then to gas. So the primary use of stoker type furnaces during the last half-century has been for wood chips and waste fuels – mostly in the forest products industry and for municipal solid waste. Coal stokers are still in use, but many date to the first half of the last century. Burning fuel on a stoker is little different from a campfire or the fire in a fireplace. The evolution of the stoker from the common hearth or campfire has been automation and adaptation for the larger physical size of a stoker furnace. Fuel is introduced with some type of mechanical feeder – the actual stoker. Ash is removed either by hand in smaller furnaces or by some variety of automated mechanical grate in larger systems. Airflow is no longer natural draft, but is supplied by a forced draft fan. Air flow is divided, some supplied under the grate and some supplied to the fire above the grate as overfire air. Figure 2-14 shows the key features of a stoker. The traveling grate shown here is one of many grate varieties.

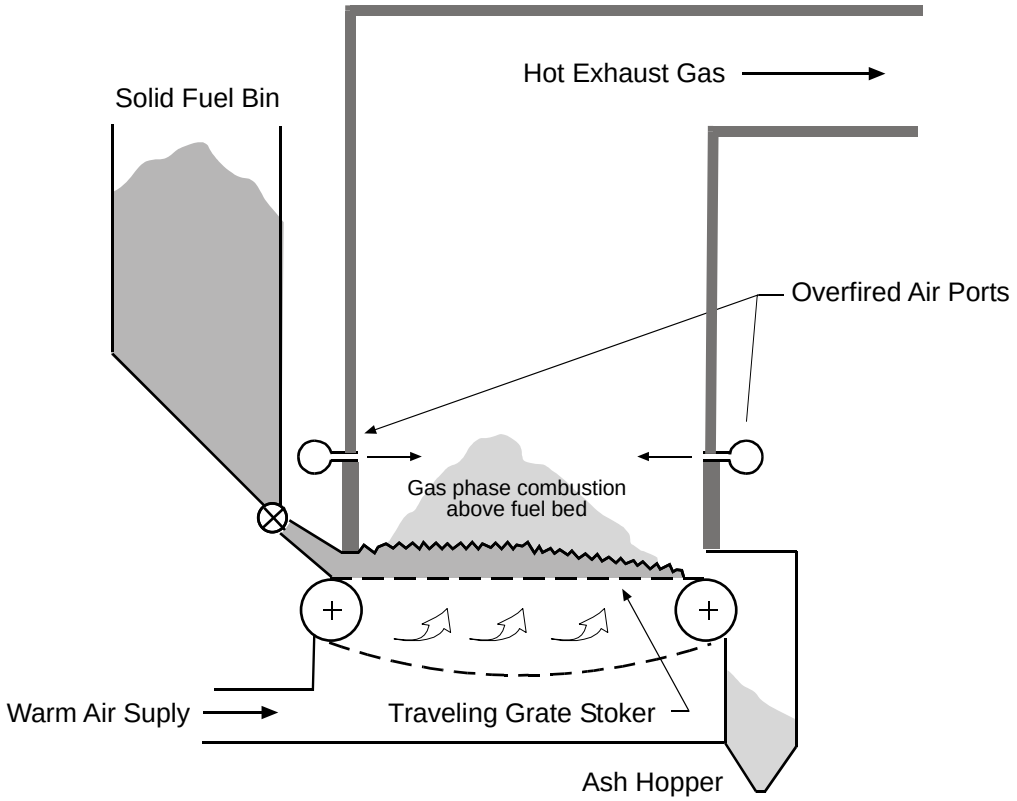

Figure 2-14. Stoker Firing Concept

Fuel Burning on a Grate

The length of time it takes for fuel to burn on a stoker grate depends on how large the pieces are because solid fuel burns primarily on the surface. A large piece of fuel burns faster if it is broken up into smaller pieces. So there has to be a correlation between the size of fuel particles fed to the furnace, the expected firing rate, and the transport rate on an automatic grate. For example, one can put pieces of railroad ties into the furnace, but they will probably take two or three hours to burn completely. So the speed of the grate must be adjusted accordingly and the furnace will probably need a supplemental fuel of wood chips or crushed coal in order to sustain its normal load. Typically, coal or wood is crushed or chipped into pieces smaller than 3/4".

The other aspect of stoker fuel particle size is the behavior of small particles. A stoker can be operated with fairly small fuel particles, but the result is that the fuel burns up quickly and the firing rate can actually be somewhat unstable – burning furiously then dying down. So one normally does not want a lot of fine particles. Another more serious problem with particles less than about 1/8" (3 mm) is that the air velocity is sufficient to blow them off the grate and out of the furnace. Clearly there is a need to limit the minimum size and the amount of small particles. Chapter 3 provides a description of standard methods for stoker fuel sizing.

Most stokers use some kind of automatic fuel feeder to spread fuel onto the grate. This device must have an adjustable feed rate to control the average furnace-firing rate and may have other adjustable features. One essential objective of the feeder is to generate a uniform distribution of fuel on the grate. If the fuel layer on the grate is a series of mounds and valleys, it affects the distribution of air coming up through the grate. The air tends to flow up through thin spots in the fuel layer and is blocked from flowing through the thicker mounds. Good combustion dictates more air where there is more fuel – not less. Thus fuel mounds burn slowly and the air that should be used to burn them carries unused oxygen out of the furnace.

Solid fuels take considerable time to burn, depending on the moisture content and on the size of the pieces of fuel. This means that a stoker boiler cannot respond rapidly to load changes. The boiler can take 10 or 15 minutes to burn down fuel that is already in the furnace in response to decreased load. There is a similar restriction on building up a supply of fuel in the furnace to respond to load increases. The operator can use air flow controls to increase or decrease the load rapidly. However, dropping the air flow too much will cause the boiler to smoke and raising it will rapidly decrease the amount of fuel in the furnace, which limits the use of air flow for load control.

Fuels like green wood chips and municipal waste can contain 50% to 60% water which requires hot air to dry the fuel before it will burn. So these stokers require hot air under the grate (400°F – 500°F). On most of these systems the fuel is moved progressively from one end of the grate to the other. As the fuel moves, it dries and then begins to burn so that eventually only the ash remains. The traveling grate shown in Figure 2-14 is one way to achieve this. A stoker boiler can also burn wet fuel in a thick stationary bed. Once the fire is started, fresh fuel is continuously spread on top where it dries, burns down and leaves only ash at the bottom against the grate. Eventually, the fire is allowed to burn down in order to remove the ashes.

Fuel Feeders

A great many feeder devices have been designed in response to various fuels. They all have various features intended to improve their reliability and support the objective of a uniform fuel distribution across the grate. These details are beyond the scope of this text, but a basic description will be provided of two broad groups of feeders: (1) spreaders, and (2) bottom feeders.

Spreader stokers throw fuel onto the grate as indicated in sketch (c) of Figure 2-15. The spreader is located two to four feet above the grate. Coal spreaders use a small paddle wheel device spinning fast enough to throw larger coal particles across the furnace. There may be several of these across the width of the furnace. Wood waste spreaders commonly use a pneumatic puffing device in place of the paddle wheel.

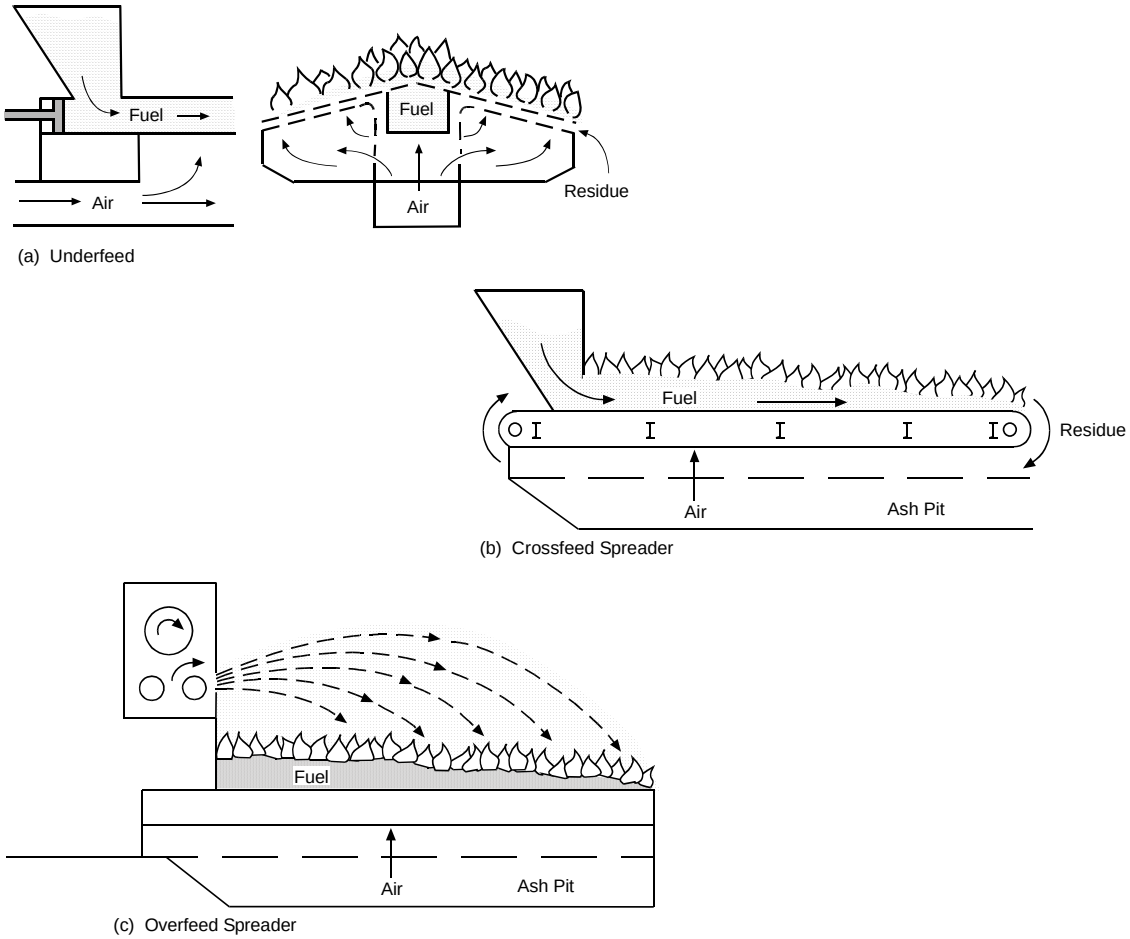

Figure 2-15. Example Configurations of Industrial Stokers

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Bottom feeders, such as those shown in sketches (a) and (b) of Figure 2-15, are slow moving. The traveling grate shown in Figure 2-14 and sketch (b) of Figure 2-15 can take up to an hour to traverse the length of the furnace, corresponding to the time it takes for the fuel to burn completely. The height of the bed in sketch (b) of Figure 2-15 or speed of the ram in sketch (a) of Figure 2-15 is used to control the furnace's average firing rate.

Air Flow

Early stokers had no fans. They had tall stacks that generated enough draft to draw air into the combustion zone and through the boiler. A single damper near the stack controlled air flow. Essentially all furnaces now use forced draft (FD) fans to supply air to the furnace. Larger furnaces also use an induced draft (ID) fan to maintain a

negative pressure in the furnace and move the exhaust gas. Some smaller boilers may still use stack draft to move the flue gases downstream of the combustion zone.

Overfired Air

Nearly all stokers distribute some of the air above the grate as overfire air. As solid fuel is heated and burned it releases various hydrocarbons – volatile matter which can burn in the gas phase above the grate. Volatile matter can account for more than 50% of the heat release, which implies that a major portion of the combustion air needs to be supplied as overfired air to burn some fuels. This poses a dilemma for older stoker systems. Unless the grate is water cooled, it needs about 2/3 of the total air flow to keep it cool and prevent long term thermal damage, which leaves insufficient overfired air for typical fuels. As a consequence, stoker furnaces generally use much more air than is theoretically necessary for combustion. Excess air levels are usually at least 35%, but are frequently more than 50% in order to prevent smoking.

Overfired air is necessary to burn all the volatile gases that are released from the fuel bed as it burns. If the amount and/or distribution of overfired air is inadequate the furnace will smoke and emit CO. Overfired air does not have to be preheated, but it does have to be an adequate amount to mix well with the gases coming off the fuel bed. Usually about 50% or more of the combustion air needs to be supplied by a high pressure fan and the ports into the furnace need to be the right size and spacing.

Grate Concepts

The grate supports the burning fuel and has openings that supply air to the bed. Air will be evenly distributed around the grate if there is some pressure drop across the grate, typically 0.5" w.g. or more. The lower the pressure drop, the more the air will tend to follow the path of least resistance. Air will not go where the fuel is most deeply piled on the grate. The operating problems associated with inadequate pressure drop begin to appear when the grate holes become enlarged or the seals around the edge of the grate become worn. Thus deterioration of the grate system will have significant impact on operation before there is obvious need for repair or maintenance. There are many types of grate design that serve a variety of purposes with different fuels. General descriptions of a few types follow.

- *Stationary Grates.* Stationary grates are the oldest as well as some of the newest designs. They are common in wood chip and wood waste fired facilities. A stationary grate can be water cooled, which allows most of the combustion air to be overfired. The problem with a stationary grate is that the ash must be removed by some other mechanism. Small to medium grates can be raked by hand. Larger stationary grates require a mechanical rake.

- *Traveling Grate.* Traveling grates, such as the one shown in Figure 2-14 provide automatic transport of the fuel bed and removal of the ash, but they require a lot

of air for cooling, which limits the amount of overfired air and the ability to control smoking. Traveling grates are common in coal-fired systems.

- *Oscillating Grates.* There are a wide variety of oscillating grate designs where portions of the grate move periodically and gradually push the fuel downhill toward an ash hopper. This concept is favored for municipal waste combustors because the grate action tends to stir the bed and help to expose and burn wet or non-uniform fuels. Some of these designs also tend to be self-cleaning to remove molten glass or other sticky ashes.

Stoker Summary

Most of the major components of a stoker-fired boiler are shown in Figure 2-16. Starting from the left side there is a fuel supply system that controls the rate of fuel feed and spreads it onto the grate. The air supply is split into under-grate and over-fire flows. Hot combustion gases pass out the top of the boiler past convectively heated tubes that superheat the steam. Although the walls of the furnace are normally water tubes, this boiler also has a convective steam generating section as shown by the tubes connecting the mud drum to the steam drum.

The exhaust gases from a stoker tend to carry a lot of course particulate, and virtually all stoker boilers employ a pre-treatment system such as the multiple cyclones shown here. Some of the particulate will still be burning, particularly if the fuel is waste wood or bio-fuel, and a cyclone is not damaged by flaming embers. The air heater provides the hot air necessary for firing wet fuel as well as saving energy by cooling the exhaust gas. Gas flow through the system is provided by a pair of fans, forced draft (FD) to supply air and induced draft (ID) to maintain a negative draft in the combustion chamber.

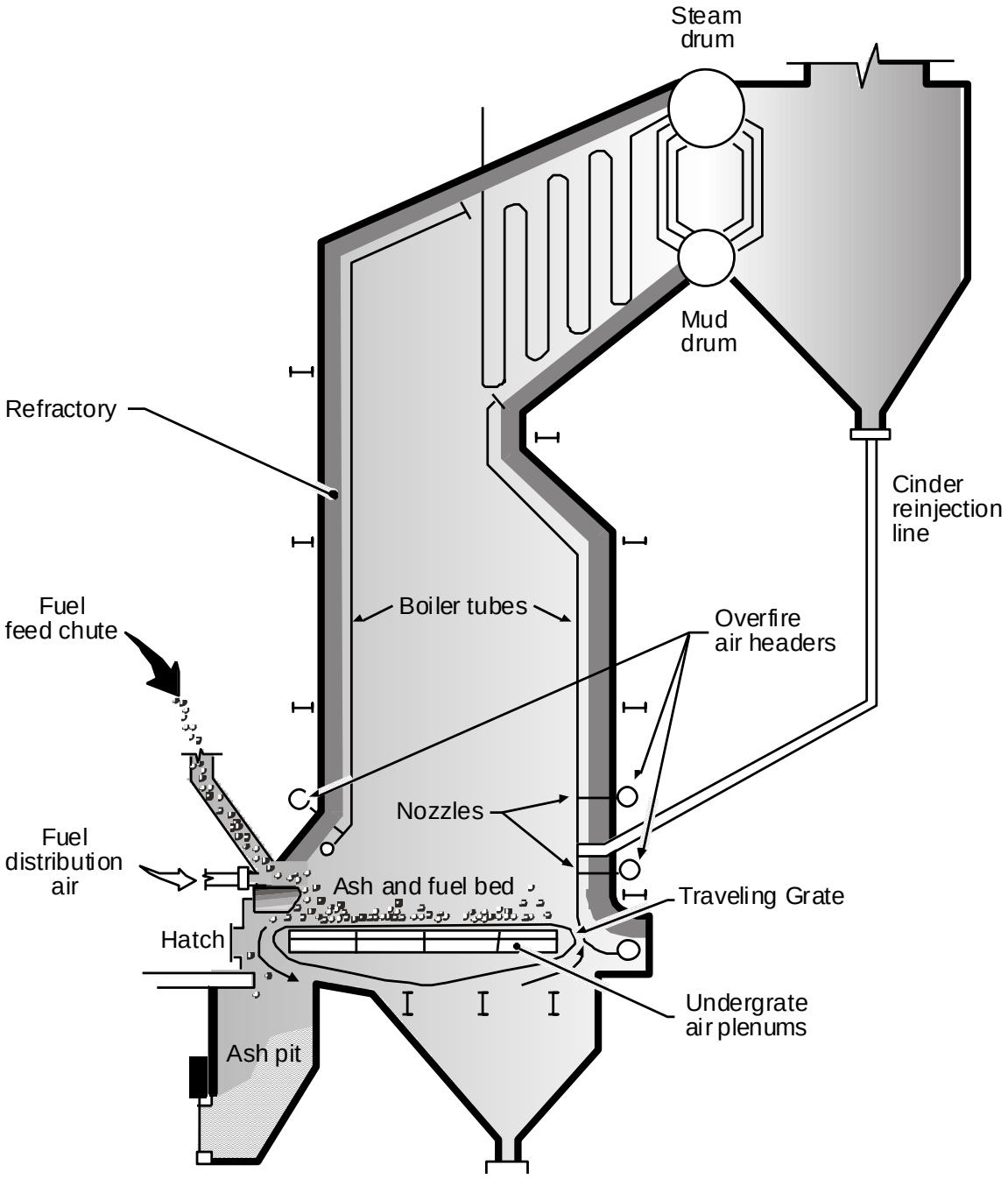


Figure 2-16. Stoker in a Large Boiler

2.2.2.6 Fluidized Bed Combustors

The fluidized bed combustor is the most recent type of solid fuel combustor. In fact, this combustor has come into common use only since about 1975. Fluidized bed combustors can fire a wide variety of solid, liquid or gaseous fuels and they overcome most of the problems associated with fuel and air misdistribution across a stationary

grate. Figure 2-17 shows a version of a fluidized bed. The basic device appears similar to a stoker except that a bed of ordinary sand, about a foot deep, replaces the grate. When air is blown up through the bed nothing happens until the air exceeds a critical flow rate, at which point the bed begins to lift. Air flow causes the bed to expand to a depth of more than three feet, and the air bubbles through it like steam in a pot of boiling water. The temperature of the sand is raised to about 1500°F by adding gas to the air and igniting it. Once the bed is up to its normal operating temperature, small pieces of virtually any solid fuel can be added and they will burn.

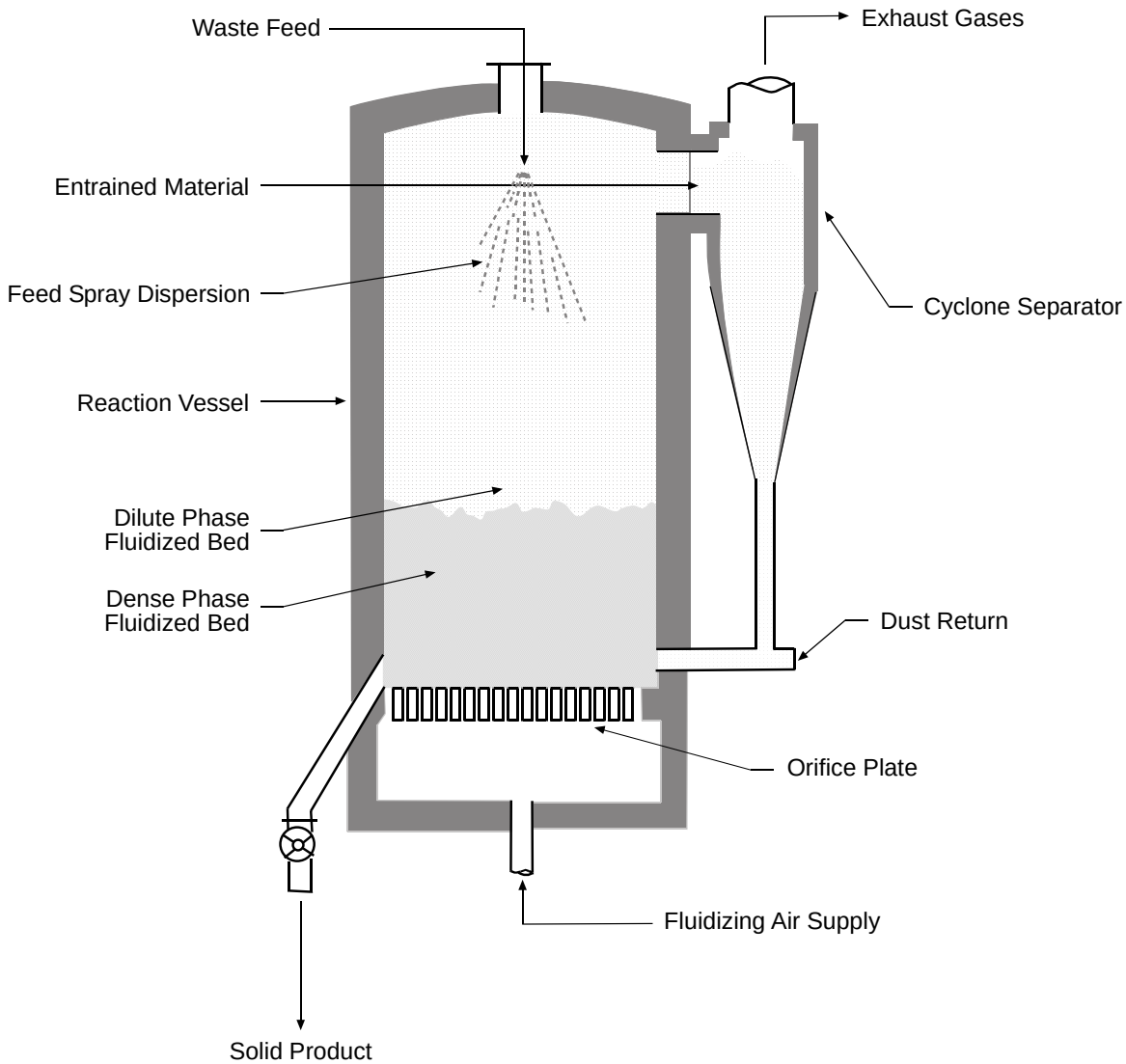


Figure 2-17. Fluidized Bed Combustor

The stirring action of the bubbling air causes the fuel to mix throughout the bed and constantly come in contact with fresh air as it rises through the bed. Fuel can be added at any location and it fairly rapidly disburses through the bed, so the problem of trying to evenly distribute the fuel disappears. Fuel particles either float randomly on the

surface or mix down into the bed. In either case they burn rapidly. Combustion is very stable because the bed temperature cannot be changed rapidly, so unlike a flame, it cannot be blown out. In fact, the bed can be shut down by shutting off the air. An inactive fluid bed takes several hours to cool and during that time it can continue operation simply by restarting the air and fuel flow.

A fluidized bed requires a system to continuously make up sand that is lost. Some of the sand as well as ash from the fuel are continuously carried out of the bed by the exhaust gas. A cyclone or inertial collector is used to capture the coarser particles that are returned to the bed. Finer dust particles pass through the cyclone and must be captured with a dust collector.

A fluidized bed is ideally suited to firing solid waste fuels or very low-grade fuels such as those with high moisture contents or low heating values. This type of combustor can be set up to fire fuels in almost any combination. A side benefit of operating at a very low temperature is that it produces fairly low levels of NOx. In some cases, adding lime or limestone to the bed has reduced SOx emissions.

Given the advantages of the fluidized bed combustor, why are there are so few of them? The primary answer is that as long as traditional fuels like natural gas or oil are cheap, there is little economic incentive to use other fuels. Fluidized bed combustors have some significant costs that are not incurred by systems fired on standard fuels.

- *Electrical Energy Costs.* Lifting the bed of sand requires 30" or 40" w.g. pressure that is easily four times as much as the forced draft (FD) pressure of a standard boiler. So the fluidized bed has a substantially higher electrical energy cost to run the combustion air fan.

- *Cost of Bed Cooling.* In order to keep the bed temperature low enough that the sand does not melt it has to be cooled. One approach is to put water tubes in the bed, which makes a very effective steam generator. However, the erosion rate from sand scrubbing the tubes is very high, so the tubes have to be replaced quite frequently. Another approach is to operate with about three times the normal excess air level. This increases the size of the bed by a factor of three and triples the electric bill for running the air fan. A third alternative is a system called a circulating fluidized bed in which the bed sand is continuously circulated through a heat exchanger to cool it off before it is returned to the combustor bed. This incurs a significant amount of additional hardware, but avoids most of the problems with the first two alternatives.

- *Ash Management Costs.* A fluidized bed combustor, even if it is burning clean fuel, requires a dust collector to control particulate emissions with associated ash management systems. Of course it also requires systems to make up sand that is gradually lost as the system operates.

2.2.3 Thermal Oxidizers and Other Combustion Systems

Although combustion systems can generate air emissions, they are used effectively as pollution control systems in a number of applications. The word *incinerator* has acquired a negative political connotation leading to the use of other terms, such as *thermal oxidizer*.

A variety of thermal oxidizers are used to control the emission of organic gases from other (non-combustion) types of sources. Various industrial processes generate solvent vapors or other organic gases and combustion is an effective way of controlling the emission of these pollutants. When properly operated, thermal oxidizers achieve nearly complete destruction of virtually all organic compounds, converting them to carbon dioxide (CO_2) and water vapor (H_2O).

2.2.3.1 High Temperature Oxidizers

Figure 2-18 shows the elements of the basic thermal oxidizer. Air from a process such as a coating operation is blown into a refractory lined chamber. A gas-fired burner maintains the chamber temperature above the minimum destruction temperature, typically 1400°F. If the incoming air is well mixed with the hot gas from the burning flame, there will be non-detectable levels of organic compounds in the exhaust. However, if the mixing is poor, there will be large spatial temperature gradients in the exhaust and some of the incoming air will carry its pollutants up the stack. The quality of mixing is determined primarily by the geometry of the chamber. The partition wall in the chamber suggests the sort of geometry necessary to assure mixing. In practice, a thermal oxidizer should be tested when it is commissioned to be sure it is working properly. Once the design is shown to work well, at or above a given temperature, its performance can be reasonably assured by simply maintaining the exit temperature above the demonstrated level.

While a basic thermal oxidizer, such as the one pictured in Figure 2-18 is a very effective pollution control device, it uses a lot of fuel and the resulting hot air is dumped into the atmosphere. One way to reduce energy costs is to install a heat exchanger, which can reduce fuel consumption by 70% or more. The applicability of a heat exchanger depends on the kinds of organics being controlled and the type of heat exchanger used. For example, chemicals like phenolic resins may condense in the cold end of a metal plate or tube heat exchanger and make it inoperative. Other types of equipment such as a regenerative heat exchanger can be more tolerant of troublesome chemicals. Any type of heat exchanger can develop leaks or a valve malfunction resulting in organic material bypassing the oxidizer. Thus the heat exchanger becomes the primary cause of low destruction efficiency.

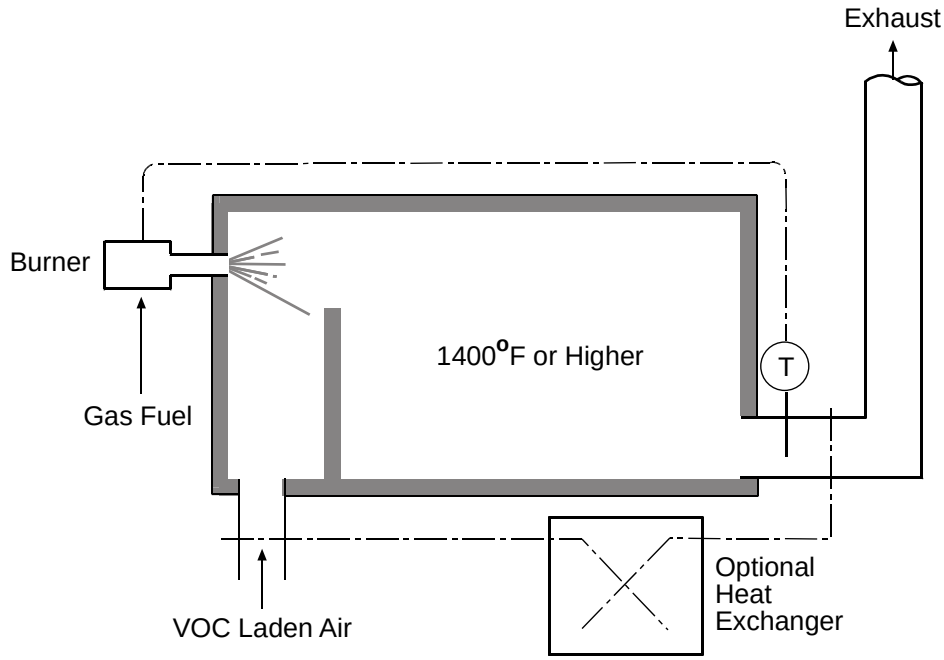


Figure 2-18. Thermal Oxidizer (Gas Incinerator)

2.2.3.2 Catalytic Oxidizers

Catalytic oxidizers are similar to high temperature oxidizers, except that they work at much lower temperature and are therefore cheaper to operate. By passing the contaminated air through an oxidation catalyst, organic compounds are oxidized at temperatures as low as 500°F or 600°F. Oxidation catalysts are precious metals – usually platinum, but rhodium and palladium have been considered. The configuration is not very different from Figure 2-18, except that the burner only has to heat the air to the catalytic reaction temperature and there is a catalyst between the burner and the stack. The catalyst can be on the surface of a fixed support, like a honeycomb grid, or on the material in a bed.

The destruction efficiency of a catalytic oxidizer depends on a number of factors including the type of catalyst and the organics species being oxidized. Oxidation catalysts work better at higher temperatures, so low temperature regions in the oxidizer can cause reduced destruction efficiency. Performance also deteriorates if there is insufficient catalyst surface area or if the air velocity through the catalyst is too high. These are concerns that can be evaluated by the manufacturer during design or by demonstration tests after the system is operational.

The performance of a catalytic oxidizer will deteriorate if the catalyst is damaged or poisoned. Catalysts work by reacting with or adsorbing molecules of the original species and then, when the reaction is completed, the catalyst is returned to its original state. If there are species in the gas that react with or absorb on the catalyst permanently, the catalyst does not return to its original condition and it gradually becomes deactivated. The vulnerability of the catalyst to any particular type of

poisoning or contamination depends on the exact composition of the catalyst, its operating temperature and other factors. Catalyst manufacturers invest heavily in the development of proprietary formulations suited to specific applications. There is no "silver bullet" and all catalysts are vulnerable under certain conditions. Thus there needs to be some method to periodically monitor or measure the performance of a catalytic oxidizer to be sure that it is still operating as intended.

2.2.3.3

Elevated and Ground Flares

Historically, elevated flares were used by chemical processors and refineries to destroy waste gases. Many of these served primarily as safety devices. Combustible gases that are released accidentally can accumulate and pose an explosion hazard unless a continuous ignition source at the point of release prevents inadvertent accumulation.

The effectiveness of using a ground flare for pollution control is a relatively recent issue. Flares are extensively used today at landfills, where the odorous gases generated in the landfill are sucked out of the fill and fed to a flare for destruction. In this case, the effective destruction of the gases is the primary purpose of the flare. At larger landfills the gases are used beneficially as fuel to operate engines that generate power.

A flare has two basic purposes: (1) assure stable continuous combustion, and (2) consume the organic gases efficiently with minimum emissions. The design usually must accommodate variable rate gas flows and sometimes a significant variation in heating value. Figure 2-19 is one design concept that achieves these objectives.

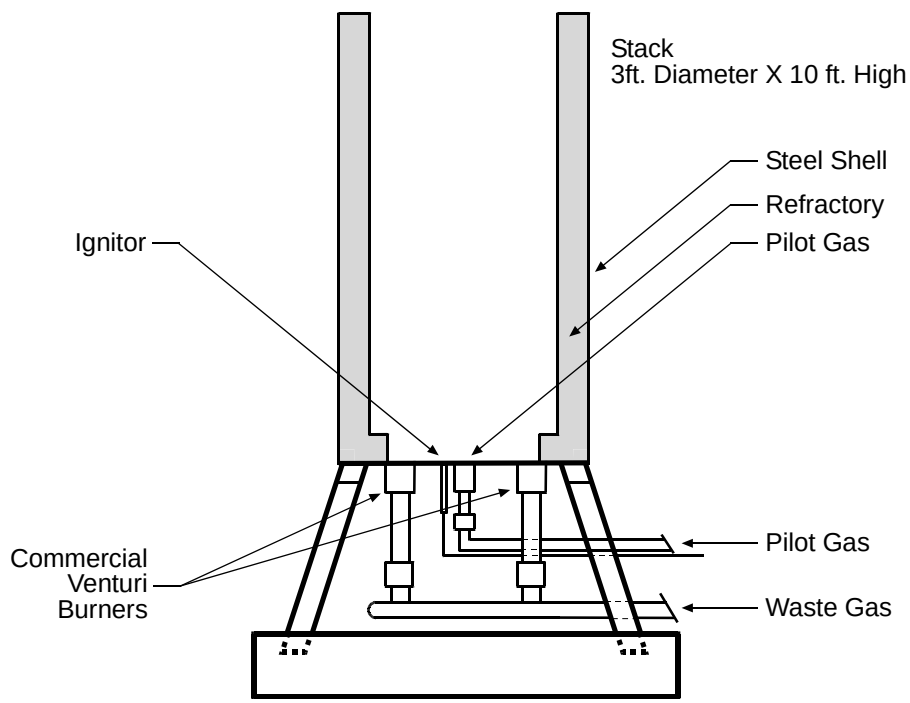


Figure 2-19. Ground Flare Concept

Combustion occurs inside the refractory tube, which makes the flare relatively insensitive to wind disturbance, and makes it feasible to measure the emission performance of the flare. A number of venturi burners at the base give stable fires. These burners use jets of gas (fuel) to draw in the right amount of air to give a flammable mixture. The amount of air entrained by the venturi is directly proportional to the amount of gas passing through the jet, so the fuel-air ratio is held fairly constant and the flame does not smoke or blow out. The pilot gas at the base provides continuous ignition. This is one of numerous flare designs.

2.2.3.4 Kilns and Other Devices

Cement Kilns

Cement kilns are large combustion devices used in the manufacture of Portland cement. Their basic function is to heat a pulverized mixture of lime, silica and other constituents to a temperature above 2300°F to create clinker, the principal ingredient of Portland cement. Any lower temperature does not form the crystal structure of clinker. Figure 2-20 shows the key elements of a cement kiln. The kiln is a long sloping tube that rotates slowly. Meal, a careful blend of limestone, silica and other minerals in powder form is fed into the upper end. The carbon is liberated from the limestone as carbon dioxide and the remaining constituents partially melt and fuse into the substance called clinker. After it leaves the kiln, the clinker is cooled and is ground down to a powder that is Portland cement.

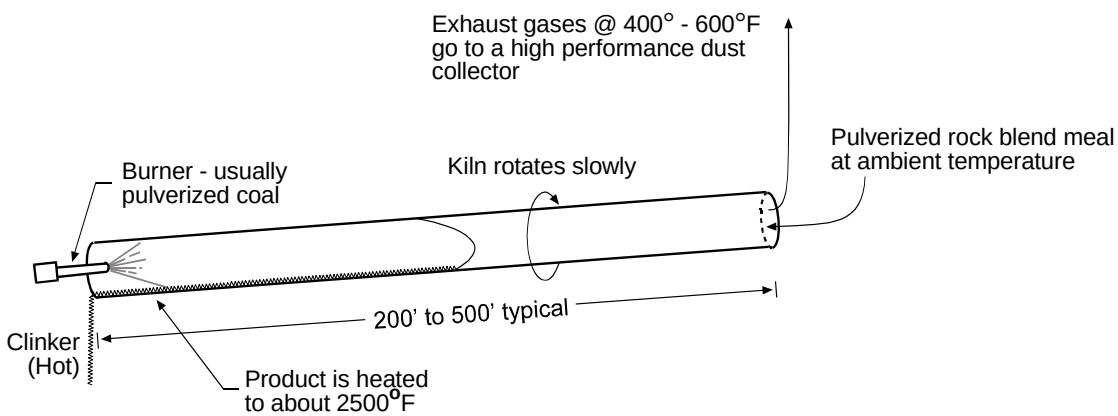


Figure 2-20. Rotating Cement Kiln

Kilns can burn any reasonably dry fuel; usually the most inexpensive is medium to high sulfur coal. The coal is pulverized and blown into the lower end of the kiln through a single burner. Air comes in parallel to the burner and is preheated by the hot clinker that has left the kiln. The hot combustion gases flow up the kiln, transferring heat to the meal and the meal flows in the opposite direction. The kiln is

a counterflow heat exchanger. In the process, much of the coal ash and any other incidental minerals are combined into the clinker. The process also absorbs much of the coal sulfur into the clinker as part of the crystal structure, so SO_2 emissions are reduced. In short, the process operates at a very high temperature and most of the minerals introduced to the kiln are absorbed into the clinker. Cement kilns exhaust to a large and very efficient dust collector.

Kilns can be significant sources of NOx, although progress in kiln burner design since about 1980 has reduced these emissions. The one thing that kilns cannot easily control is organic emissions originating in the minerals fed to the kiln. As the mineral feed moves down the kiln, it is heated and any volatile constituents in the meal are released and carried out by the exhaust gases. Only those that volatilize at very high temperature and are carried far down the kiln will encounter gases hot enough to destroy them. Some minerals contain traces of fossil organics (oil shale) or compounds that break down to form ammonia. The normal cement kiln cannot control these resulting emissions.

The fact that kilns are large stable combustors, which operate at a very high temperature and have very efficient dust collectors, makes them attractive for hazardous waste incineration. In fact, a number of commercial cement kilns have permits to manage and destroy hazardous wastes. They compete with facilities built specifically for hazardous waste incineration. Organic wastes are fuel for the kiln and their use reduces the consumption of purchased fuel, sometimes by 50% or more. For some older less efficient kilns, this has made the difference between economic operation and having to shut down.

In addition to liquid wastes, some kilns can fire solid wastes. Long kilns as shown in Figure 2-20 can be fitted with a mechanism that inserts a five-gallon pail into the middle of the kiln once each revolution. This location is hot enough that the waste burns completely. With other kiln systems, such as a preheater design, a short kiln is used that includes only the hottest part of the process. The cooler part of the process is handled in a separate preheater tower so the kiln feed is already at a temperature above 1500°F. These kilns can accept whole tires as well as containers of solid waste into the upper end of the rotating kiln. The steel in the tire cords is incorporated into the clinker and the rubber provides energy at useful point in the process.

Sludge Burners

Wastewater treatment plants generate a semi-solid sludge, which tends to be odorous and can be a disposal problem. This sludge typically contains as much as 80% water. At one time most sewage sludge was land applied; that is once again becoming an attractive and viable alternative. However, the contents of sludge can be a problem for land application and the sludge needs to be dewatered in order to make transportation viable from urban treatment plants to remote rural sites. So treatment facilities that dewater, pelletize, and track the composition of the resulting product are becoming more common. Disposal by incineration continues to be an option particularly with dry pellets that have significant fuel value. Sludge pellets can be fired in a stoker or fluidized bed boiler that is part of a waste to energy facility.

Historically, sludge incinerators were primitive devices intended primarily to get rid of the sludge, with air emissions being a secondary consideration. The traditional device is a multiple tray sludge burner as shown in Figure 2-21.

The multiple hearth furnace is a counterflow heat exchanger. Sludge is fed in the top and drops by gravity gradually from one hearth to the next. As the sludge moves downward, it is heated, dried, and eventually incinerated near the bottom of the furnace. The heat produced by the sludge incineration near the bottom of the furnace provides some of the heat necessary for drying sludge in the upper furnace. Residual ash drops out the bottom. Drying removes not only water, but also any other volatile constituents including much or most of the organic material in the original sludge. These gases with much of the resulting organic vapor are emitted with the exhaust.

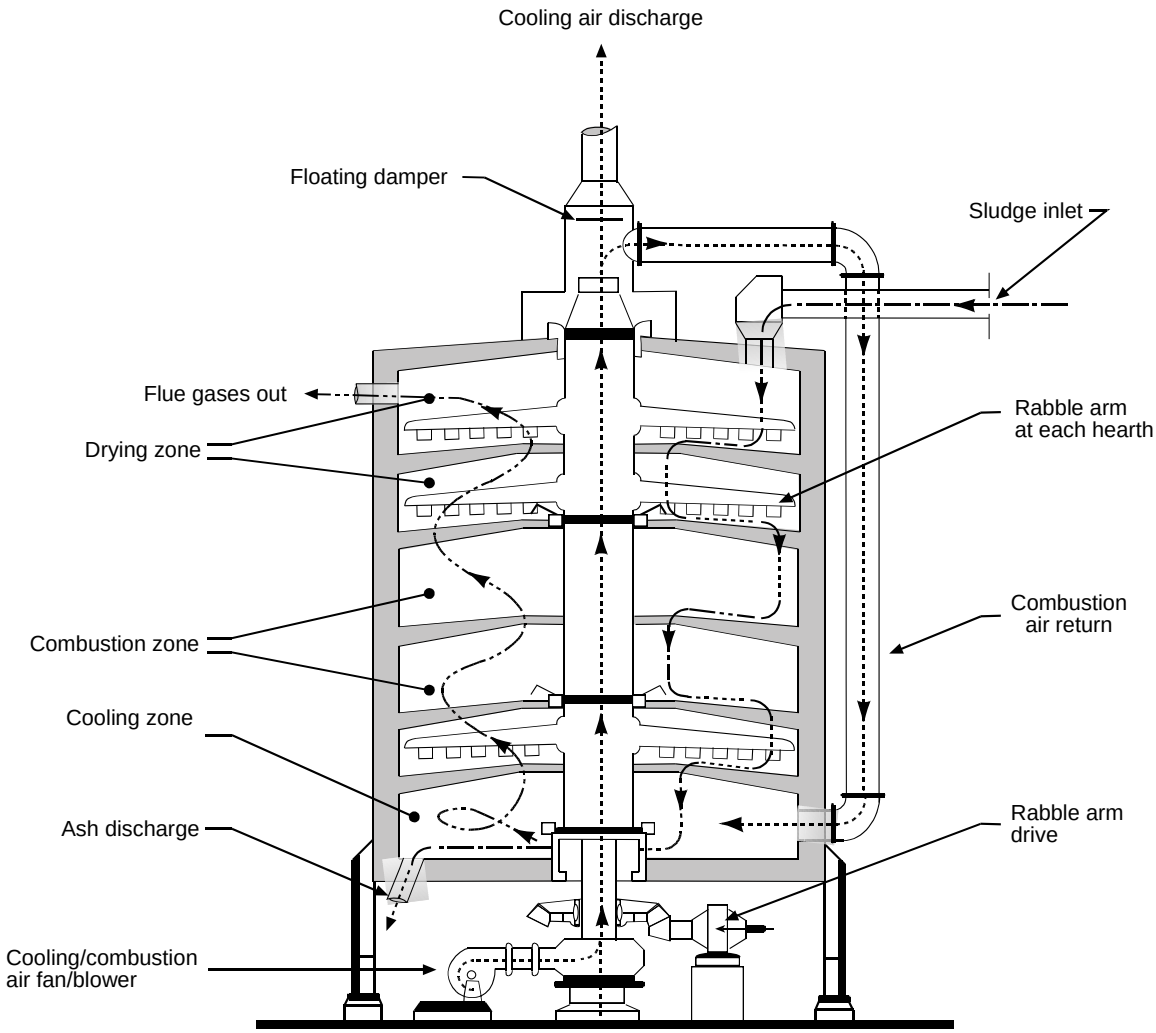


Figure 2-21. Multiple Hearth Sludge Burner

The multiple hearth furnace is also used in some industrial processes. If the feed material is free of volatile contaminants, the only pollutants will be from the combustion process as well as any particulate generated from the product.

2.3 FUEL STORAGE, HANDLING AND PROCESSING

2.3.1 Natural Gas and Oil

Natural gas is the cleanest and easiest fuel to handle. However, because it is delivered by pipeline, large end users must install branch piping from the gas company's line to their facility. In addition, smaller facilities use gas at pressures of only a few psi, while larger facilities take gas at more than 100 psi. However, long distance pipelines operate at pressures on the order of 1000 psi. Therefore, both large and small end users must install a pressure reduction station.

In many locations, the price of gas is reduced if the user is willing to accept an interruptible supply. During times of high demand (typically winter) a gas company may run short of supply unless it has customers willing to have their gas shut off. Thus it pays some companies to install hardware to fire a different fuel (usually oil) and therefore be able to accept a gas curtailment. This may apply both to engines that can burn No.2 oil and to large boiler facilities that typically burn No. 6 oil.

Oil may be delivered by pipeline in some locations, but typically it is delivered by truck, barge or rail. Small to medium size facilities typically take delivery by truck. Oil-fired electric utilities use too much fuel to make truck delivery practical and typically take delivery by barge or rail. In some cases, they run a pipeline a few miles from the nearest barge delivery point to the facility. Virtually all oil-fired facilities have oil storage capacity, usually at least enough to operate one full day. Some oil-fired utilities have large tanks that allow the plant to operate all winter when barge deliveries are not possible.

No. 2 oil is usually stored at ambient temperatures and it can be pumped even when the temperature is less than 0°F. By contrast, No. 6 oil has a pour point temperature below which it is too viscous to be pumped. Pour points are commonly in the range of 60°F to 100°F, but it can be higher. Therefore, No. 6 oil storage tanks must be insulated. If the oil is not used rapidly, supplemental heaters are used to keep the oil above its pour point.

Another concern with No.6 oil is stratification in the tank. If there is no mixing device, oil added to the tank can form a layer above or below the existing oil. When this transition layer drops past the oil pick-up line, it can cause a minor upset in the source operation or it can alter the emissions. Water is also a concern because No. 6 oil deliveries occasionally contain significant amounts of water. Normally the water settles to the bottom of the tank where, if there is enough of it, it will begin to interrupt combustion as slugs of water are fed to the burner. Occasionally, No. 6 oil is dense enough to cause water to float on the surface of the oil.

2.3.2 Solid Fuels – Storage, Feeding

Solid fuels, primarily coal and wood chips, are transported by truck or rail and occasionally by barge or ship. Figure 2-22 shows the primary elements of solid fuel handling. Perhaps the most significant element of solid fuel handling is the exposure to weather. Rain during transport or on-site storage can substantially increase the water content of the fuel with significant impacts on combustion performance. Thus a source can have seasonal emission characteristics that are governed by the accumulation of rainwater in the fuel. When the fuel is fed to the plant it may pass through a crusher or shredder, past one or more screens to achieve a target size, and under a magnet to remove "tramp iron."

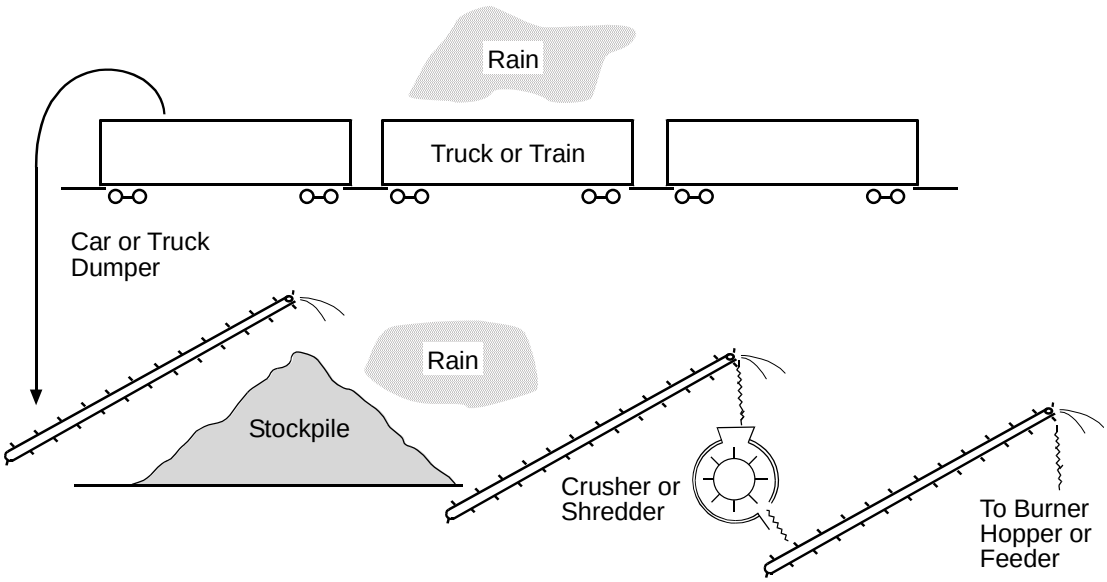


Figure 2-22. Elements of Solid Fuel Handling

2.3.2.1 Coal

Coal is hauled from mines to electric utility plants in unit trains, where the entire train carries coal to one plant. At one time many plants were located at or close to the primary supply mine. However, with the advent of SO_2 emission limits, a number of plants switched to low sulfur coal. In a number of cases, coal is hauled from Wyoming and Montana to the eastern or midwestern U.S. to meet the increased demand for low sulfur coal. Natural moisture content for bituminous coal is less than 4%; however, surface moisture from rain can raise that figure to 10%. Wet coal burns quite well, especially if it is pulverized, but it tends to stick to conveyors and hopper walls which can make a lot of work for operators to keep all the coal feed systems operating in a large plant.

Coal is stored in very large piles at the plant site. A car dumper empties coal rail cars one at a time, and the coal is moved to an initial pile by a conveyor. Then it may be pushed to another part of the pile by a large bulldozer. A key part of the bulldozer's operation is to compact the coal and shape the pile to promote drainage of any rainfall. If the pile is porous and it absorbs a lot of water, spontaneous combustion can ignite a section of the pile. The concept of water promoting combustion seems contradictory, but the water enables chemical oxidation, which begins to warm the coal ultimately leading to combustion. If properly managed, coal can be stored in a pile almost indefinitely.

2.3.2.2 Wood and Waste

Wood chips and wood waste are usually consumed fairly close to the place they are generated. Truck hauls of more than 100 to 150 miles are typically not economical. As a general rule, good quality wood chips are used to make paper or engineered lumber. Most of the fuel wood comes from the residue that remains after logging, or is generated at the mill from bark or trimmings that cannot be used for product. Construction and demolition activities also generate a significant amount of wood scrap that can be burned as fuel if there is a facility nearby.

Combustion performance and air emissions are strongly influenced by the moisture content of the wood being fired. Green or wet wood can contain 55% moisture or more. Dry wood is usually less than 15% moisture. Wood from demolition activity or waste trimmings at a wood products factory is usually fairly dry if it has not been stored outdoors.

Wood stored in a pile deteriorates with time and, like coal, can catch fire. Unless wood is kept dry, it promptly begins to rot and can lose 1% to 2% of its value every month, either as fuel or for wood products. Hence a wood chip pile is a perishable commodity that should be used as promptly as possible.

2.4 COMBUSTION AIR POLLUTION CONTROLS

2.4.1 Load Variations – Base, Swing, Peaking, Emergency

Most combustion systems are a part of a facility in which the load varies with time. Electric utility generators can be broken into three categories:

- *Base load.* Base load units are the first to be brought to full load and they operate at steady full load most of the time.

- *Swing load.* Swing load or topping units are intended to follow load swings and make up the difference between base load and current demand.

- *Emergency*. Emergency units are normally off line (shut down) and are used only when there is extraordinary demand or when there is a failure of the normal generating and supply system.

2.4.2 Control Systems

With any of these types of systems, a control system is required to drive the fuel feed system, match the air flow to the fuel flow, and operate other elements of the system. A simple example of the type of load variation seen by a typical system is shown in Figure 2-23, a hypothetical load versus time for a swing load electric utility boiler. The boiler is shut down when the trace starts about midnight. About 0300 it is started and runs at minimum load till 0700 at which time the demand for electric power increases and the boiler load rises to near maximum. The boiler then operates at varying high load throughout the day, dropping to a minimum load about 2100 and is finally shut down shortly after midnight.

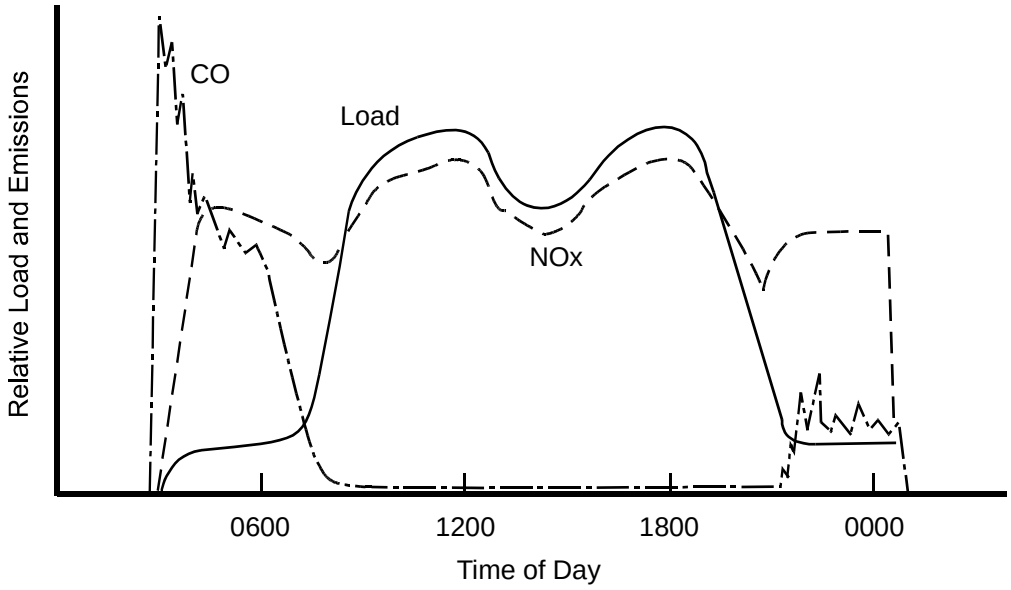


Figure 2-23. Example of Load Change Effects

Until about 1980, control systems relied entirely on mechanical, pneumatic and electro-mechanical devices. Then the programmable logic controller (PLC) appeared and control systems became much more sophisticated. Thus the population of systems in service today is a mix of pre-1980 systems, those that have been at least partially converted with modern controls and modern electronic systems. There has been a rapid evolution of control systems since 1980 and some work much better than others.

2.4.2.1 Fuel and Overall Control

Fuel control is relatively simple. The basic operation of the control is to add more fuel when load demand rises and decrease fuel flow when demand drops. The control needs to be stabilized, so it does not fluctuate. The control may also set limits on the minimum load, maximum load and rate of load change. A PLC controller can also compare flow control position to measured fuel flow or to actual load in order to detect abnormal operating conditions.

2.4.2.2 Air Flow and Controlling Fuel-Air Ratio

Air flow should vary with the fuel flow in order to keep a fixed ratio of air flow to fuel flow. A good controller should be able to keep this ratio steady within 1% to 2% of an operating set point. This may be possible based on measured fuel flow and measured air flow, but if the system uses measured exhaust O_2 concentration, then air flow can be controlled much more precisely. Exhaust O_2 is a direct indicator of the actual air flow relative to the theoretically required amount. Measured O_2 is about one order of magnitude more sensitive an indicator than using the comparison of measured fuel and measured air flow. Figure 2-24 shows one form of a current PLC control system. The measured fuel and air flow signals are the basis for setting an approximate air damper position. Measured O_2 is then used to trim the damper to a more precise position.

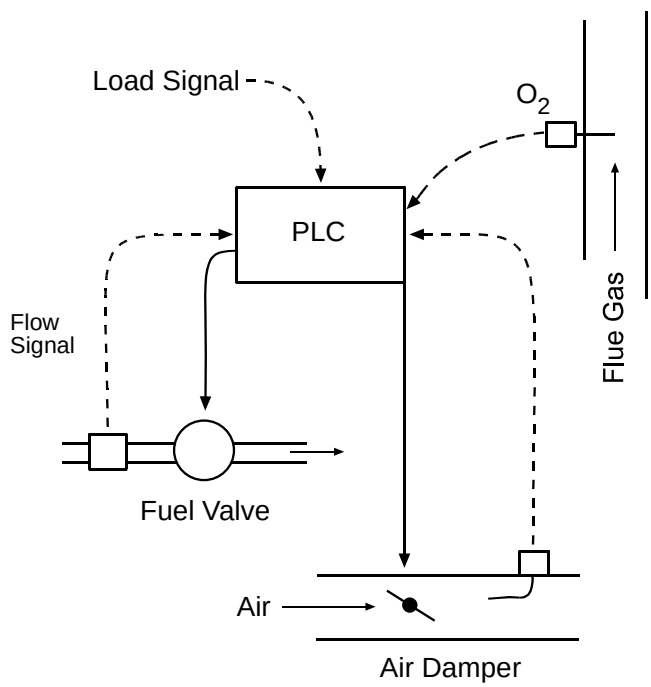


Figure 2-24. Example of a Computer-based Control System

2.4.3 Air Moving Components – Fans and Draft Levels

Air flow through a boiler is driven and controlled by components illustrated in Figure 2-25. Flow through the system shown here is driven by a pair of fans, *forced draft* (FD) and *induced draft* (ID). This is a *balance draft* system that is common for large boilers. The term draft refers to the difference in pressure between ambient atmosphere and the gas pressure inside the boiler. Some large boilers and most small package boilers use only a single FD fan. Either system is capable of pushing air and flue gas through the system. The difference between the FD fan and balanced draft systems is the gas pressure at various places in the boiler. A balanced draft system keeps the combustion zone and exhaust gases below atmospheric pressure. Any leaks in the boiler walls or ducts will cause air to leak into the system rather than exhaust to leak out of the system. If the boiler is built inside a building (typical of northern climates) a balanced draft system prevents accumulation of flue gas in the building. Another advantage of the balanced draft system is that it prevents very hot gases from leaking out of the firebox with resulting damage to adjacent hardware.

In most systems, the flow through the FD fan is governed by the boiler air flow requirement. The ID fan is linked to the firebox draft, so the ID fan normally follows the movement of the FD fan. Although for all practical purposes, the two fans move in unison. Flow through a fan is usually controlled by a damper as indicated in Figure 2-25. Newer systems might have a variable speed drive in addition to the fan damper.

In a typical arrangement, the FD fan draws air at ambient temperature; although, some systems may include a preliminary air heater to keep the fan above freezing during winter weather. The air heater raises the combustion air temperature with heat drawn from the flue gas. Most utilities use rotating regenerative air heaters built by Ljungstrom. The heated combustion air is supplied to the burners and/or under the grate of a stoker. In the firebox, the flame heats the water walls by radiation to generate steam. In the top and back of the boiler are convectively heated tubes, most of which superheat the steam. Then the gas passes through the other side of the air heater to the ID fan and up the stack. There is a pressure drop across the burners and across each of the heat transfer elements. So the draft steadily decreases in value from the exit of the FD fan to the inlet of the ID fan. Typical values in inches of water are indicated. In a balanced draft system, the firebox is normally maintained at -0.3" w.g. to -0.6" w.g.

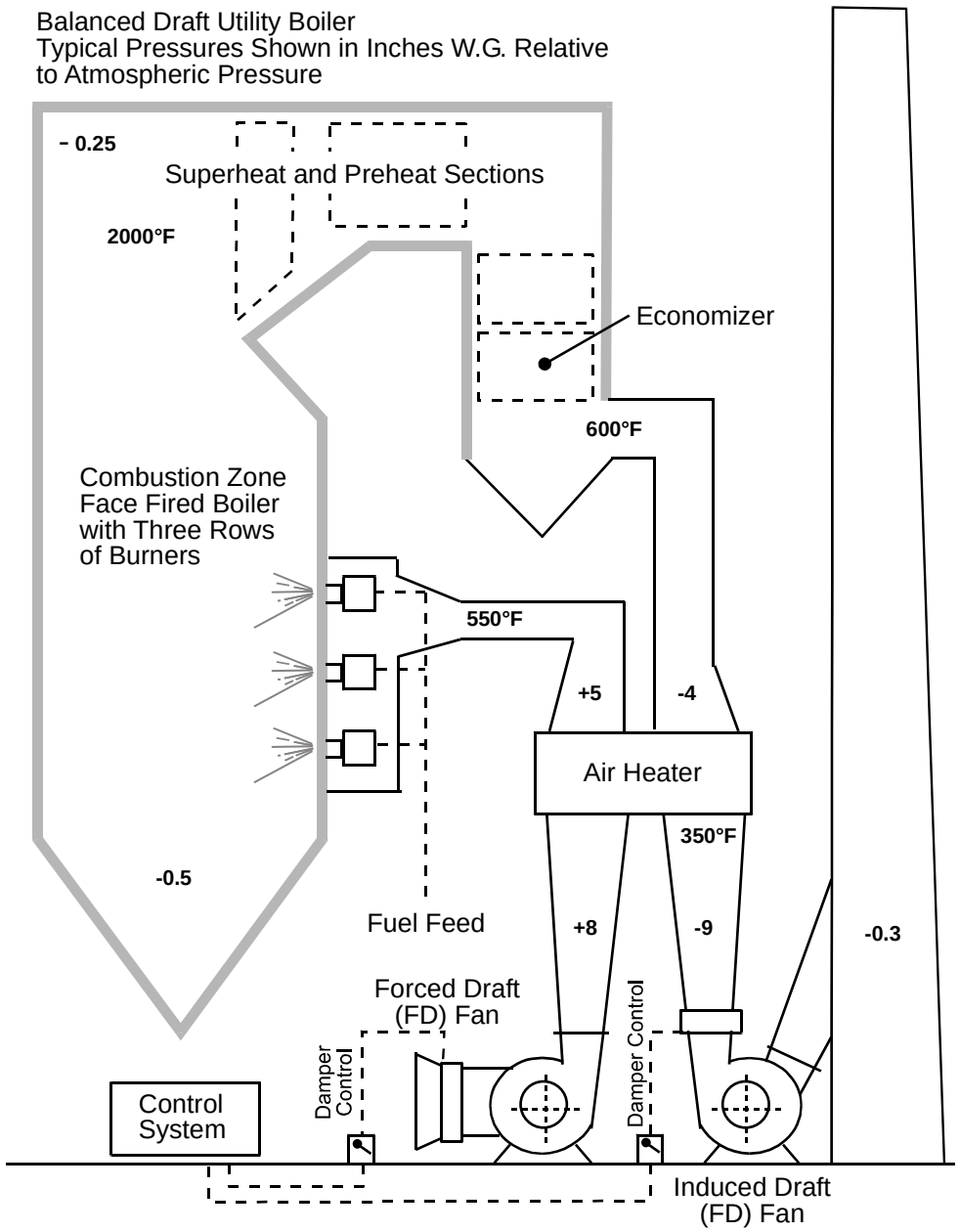


Figure 2-25. Air Flow and Draft Controls

2.5 STEAM SYSTEM COMPONENTS

The gas side and water side of a boiler are physically separate, but they are operationally linked. While the focus here is on the gas side, one invariably needs to understand the basic elements of the water side and how they relate to the gas side. Figure 2-26 provides a somewhat detailed cross section of a typical large utility boiler. A smaller boiler will have many of the same components.

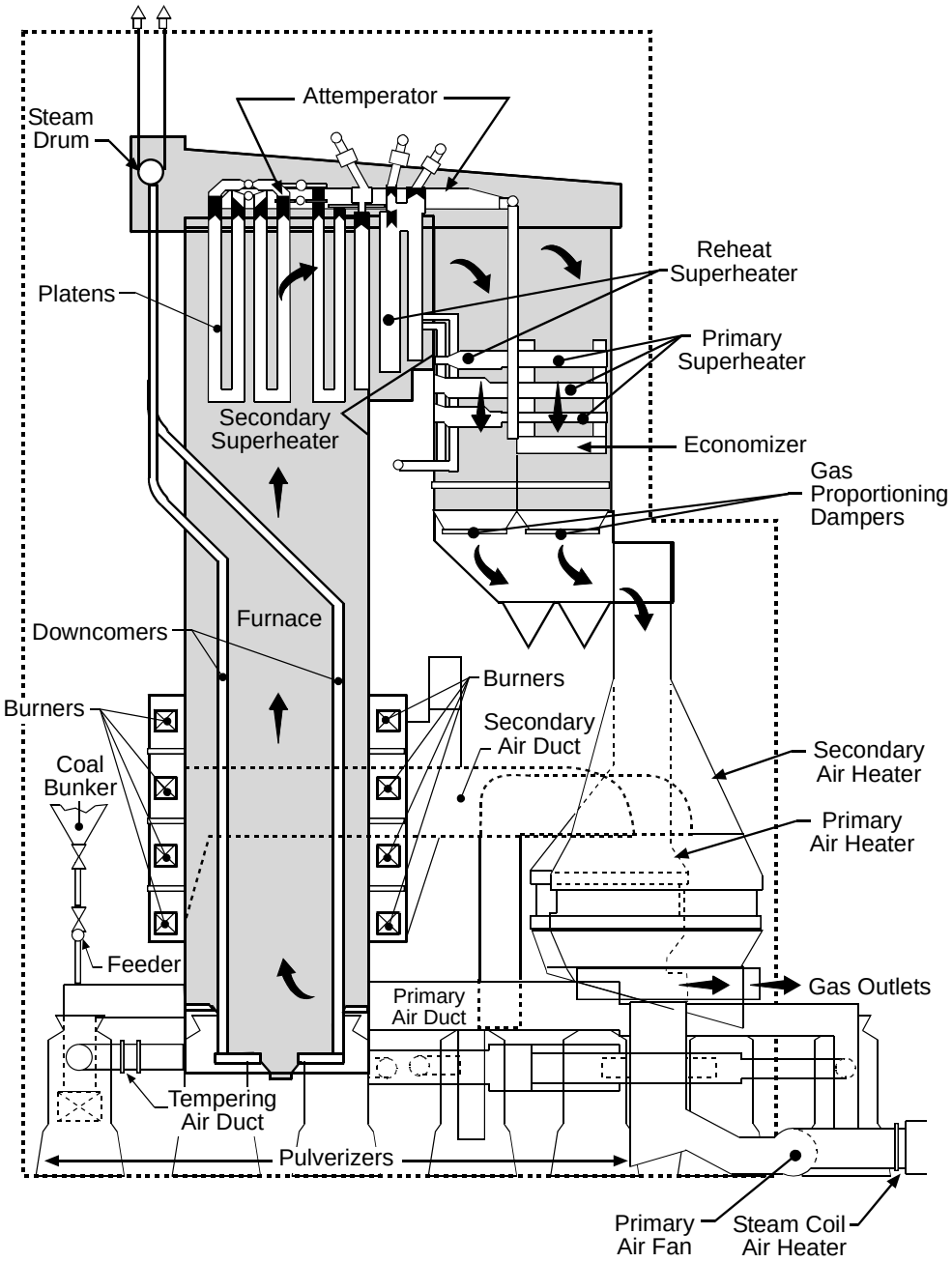


Figure 2-26. Boiler Steam and Water Components

Adapted from a drawing in Steam – 40th Edition by Babcock & Wilcox, 1992

2.5.1 Steam Generation

Perhaps the simplest way to go through the boiler is to follow the water as it passes through the system. The amount of water flowing into the boiler is at least as large as the amount of steam flowing out of the boiler. In larger boilers water is preheated, sometimes in several steps beginning with a steam heater. One or more *boiler feed*

pumps operate at high enough pressure to supply water to the boiler. The first water heater in the boiler is called an *economizer*. The economizer may be the last heat exchanger in the gas pass or located just ahead of the air heater.

When water leaves the economizer it enters the steam generating part of the system and is piped directly to the *steam drum*. The *steam generator* consists of a steam drum at the top, water tubes which transfer heat to the water, and a manifold or *mud drum* at the bottom. In a circulating boiler (most of them), there are also *downcomers* that pipe water from the steam drum to the mud drum. Water boils in the tubes and the steam-water mixture enters the steam drum that separates the steam from the water. Water flows from the steam drum, through the downcomers to the mud drum, and then back into the tubes to generate more steam. The amount of water circulating in this manner can be six to eight times as much as the steam flow; that is equivalent to saying that water passes up through the tubes an average of six times before it is converted to steam. Some boilers rely on *natural circulation* while others have pumps for *forced circulation*. Still other boilers have no water recirculation at all. In a *once-through* design, all the water changes to steam before it reaches the drum, which simply serves as a manifold to collect and distribute the steam.

Saturated steam leaving the drum can be used directly or it can be *superheated* to a temperature higher than the boiling point. Small commercial boilers generate steam for heating at pressures less than 15 psi, with corresponding saturated steam temperatures below about 250°F. However, steam used to drive a power turbine is superheated. Steam conditions in electric utility boilers can have steam pressures up to 3600 psi at superheat temperatures of 1000°F and higher. In Figure 2-26 steam goes from the drum at a temperature of about 690°F to a *primary superheater* that might raise the temperature to 850°F before it goes to the *secondary superheater*, which raises the temperature to 1000°F. The final steam temperature is controlled primarily by an *attemperator* between the primary and secondary superheaters, which can spray water into the steam to cool it. Superheated steam is then used to drive a turbine – usually connected to an electric generator.

When water is converted to steam any mineral contaminants stay in the water or are deposited on tube and drum surfaces. These deposits interfere with heat transfer and can lead to corrosion and tube rupture. If the steam drives a turbine, the turbine blades will be adversely affected by contaminants in the steam. As a general rule, the higher the steam pressure, the cleaner the water must be. Thus any facility with a medium to high pressure boiler must install equipment to purify the water used in the boiler. Purified water fed to the boiler is called *makeup*. The facility will also have instrumentation and at least some simple chemical analysis ability in order to track water quality. Steam used for heating or to operate turbines is usually condensed and returned to the boiler. The method of removing contaminants from this loop is to dump some of the water, a process called *blowdown*. Blowdown valves in the mud drum are opened periodically (as necessary) and the blowdown rate can be 1% or 2% of the steam flow rate.

2.5.2 Steam Turbines

Most steam-electric power plants have two turbines: a *high pressure turbine* and a *low pressure turbine*. Steam leaving the high pressure turbine is sent back to the *reheat superheater* in the boiler where the steam temperature is again raised to 1000°F. The steam then drives the low pressure turbine. Steam conditions at the exhaust of the last turbine are typically less than 100°F and pressures measured in inches of mercury absolute – a substantial vacuum. A *condenser* maintains these conditions, which is either water or air-cooled. A water-cooled condenser's performance is usually influenced by seasonal water temperature variations and by any tidal variations in water level. Any influence that raises condenser temperature reduces turbine efficiency and this telegraphs back to the boiler, which has to fire harder to make more steam to make up for the lost efficiency.

There are two other factors that commonly reduce steam turbine efficiency. One is mechanical deterioration of the turbine, which normally occurs over a period of many years. This can reduce turbine efficiency, and thus peak power output, by 5% or more. The second is turbine inlet steam temperature. Normal steam temperatures on newer units (since about 1955) are 1000°F. If steam temperature drops by even 15°F, there will be a measurable increase in boiler fuel flow to make up the difference. A discussion of the factors affecting superheated steam temperature is beyond the scope of this text, but some of the significant factors are listed below.

- Size of the superheater
- Deposits on the inside or outside of the superheater tubes
- Type of fuel being burned – gas, oil or coal
- Excess air level
- Boiler load
- Burners in service

Note that conditions on the gas side of the boiler are as important as conditions on the water/steam side in determining steam temperatures.

2.6 ASH HANDLING

2.6.1 Boiler Surface Deposits

Gas and distillate oil fuels carry little or no ash into the combustion zone. Residual oil carries a small amount of ash, which can, over a period of weeks or months, generate a fairly thick coating on tubes throughout the boiler. Coal is about 10% ash (or higher), which means that a ton of coal carries 200 pounds of incombustible rock into the

combustion zone. In a stoker furnace most of the ash stays on the grate, but in a pulverized coal furnace all the ash is carried through the flame zone in suspension. There are two major consequences: (1) an efficient dust collector is necessary on all pulverized coal-fired boilers in order to control particulate emissions, and (2) accumulation of dust and slag on boiler surfaces is a major factor in the design and operation of pulverized coal boilers.

The dust generated by firing pulverized coal is a dry powder at room temperature. The composition is silica, alumina, iron oxide and other mineral oxides – essentially pulverized rock. In the combustion zone, much of this dust is semi-molten and some constituents actually vaporize. The dust cools very rapidly after it leaves the flame zone, but if it is semi-molten when it hits a surface it sticks and accumulates. Thus furnace temperatures and the melting temperature of the ash are key variables in determining how much dust will stick to the walls and where it will do so. Any deposit on the boiler walls and tubes reduces the heat transfer rate. Deposits that grow uncontrollably also present a physical hazard inside the furnace. They block the normal gas passes and if large deposits break free, they can damage the bottom of the boiler. In general, the operators attempt to keep the deposits relatively dry and avoid situations where liquid slag is running down the walls of the firebox.

Boiler operators use several methods to control gas side deposits inside the boiler:

- Purchase coal with an appropriate ash melting or softening temperature.
- Use soot blowers to remove deposits.
- Limit the load, excess air or other parameters to minimize problems.

Utility power plants are selective about which mines supply their coal. Anytime a plant proposes to fire coal from an untried mine, it will conduct a test burn to determine if there are any unmanageable problems.

Soot blowers are devices that can create local disturbances adjacent to the walls or tubes with jets of steam that remove loose deposits. They are permanently mounted on the boiler walls and positioned on long pipes that penetrate deep into all the convective heating tube banks in the boiler. The soot blowers are controlled by the boiler operator with the objective of maintaining normal steam temperatures. The operator selectively cleans certain surfaces to restore heat transfer rates that control the temperatures.

Increasing load or decreasing excess air tends to raise boiler temperatures and high temperatures lead to liquid or sticky slag. Load, excess air, and the choice of which burners to use are parameters that the operators use from experience to control ash accumulation problems.

2.6.2 Bottom and Fly Ash Management

In a stoker boiler most of the fuel ash stays on the grate and is dumped into a hopper for disposal. However, in a suspension-fired boiler, less than 20% of the fuel ash drops out in the boiler hoppers; the remainder, fly ash, must be captured in the dust collector. Bottom ash is usually dropped into water to cool it. The recovered material has the consistency of gravel. Coal bottom ash has been used for fill in most of our coastal cities and can also be used on icy streets in the winter. Fly ash recovered by a dust collector is a fine powder that is frequently mixed with water to prevent fugitive emissions. Almost all fly ash is land filled somewhere close to the power plant.

2.6.3 LOI and Introduction to Ash Chemistry

Bottom ash typically has a furnace residence time of an hour or more. This is long enough to burn out any residual carbon from the fuel so bottom ash usually has very little carbon. However, biomass-fired stokers are an exception because the ash is frequently removed before the fuel is completely burned. Fly ash carbon contents can be significant, particularly from biomass-fired stokers. On pulverized coal-fired boilers, fly ash carbon contents should normally be less than 4% and at this level represent a heat loss of less than 0.3%. Ash carbon content is usually characterized by a Loss on Ignition (LOI) laboratory test. The sample is heated to about 1400°F and the change in weight is attributed to carbon loss.

Ash chemistry reflects the composition of ash in the fuel. However, the proportions of various elements in the fly ash will be skewed from the original as discussed in Chapter 5. This change is caused by ash constituents that are volatile or semi-volatile at flame temperatures. Any substance that vaporizes in the combustion zone will condense as the gas cools and deposit on all available surfaces. Most of this condensation will be on ash particles and, since fine particulate matter has more surface area than course particulate, these volatile species will appear preferentially on the finest fly ash particulate. This can result in the fly ash having a very different chemical signature from the bottom ash.

2.7 CONCLUSION

This chapter has attempted to provide a brief description of the types of combustion sources that someone in the regulatory community might reasonably expect to encounter. The focus is on an overview and general description of combustion sources. A more detailed description of the specific types of sources can be found in one or more of the references indicated in this section. Subsequent chapters of this text will present more information relevant to air emissions from these sources.

Review Exercises

1. Reciprocating engines are commonly found in a(n) _____.
   a. jet aircraft
   b. gas turbine power plant
   c. automobile
   d. steam electric generating plant

2. Combustion turbine power plants differ from steam power plants because they _____.
   a. typically have 10 to 100 times less power
   b. have more operating parts that require greater maintenance
   c. have less thermal efficiency
   d. can only burn clean fuel, such as natural gas or distillate oil

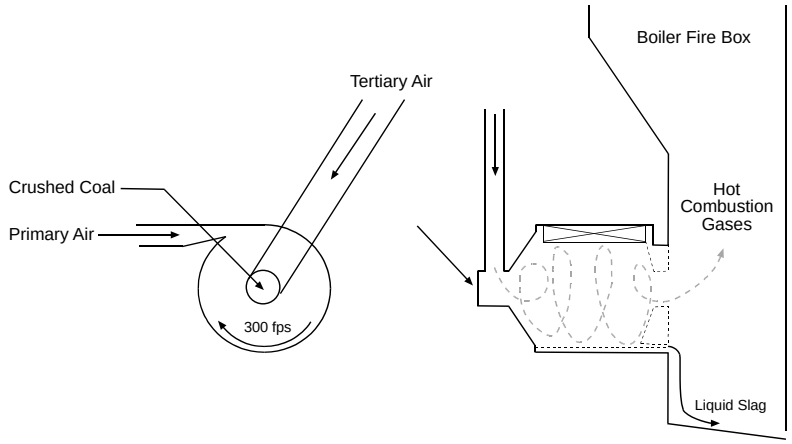
3. A chief characteristic of a rich burn reciprocating engine is that it _____.
   a. has less power, but lower emissions than a lean burn engine
   b. has more power, but higher emissions
   c. is spark ignited with a lean gas mixture in the intake air
   d. is exclusively used with diesel oil

4. Which of the following boilers has the largest thermal capacity?
   a. Electric utility boilers
   b. Large factory built boilers
   c. Residential furnace
   e. Commercial building HVAC boilers

5. Which of the following is **not** true of suspension type burners?
   a. Allows better control of the combustion process than stoker firing.
   b. Operates by injecting fuel into the combustion zone.
   c. Capable of burning almost any solid fuel.
   d. Permits greater control of fuel-air mixing.

6. Which of the following correctly characterizes the evolution of electric power generating plants in the U.S.?
   a. Pulverized coal furnaces / stoker combustors / oil-fired boilers / gas turbines
   b. Stoker combustors / pulverized coal furnaces / oil-fired boilers / gas turbines
   c. Oil-fired boilers / stoker combustors / pulverized coal furnaces / gas turbines
   d. Pulverized coal furnaces / oil-fired boilers / stoker combustors / gas turbines

7. Which combustion system correctly identifies the following illustration?



   a. Large industrial boiler
   b. Cyclone burner
   c. Combustion gas turbine
   d. Fluidized bed combustor

8. Which of the following stoker grates would be preferred for burning municipal waste?
   a. Stationary grate
   b. Traveling grate
   c. Oscillating grate
   d. A and C

9. Which of the following oxidizers or combustion systems operate at a relatively low temperature?
   a. High temperature oxidizer
   b. Catalytic oxidizer
   c. Utility boiler
   d. Cement kiln

10. In a suspension-fired boiler, approximately _____ of the fuel ash drops into the boiler hopper for disposal.
   a. 20% or less
   b. 50%
   c. 70%
   d. 100%

11. Air flow through a combustion turbine is _____.
   a. about the same as a boiler that fires a comparable amount of fuel
   b. kept low to minimize exhaust noise
   c. very high in order to keep the turbine at an acceptable temperature
   e. very high in order to maximize fuel efficiency.

Review Answers

1. c. automobile

2. d. can only burn clean fuel, such as natural gas or distillate oil.

3. b. has more power, but higher emissions.

4. a. Electric utility boilers

5. c. Capable of burning almost any solid fuel.

6. b. Stoker combustors / pulverized coal furnaces / oil-fired boilers / gas turbines

7. b. Cyclone burner

8. c. Oscillating grate

9. b. Catalytic oxidizer

10. a. 20%

11. c. very high in order to keep the turbine at an acceptable temperature

References

1. Babcock and Wilcox Company. *Steam: Its Generation and Use*, (Babcock and Wilcox Company, Barberton, Ohio, 1992). A huge book with in depth coverage of large boiler furnaces, particularly coal-fired boilers. It also covers fluidized beds and refuse firing. The book has grown over the years and the material covered has changed.

2. Bryers, Richard W. *Ash Deposits and Corrosion Due to Impurities in Combustion Gases*, Proceedings of an International Conference in Henniker, NH, (Hemisphere Publishing Corp in association with McGraw-Hill International Book Co, 1977).

3. Gill, James H. and Quiel, John M. *Incineration of Hazardous, Toxic, and Mixed Wastes*, (North American Mfg. Co., Cleveland, OH, 1993). This book focuses on waste combustion in rotating kilns, but much of the data is broadly applicable to other systems and fuels.

4. Pritchard, R., Guy, J.J., and Conner, N.E. *Handbook of Industrial Gas Utilization*, (Van Nostrand Reinhold Co., 1977). The authors are/were at the University of Salford (GB) and the detail/clarity are typically British. The book covers all aspects of combustion hardware and furnace design for any system that fires gas or gas in combination with other fuels.

5. Reed, Richard J. and Schilster, Robert E. *North American Combustion Handbook*, (North American Manufacturing Company, Cleveland, OH, 1993). A good basic reference for small to medium size gas and oil-fired combustion systems.

6. Reed, Richard J. and Schilster, Robert E. *North American Combustion Handbook*, Volume II, (North American Manufacturing Company, Cleveland, OH, 1995). Provides good detail on burner types, control systems, emissions, heat recovery and other special topics.

7. Singer, Joseph G. Combustion Fossil Power Systems, (Combustion Engineering, Inc., Windsor, CT, 1981).

8. U.S. Environmental Protection Agency. *Alternative Control Techniques Document: NOx Emissions from Stationary Gas Turbines*, January 1993, EPA Report 453/R-93-007, NTIS PB93-156586. This weighty document is a fairly a comprehensive, if slightly dated, description of combustion turbine technology with a significant database included.

9. U.S. Environmental Protection Agency. *Alternative Control Techniques Document: NOx Emissions from Stationary Reciprocating Internal Combustion Engines*, July 1993, EPA Report 453/R-93-032, NTIS PB94-104494. This weighty document is a fairly a comprehensive, if slightly dated, description of engine NOx technology with a significant database included.

10. U.S. Environmental Protection Agency. *Introduction to Boiler Operation: Self-instructional Guidebook*, APTI Course SE:428A, 1984. The descriptions of boilers and related combustion systems in the Student Manual are clearly written and well illustrated.

11. Wilber, Leslie C. Handbook of Energy Systems Engineering, (John Wiley & Sons, New York, 1985). A hefty handbook that covers many areas including useful sections on gas, oil and coal combustion.

Chapter 3: Fuel Characteristics

LESSON GOAL

Demonstrate an understanding of how various gaseous, liquid, solid, and emulsion fuels are used in combustion sources through successful completion of the chapter review exercises.

STUDENT OBJECTIVES

When you have mastered the material in this chapter, you should be able to:

1. Describe past and current trends in the types of fuel used in stationary sources in the U.S.
2. Describe the trends in fuel production in the U.S. over the past 30 years.
3. List the differences between fuel analysis based on “as received” and “mineral and ash free” basis.
4. Describe the difference between an ultimate fuel analysis, a trace element analysis and a market driven analysis such as a proximate analysis.
5. Discuss the issues involved in obtaining a representative fuel sample for lab analysis.
6. Describe the difference between the lower and higher heating value of a fuel.
7. List the primary non-fuel contaminants in bituminous coal and No. 6 oil.
8. List the typical ranges in sulfur and ash content in No. 2, No. 4, and No. 6 fuel oils.
9. Describe how the size distribution of solid fuels is obtained in the laboratory.
10. List some of the common minor constituents present in natural gas.
11. Describe the difference in potential air pollutant formation between residual and distillate oils based on how they are manufactured.
12. Describe the differences in heating value, ash content, and sulfur levels among anthracite, bituminous, sub-bituminous, and lignite coals.
13. Describe how agglomerating/caking tendencies may affect stoker coal combustion.

14. Describe how ash softening and fusion temperatures can affect pulverized coal combustion.
15. Describe the range in mercury levels in coals throughout the U.S.
16. List the various types of wood fuels used in combustion processes.
17. List various types of solid waste and describe their general characteristics.
18. Describe the common factors that affect the moisture levels in municipal waste fuels.

Chapter 3: Fuel Characteristics

3.1 INTRODUCTION

Fuel characteristics are the single most important factor that must be considered in the design and operation of a combustion process. The fuel characteristics significantly affect almost every aspect of the combustion system from (1) the fuel storage and handling equipment, (2) the configuration and size of the combustion furnace and burners, (3) the air pollution control systems, and (4) the ash handling systems. Fuel characteristics also have a major impact on the quantity and types of air pollutants generated during combustion. The variability of fuel quality over time introduces routine variability in the performance of combustion systems.

This chapter begins with a general summary of the wide variety of fuels used during the combustion process. Information concerning ultimate and proximate analyses is presented because these data are frequently used to evaluate the fuel properties. In later sections of this chapter each of the major fuels is discussed. The emphasis in the fuel specific sections is on the fuel characteristics that are most relevant to air pollution control and emission oriented projects.

3.2 FUEL CHARACTERISTICS AND USAGE TRENDS

In the 19th century wood was the most common fuel. By the beginning of the 20th century it was replaced by coal in stationary sources. Coal supplied more energy and was available in larger quantities. In the early 1960s oil began to compete with coal in terms of cost and usually generated lower air emissions than coal. By the end of the 20th century natural gas had become a preferred fuel for new stationary sources, but coal and oil continued to be used where they were practical and when they were more economical than natural gas. The Clean Air Act Amendments of 1990 (CAAA 1990) have encouraged the use of clean fuels to reduce emissions that contribute to acid rain and ozone formation. Concerns over carbon dioxide emissions are tending to increase the use of biomass and other renewable types of fuels. Decreasing landfill capacity and concerns over the environmental adequacy of landfills have also stimulated interest in the increased firing of waste materials. Collectively, these trends have begun to have an impact on combustion process design and on a facility's choice of fuel. In the future we will probably see the processing of coal, waste or bio-fuels to create clean gas and/or liquid fuels.

3.2.1 General Types

There are five major categories and numerous subcategories of fuels used in combustion processes as indicated in Table 3-1. However, this list omits most of the minor fuels. Furthermore, new fuel types – based on wastes or biomass – may be commercially developed and used in the future.

Table 3-1. Fuels

Fuel Category	*Examples*
Solids	Bituminous coal, sub-bituminous coal, lignite, peat, wood
Liquids	Kerosene, No. 2 oil, No. 6 oil, coal-water emulsions, oil-emulsion
Gaseous Fuels	Natural gas, propane, landfill and biological gases
Wastes	Municipal and medical wastes, hazardous wastes, sewage sludge, tires
Biomass	Wood and wood waste, bagasse, straw

The dominant fuels for stationary sources since 1990 have been coal, natural gas, oil and wood, generally in that order. The consumption and production of dominant fuels in the U.S. is indicated in Figure 3-1. Note the steady increase in the production of coal and the decrease in the production of oil. The steady increase in coal use is due primarily to increased demand for electrical power and abundant U.S. coal supplies. However, total oil consumption has actually increased with the growth in transportation use; although stationary source use has been partially displaced by natural gas. The decrease shown in Figure 3-1 is offset by an increase in imported oil.

Table 3-1 collectively addresses all types of coal including anthracite, bituminous, sub-bituminous, and lignite coals. Due primarily to the cap in SO_2 emissions mandated in the CAAA of 1990, there has been a trend toward sub-bituminous and lignite coals that have low sulfur content. Most wood fuels are used near the point of generation, primarily in the forest products industry (paper and saw mills) as well as in furniture manufacturing plants. Although there has been some shift from the use of No. 6 to No. 2 oil, driven primarily by the need to minimize sulfur dioxide emissions, the use of No. 2 oil has remained relatively steady.

A variety of liquid fuels are beginning to be applied for electrical power generation and industrial process heating. One of these new fuels includes ori-emulsion, an oil-water emulsion extracted primarily in Venezuela. Large deposits of ori-emulsion appear to be available for future years. In addition, various energy companies are experimenting with coal-water emulsion fuels that burn like No. 6 oil, but require major air pollution control devices. Depending on market prices and other factors these fuels may compete for fuel oil combustion process applications at some time in the future.

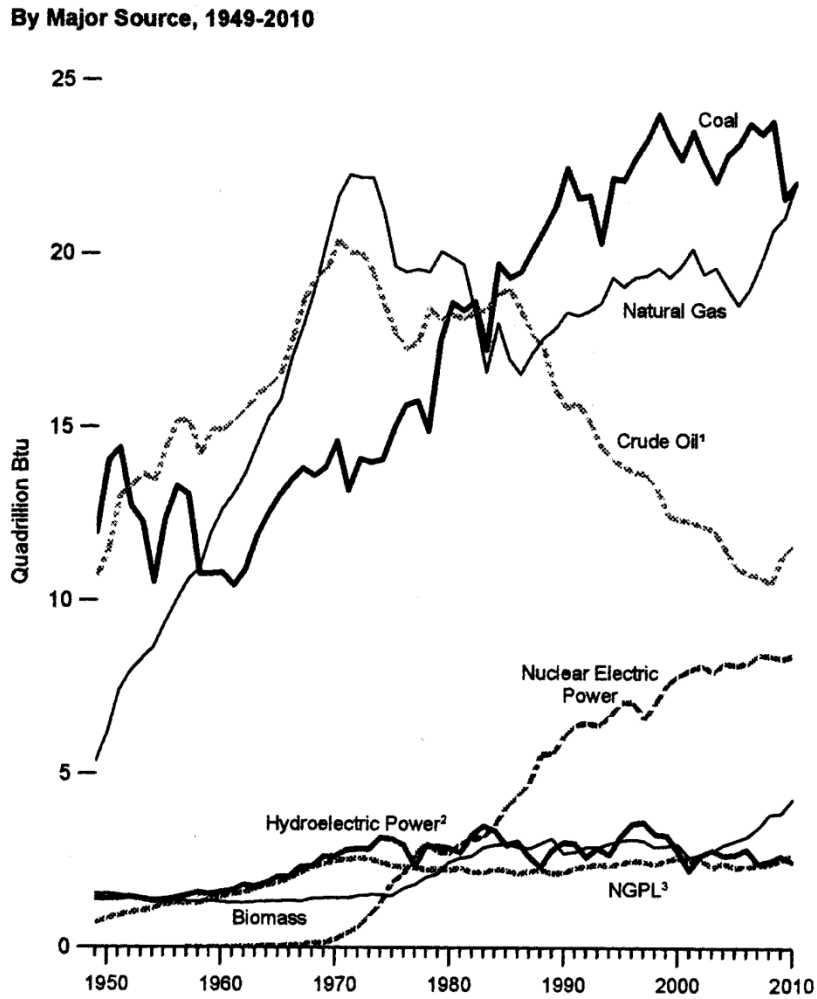


Figure 3-1. U.S. Energy Production Trends
US Department of Energy, Energy Information Agency, Annual Energy Review 2010

As indicated in Figure 3-1, the use of natural gas increased substantially between 1990 and 2010. However, a marked increase in the consumption of natural gas for electrical power production has played a large part in driving up total consumption.

Natural gas use peaked about 1970 then significantly decreased from 1973 through the early 1980s. There was a perception that gas supplies were dwindling and that a crisis loomed. The oil crisis of 1973 spurred Congress to pass a law that prohibited new applications of natural gas for electrical power generation. However, the law was repealed in 1990 after it became apparent that natural gas supplies were more than adequate for the foreseeable future.

Natural gas use for electrical power production has increased significantly since the mid-1980s. This increase is due primarily to the availability of natural gas at competitive prices. As a result, a number of coal- and oil-fired boilers have been converted to primarily gas-fired units. This change has reduced both sulfur dioxide

and nitrogen oxide emissions. Natural gas use has also increased due to the construction of new power plants driven by gas turbines.

A small increase in natural gas use is associated with thermal oxidizers used for air pollution control that was mandated by the promulgation of Maximum Achievable Control Technology (MACT)-based standards for hazardous air pollutants.

Natural gas will be the dominant fuel used in a wide variety of small combustion units installed during the next twenty years as the electric generation industry increases "distributed power" capability. Almost certainly this will result in the increased use of electrical generation at or near the point of use rather than at large centralized power stations.

Table 3-2. U.S. Energy Consumption, 2006-2010
Energy Use Expressed in Quadrillion BTU

Energy Source	*Energy Type*	*2006*	*2007*	*2008*	*2009*	*2010*
Fossil Fuels	Coal	22.447	22.749	22.385	19.692	22.817
	Natural Gas	22.224	23.702	23.834	23.344	24.644
	Petroleum	39.955	39.774	37.280	35.403	35.970
Total Fossil Fuels		84.626	86.225	83.499	78.439	81.431
Renewable Fuels	Hydroelectric Power	2.869	2.446	2.551	2.669	2.509
	Geothermal Energy	0.181	0.186	0.192	0.200	0.212
	Biomass	3.276	3.502	3.852	3.899	4.295
	Solar Energy	0.068	0.076	0.089	0.098	0.109
	Wind Energy	0.264	0.314	0.546	0.721	0.924
Total Renewable Fuels		6.658	6.524	7.230	7.587	8.049
Nuclear Energy		8.215	8.455	8.427	8.356	8.441

Source: DOE/EIA –Annual Energy Review 2010 Energy Information Administration [2]

Table 3-2 shows data for fuel use over a recent five-year period. Note that renewable energy is only about 10% of the total, so the U.S. has a long way to go to substantially replace fossil fuel with renewable energy. Much of the renewable energy has come from hydroelectric power and it is unlikely that many more dams will be built in this country. Also siltation has reduced the capacity of our reservoirs. Large land areas will be required for a significant expansion in the use of bio-fuels. Wind and solar energy production can be expanded, but these sources also will have to grow by two orders of magnitude in order to begin to significantly displace fossil fuel. Although displacement of fossil fuels with renewable energy is a highly desirable goal, its implementation is challenging.

3.3 FUEL ANALYSES

3.3.1 Basis of Fuel Analysis

A fuel analysis is a laboratory report with information useful to the combustion source operator, regulatory agency and others. Originally the purpose of a fuel analysis was to help assure that a fuel was suitable for a particular combustion system, or to determine the economic value of the fuel. The octane rating of gasoline is an element of a fuel analysis that is most familiar to the general public. Each automobile engine has specific requirements and the analysis of the gasoline must show that the fuel meets or exceeds these requirements. The fuel requirements for stationary sources are related to the ability of the source to burn the fuel as well as environmental issues. In this section we will examine those fuel analyses that are most commonly conducted and relate their significance to stationary combustion sources.

A fuel analysis is the product of a series of laboratory tests on a small sample of the fuel. When reviewing any analysis we need to know what was analyzed, or the basis for the analysis. Examples of the basis for fuel analysis include:

- *As-received:* The fuel as it was received in the laboratory.
- *Air dried:* The fuel was dried at room temperature to remove surface moisture.
- *Moisture free:* The fuel was dried in an oven to remove moisture.
- *Mineral free:* The ash and inorganic materials were subtracted from the analysis to report the composition with mineral and ash excluded.

As-received fuel is undried fuel in the same condition as it was received at the laboratory. Due to the possibility of surface moisture loss from solid fuels and wastes during sampling and shipment, the reported as-received moisture level can be slightly lower than the as-fired fuel.

Air-drying is conducted at room temperature, which removes surface moisture that reflects water accumulated during transportation and storage. This basis is sometimes used in the analysis of coals that are being fired in pulverized coal boilers. The fuel analysis expressed on an air-dried basis is a reasonable description of the fuel as it leaves the pulverizing mill enroute to the combustion zone. ASTM procedure D3302 is used to determine the amount of air-dried moisture that is used to convert the fuel analysis data to an air-dried basis.

Moisture-free fuel has been oven dried in accordance with ASTM D3302 to remove the inherent moisture trapped in pores and cracks of solid and waste fuels. Fuel must be dried very carefully to avoid excessive volatilization of organic vapors from the fuel. Loss of volatile matter will reduce fuel heating value and alter elemental

composition. Fuel analyses are often expressed on a moisture-free basis to eliminate variability introduced by the moisture in the fuel.

A *mineral-free* fuel analysis allows comparison of different fuels without the variable influences of ash and water. However, the mineral content of many solid fuels can vary widely.

Analysis can be broken into three types: (1) market driven (includes proximate), (2) ultimate and (3) trace element. What we have called the *market analysis* gives a description that is useful to buyers and sellers in a fuel market. *Ultimate analysis*, gives a detail listing of the elemental composition of the fuel. *Trace element* analyses are supplemental analysis conducted for whatever elements are requested. Table 3-3 lists common constituents of these analyses.

Table 3-3. Fuel Analysis – Common Elements

Type of Analysis	*Coal and Solid*	*Oil*	*Gas*
Market (Proximate)	• Heating value per lb. • Moisture • Sulfur • Volatiles • Fixed carbon • Ash	• Heating value per gal. • Density or API gravity • Sulfur • Viscosity • Pour point • Water & sediment	• Heating value per ft^3 • Specific gravity
Ultimate (Chemical)	• C, H, S, N • Oxygen by difference • Moisture • Ash	• C, H, S, N • Oxygen by difference • Moisture • Ash	• CH_4, C_2H_6, C_3H_8, etc. • CO_2, N_2, H_2O • O_2
Ash or Trace Element	• SiO_2, Al_2O_3, TiO_2 • Fe_2O_3, CaO, MgO • K_2O, Na_2O, Cl, Hg • Others by request	• V, Na, • Others by request	• Others by request

A fuel analysis is the result of a series of laboratory tests that begin with a one or two pound fuel sample. The results are representative of the fuel only if the sample is representative; however, it is not difficult to obtain a representative oil sample. Most facilities have a hand valve located on a tee off the main line leading to the burners. The sample is taken some time during an air emissions test (or other pertinent event). Some oil is drained from this tee before filling a quart sample bottle that is then sent to the lab for analysis.

Sampling coal, wood or any other solid is another matter entirely. Solid fuel is not homogeneous and a small sample taken from one place at one point in time can be very different from the average. The original procedures used to sample coal illustrate the difficulty in obtaining a representative sample. Coal is transferred into a combustion facility on one or more conveyor belts. At the beginning of a test that requires a fuel sample, a technician is stationed at each feed belt. At five or ten minute intervals the technician rakes a two or three pound sample off the belt into a

large garbage can. At the end of the test all the garbage cans, perhaps totaling half a ton, are collected and emptied onto a pile on a clean floor or a tarpaulin. Using shovels, this pile is mixed to the maximum degree practical. The pile is then divided in half; one half is discarded and the other is divided again. One of these quarters is then divided again. This process continues until the sample is reduced to about 10 pounds, which can be sent to the lab. The lab then takes out about one pound and grinds it up to obtain smaller samples for each of the tests. Mechanical samplers have largely replaced the need for technicians to rake the belts, but the challenge of getting a representative sample remains.

While representative sampling of coal and wood chips is feasible, it is all but impossible to obtain a small, representative sample of municipal waste. Many of the individual items in the waste stream are larger than the sample required by the lab. Combustion assessments of solid waste facilities must be conducted without the benefit of a representative fuel analysis.

3.3.2 Market Characteristics

When purchasing fuel, a buyer wants to know how much energy they will get and whether the fuel is suited to their use. The essential information about the fuel is contained in an analysis that goes by different names for different fuels. Proximate analysis is the term used for solid fuels (e.g., coal, etc.). No single name is used for this type of analysis of oil or gas. The normal components of this analysis are listed in Table 3-3.

3.3.2.1 Heating Value

For economic reasons the price of any fuel is expressed as dollars per million BTU ($/mmBTU). The price of fuel can be determined from the cost per pound and the heating value that is expressed as BTU per pound of solid, per gallon of liquid, or per cubic foot of gas. Heating values are determined by burning a small sample (typically one gram) in a calorimeter that measures the amount of energy released.

A British Thermal Unit (BTU) is the amount of energy required to heat one pound of water one degree Fahrenheit. The energy released when burning a pound of fuel should be equally unambiguous, but unfortunately there are two different definitions commonly used. The difference has to do with the water vapor generated by burning hydrogen in the fuel and whether or not this water vapor condenses. The higher heating value (HHV) assumes that all the water condenses, which means that the flue gas is cooled to room temperature. This is what happens in the laboratory test apparatus that measures heating value. In real combustion systems, the flue gas is almost never cooled below the water dew point, so the uncondensed water vapor carries energy with it up the stack. If one excludes the heat of condensation from the definition, you have the lower heating value (LHV). The difference is 1030 BTU/lb of water generated by combustion. Table 3-4 lists typical higher and lower heating values for several fuels.

Table 3-4. Fuel Heating Values - BTU/lb		
Fuel	*HHV*	*LHV*
Natural Gas	22,200	20,000
No. 2 Oil	19,000	17,860
No. 6 Oil	18,200	17,300
Bituminous Coal	14,000	13,600
Doug Fir – dry	9,000	8,400

HHV is used for emission calculations and is nearly always the value used in any regulatory context, but it also is used by people who operate boilers and furnaces. HHV is generally used by anyone selling fuel because no vendor would voluntarily use the lower value to characterize his fuel. On the other hand, engine and turbine manufacturers use LHV. The argument for this approach is: "since the heat of condensation is never available, we will exclude it from all calculations". A resulting benefit is that their reported engine efficiency is higher (more impressive) when they use the lower heating value. Problems arise when an unsuspecting engineer combines data from two different sources and does not realize that the BTU values from the two sources are not comparable. For example, if a permit writer combined engine efficiency data (BTU per kilowatt hour)from an engine manufacturer with emissions data (lb/mmBTU)from an EPA Method test, he could underestimate the total emissions by more than 10%. So it is important to know which definition of BTU is used and to convert everything to one basis, preferably HHV.

The significance of fuel heating value is illustrated in two example problems.

Example 1: Importance of Fuel Heating Value

A combustion process must operate at a heat release rate of 10 x 10^6 BTU per hour (10 mmBTU/hr) in order to maintain the desired boiler-operating load. Fuel A has a heating value of 11,000 BTU/lb. while Fuel B has a heating value of 12,750 BTU/lb. What is the difference in the quantities of fuel needed for alternative Fuel A and Fuel B?

Solution:

$$\text{Fuel A} = \frac{H_T\ \text{Release Rate}}{\text{Fuel HHV}} = \frac{10 \times 10^6}{11{,}000} = 909\ \text{lb/hr}$$

$$\text{Fuel B} = \frac{H_T\ \text{Release Rate}}{\text{Fuel HHV}} = \frac{10 \times 10^6}{12{,}750} = 784\ \text{lb/hr}$$

As illustrated in this example, considerably less of Fuel B is needed.

The fuel storage, feeding and processing equipment necessary for a plant designed for Fuel B could be smaller than for a plant designed to handle Fuel A.

The heating value also has a direct impact on the quantity of ash that must be handled. The relationship between heating value and ash quantities is illustrated in Example Problem 2.

Example 2: Relationship Between Heating Value and Ash Quantities

The plant in Example 1 is considering converting from coal supply B to coal supply A. Both fuels have an ash content of 10.5%. The boiler operates 7000 hours per year. What change will occur in the total quantity of ash that will have to be disposed? Assume that none of the ash escapes into the atmosphere.

Solution:

(Coal B) $$\text{Present Ash Quantity} = \frac{0.105}{12{,}750} \times 10 \times 10^6 \times 7{,}000 = 576{,}500 \ \text{lb/yr}$$

(Coal A) $$\text{Future Ash Quantity} = \frac{0.105}{11{,}000} \times 10 \times 10^6 \times 7{,}000 = 668{,}200 \ \text{lb/yr}$$

Where:

0.105	=	lb of ash/lb of coal
12,750	=	BTU/lb of coal
11,000	=	BTU/lb of coal
10×10^6	=	BTU/hr
7,000	=	hr/yr

So the amount of ash will increase by almost 92,000 lb/yr. Examples 1 & 2 illustrate that the quantity of both ash and fuel handled in the combustion system is inversely related to the heating value.

3.3.2.2 Sulfur Content

Although sulfur content is a chemical constituent included in an ultimate analysis, most market analyses report sulfur because coal and oil markets are based on fuel sulfur content. Permits that limit fuel sulfur content control SO_2 emissions from most stationary sources. So, for example, a source operator will specify oil with less than 0.5% sulfur because that limit is written in the air permit for the source.

3.3.2.3 Proximate Analysis Data

Proximate analyses are used to characterize coal and other solid fuels. The data are measured using ASTM procedure D271. In addition to heating value and sulfur, the

proximate analysis specifically includes fixed carbon, volatile matter and moisture. The analysis procedure involves heating a sample and measuring the weight loss at several temperatures. Very gentle heating or placing the sample in a dry atmosphere will drive off the surface moisture. Further heating drives off inherent moisture that is more tightly bound. In the case of coal, this is moisture that was present when it was mined. Raising the temperature further in an oxygen free atmosphere drives off volatile constituents and essentially all the hydrogen. Finally, by raising the temperature to about 1400°F with oxygen present, all the carbon is oxidized leaving just the incombustible ash (mineral matter). Each of these measured values has significant implications for combustion performance.

3.3.2.4 Moisture Content

The moisture content of the fuel can impact combustion processes in several ways. First, water increases the amount of fuel that must be fired. A ton of wood with 50% water is actually only half a ton of dry fuel. Second, the water absorbs energy when it evaporates during combustion. This increases the amount of fuel that has to be fired and the water decreases flame temperature. Third, a significant amount of water in the fuel generates enough steam to cause a measurable increase in the moisture content in the flue gas. This has implications for emissions measurement and for the performance of emissions control devices like dust collectors. Water content is particularly significant in wood and waste fuels where it can constitute more than 50% of the "as received" fuel.

3.3.2.5 Volatile Matter

Volatile matter includes organic compounds that vaporize during the heating of the fuel entering the combustion chamber. These can include methane, hydrocarbons, and carbon monoxide. A fuel with a high volatile content will be easier to ignite and burn in the combustion zone. Most pulverized coal combustion systems require a certain minimum fuel volatility in order to sustain stable flames and achieve complete combustion of the fuel.

3.3.2.6 Fixed Carbon

Fixed carbon is the combustible residue remaining after departure of organic compounds and other volatile matter in the fuel. In a stoker furnace the fixed carbon levels provide a general indication of the quantity of the fuel that will remain on a grate and burn as a char. Since solid carbon (char) burns only on the surface of the fuel particle, combustion of fuel with a high fixed carbon level will be relatively slow.

3.3.2.7 Ash or Mineral Content

A few minerals are volatile at combustion temperatures, but most of the inorganic fuel constituents remain after combustion in the form of ash. Ash must either be removed from the bottom of the furnace or collected from the flue gas to control particulate emissions. Thus the fuel ash content is an indicator of potential air

emissions as well as the amount of solid waste requiring disposal. There are also implications for the accumulation and management of dust and slag on the interior surfaces of a furnace, as discussed later in this chapter and in Chapter 7.

3.3.2.8 Fuel Oil Market Properties

In addition to heating value and sulfur content, there are several properties significant to the fuel oil market.

Oil is purchased by the gallon, and density or *specific gravity* is needed to convert heating value from BTU/lb to BTU/gallon. Since the heating value in BTU/lb is relatively constant for each oil category, the density determines the variation in BTU/gallon. There is some high density oil on the market that is heavier than water, meaning water will float on the surface or be suspended in the oil rather than settling to the bottom of the storage tank. Density is frequently reported as °API gravity, which is related to specific gravity by the following formula:

$$\text{sp.gr@60}^{o}\text{F} = \frac{141.5}{\text{API} + 131.5}$$

No. 6 oil is a viscous liquid that must be heated to thin it out before it is sprayed into a combustion chamber. In fact, it frequently is so thick at ambient temperatures that it has to be heated in order for pumps to transfer it for transportation or to move it to a burner. The minimum pumping temperature is called the *pour point,* which is about the temperature that paraffins begin to condense and form solid crystals in the oil. Storage tanks must be maintained above this temperature. No.2 oil also has a pour point, but this is usually well below 0°F.

Oil *viscosity* is measured and used to determine what minimum temperature is necessary to fire the oil. The viscosity can be measured in the laboratory at any temperature, but the oil may have to be heated to make the measurement and a common temperature used is 122°F. Viscosity is discussed further in Section 3.4.2, *Fuel Oils.*

Water and sediment can be suspended in small quantities in No.6 oil. Note that the sample analyzed by a laboratory probably does not include any accumulation of foreign material at the bottom of the tank. Any significant amount of water and sediment reported by the lab could be an indicator that there is a significant accumulation at the bottom of the tank.

3.3.3 Ultimate Analysis

An ultimate analysis is usually performed for the benefit of an air emissions assessment. The results are used to calculate the F-factor (see Chapter 4), a parameter essential to reduction of air emissions test data. The ultimate analysis presents the elemental composition of the fuel as determined by ASTM D3176. The elements include, but are not necessarily limited to the following:

- Carbon
- Hydrogen
- Oxygen
- Nitrogen
- Sulfur
- Chlorine

In addition to these elements, the ultimate analysis usually includes data on ash and moisture levels. The moisture levels presented in ultimate analyses usually represent moisture present on a "moisture free" basis after being gently oven dried. Table 3-5 gives some typical values for the ultimate analysis of coal and oil samples.

Table 3-5. Typical Ultimate Analysis for Coal and No. 6 Oil (% by wt.)

Analyte	*Coal – As Received*	*Coal – Dry Basis*	*No. 6 Oil*
Moisture	3.03	0	nil
Carbon	60.68	62.58	85.78
Hydrogen	4.35	4.49	10.59
Nitrogen	1.12	1.16	0.03
Chlorine	0.12	0.12	
Sulfur	4.29	4.42	2.13
Ash	19.18	19.78	0.10
Oxygen (diff.)	7.23	7.45	1.37
Total	100.00	100.00	100.00

Note that only one coal analysis was performed and the second column is derived from the first by adjusting for zero moisture. The fact that the composition always totals exactly 100.00% is not fortuitous. The oxygen concentration is determined by the difference after all other figures, including the total, are entered in the column. The reported oxygen concentration may be approximately correct but, by definition, it covers up any errors in the other analysis.

3.3.4 Ash Composition Data

Ash is the solid material remaining after combustion is complete and all the organic fuel is converted to gas. Coal generates large amounts of ash, but even residual oil with less than 0.1% ash can generate substantial furnace ash accumulations over a period of weeks or months. Ash settles in the bottom of the furnace, accumulates on the walls and heat transfer surfaces, and is carried to the dust collector or stack by the flue gas. Wherever it goes, it needs to be managed, cleaned off the walls, removed from hoppers or prevented from causing excess particulate emissions. The amount of ash to manage is simply the amount introduced with the fuel. For example, 150 tons of coal with 10% ash content will generate 15 tons of ash in the furnace.

The composition of the ash affects operation of the combustion source as well as several aspects of ash management. Ash chemistry determines the ash melting temperature that in turn affects if and where molten sticky ash will accumulate as slag on the furnace walls. This in turn affects the firing rate and maximum achievable load. The ash properties directly affect corrosion and erosion rates of boiler surfaces. The ash composition of the fuel can affect the ability of an electrostatic precipitator or fabric filter to collect fly ash. For example, the sodium, potassium and sulfur contents of the ash exert an influence on the dust collecting performance of an electrostatic precipitator. An additional discussion of these subjects is presented in Chapters 5, 6, and 7.

Table 3-6. Example of Coal Ash Composition (%)

Mineral	*Ash No. 1*	*Ash No. 2*
SiO_2	38.94	55.93
Al_2O_3	22.75	25.02
TiO_2	1.03	1.15
Fe_2O_3	30.97	9.73
CaO	1.59	0.81
MgO	0.94	1.07
K_2O	1.82	2.36
Na_2O	0.46	0.46
SO_3	0.31	0.85
P_2O_5	0.10	0.12
SrO	0.02	0.00
BaO	0.08	0.12
Mn_3O_4	0.10	0.02
Undetermined	0.89	2.36

Ash compositional data are often presented based on the assumption that all of the elements are present in an oxide form. A typical composition analysis for two coal ashes is provided in Table 3-6. This example is analysis of ash prepared in the laboratory from coal samples. One could also analyze samples of ash taken from the furnace hoppers or from the dust collector. On a given furnace, the results of these analyses should be similar in most respects to the results of the coal analysis. However, the ash concentrations of some of the more volatile constituents, such as sulfur, chlorine and lead may differ substantially between the fuel ash and the resulting furnace ash. These differences are discussed in more detail in Chapter 5.

The examples shown here are relevant to the behavior of ash in a pulverized coal furnace. Analysis for other elements can be requested to serve other purposes. Toxic elements such as arsenic, beryllium or lead could be requested if there was an interest

in potential air emissions. Note that mercury and its compounds are volatile and are not likely to be found in ash that is generated by burning away the organic compounds, either in the laboratory or in an actual furnace. Thus the methods of sample preparation and analysis may be critical to interpreting the results.

3.3.5 Size Distribution of Solid Fuels

Solid fuel particles burn on the surface, so large particles take longer to burn than small particles. Hence there is both fundamental and practical significance to the particle size distribution of solid fuel fed to a combustor. We will briefly discuss the effects of fuel particle size on typical combustion systems and then describe size analysis.

3.3.5.1 Measuring Fuel Size

ASTM sizing screens can be used by plant personnel to measure fuel size distribution. These are 8" or 12" pans that have an open wire mesh weave as illustrated in Figure 3-2. The pans are stacked with the largest openings at the top and smaller openings in each successive screen. The fuel sample is placed in the top pan and the entire stack is shaken for a standard period of time. After shaking the contents, each screen is weighed to determine the percentage of the sample in each size range.

Figure 3-2. ASTM Sieves, Separated and Stacked for Shaking

Table 3-7. Standard Sieve Sizes		
Mesh	*Size (mm)*	*Size (inch)*
200	0.075	0.003
100	0.15	0.006
50	0.30	0.012
35	0.50	0.020
18	1.00	0.039
10	2.00	0.079
8	2.36	0.093

Standard sieves for testing small particles are made of wire mesh and the mesh number refers to the number of wires per inch. Thus a No.8 mesh has openings a bit smaller than 1/8 inch. Standard mesh sizes run from No.8 to No.400. Sieves with openings 0.25 inches and larger are designated by the size of the openings and come either with round holes or wire mesh. A few of the standard sizes are listed in Table 3-7.

3.3.5.2 Stoker Fuel Sizes

In a stoker furnace, air is blown up through a grate that carries a bed of burning fuel. Combustion of the fuel takes a number of minutes. Maximum coal or wood particle size is typically on the order of an inch (2 cm), but these furnaces can be designed or operated with much larger particles. Typically, a facility limits the maximum allowable particle size either through a fuel purchase agreement or by on-site fuel processing (crushing, chipping, shredding, etc.). This assures no fuel particles are too large to burn completely in the available furnace residence time. Stokers may also limit the amount of fine particulate for two reasons. First, fine particulate burns rapidly while the stoker is designed and operated for fuel that takes a number of minutes to burn completely. So too much fine particulate disrupts normal stoker operation. Second, particles smaller than one or two millimeters (about 1/16 inch),.

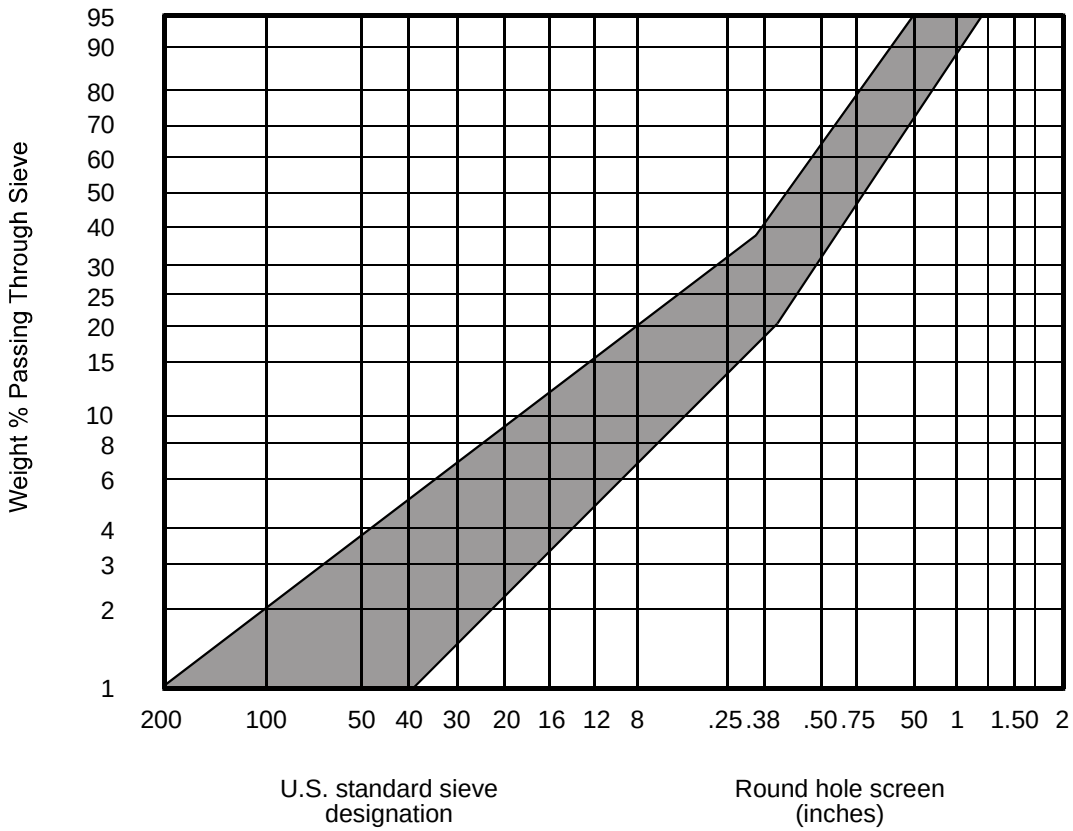


Figure 3-3. Example of Coal Size Specification for a Spreader Stoker

but larger than 0.1 mm, tend to get blown out of the furnace before they burn completely. So fuel with a lot of fine particulate tends to put a lot of unburned carbon into the fly ash that is captured in the dust collector. This wastes fuel and can make the dust a fire hazard.

An example specification for coal size distribution in spreader stoker boilers is shown in Figure 3-3. The percentage of coal in each size range should fall within the shaded area. In this example, between 14% and 32% of the coal should be nominally 0.25 inch diameter. If more than 32% passes through a 0.25 inch screen, the coal is too fine. If less than 14% reaches the 0.25 inch screen, the coal is too coarse. The problem in Example 3 illustrates how the fuel-sizing curves are interpreted.

Example 3: Interpretation of Fuel Sizing Charts

A coal supply to be used for a spreader stoker has a size distribution as indicated in the following table. Is this material appropriately sized for use in the boiler if the size curve shown in Figure 3-3 applies?

Coal Size Range, Example 3

Table 3-8. Coal Size Range

Coal Size Range	*Wt. % of Fuel (passing sieve)*
< 3/8	80
< 1/8	25
<20 mesh	8
< 50 mesh	6

Note: Mesh sizes apply to standard ASTM sizing screens

Solution:

80% is less than 3/8 inch, which is outside the required range of 18% to 40%. More of the coal should be in pieces larger than 3/8 inch.

25% is less than 1/8 inch, which is close to the required range of 8% to 22%

8% is less than 20 mesh, which is in the required range of 2% to 9%.

6% is less than 50 mesh, which is outside the required range of less than 4%. Too much of the coal is finer than 50 mesh.

Therefore, the example coal has more fines and much less larger sizes than the desired size distribution. The lack of larger sizes means the coal will burn more rapidly than intended for this grate, because smaller pieces mean more surface area. The excess of fines less than 50 mesh means that more partly burned coal will blow out of the furnace, wasting fuel and increasing particulate emissions.

Having discussed the theory of stoker coal sizing it should be noted that it is common for coal-fired stokers to burn fuel that lies outside the original size specifications. The reasons are market based. Properly sized stoker coal frequently sells for considerably more than readily available supplies that have too much fine material. It is much cheaper to take what is available than it is to require specially prepared coal.

When dealing with wood or waste-fired stokers, the subject of fuel particle sizing becomes academic. For the most part these stokers take whatever is supplied. With wood the key issues involve conveyors, feeders and other hardware that can be jammed or disrupted by oversize or odd shaped pieces. Once the fuel is in the furnace, problems with incomplete combustion are addressed by approaches other than trying to adjust particle size.

Municipal and medical wastes are usually fired in whatever form they arrive at the facility, in which case size distribution has little meaning. The furnace is fed by a large grapple that drops huge handfuls of waste directly into the chute that feeds the grate. The only exceptions are a few municipal waste facilities that prepare and burn *refuse derived fuel* (RDF). RDF is made by running municipal waste through a large shredder that reduces everything to pieces about the size of a credit card. As part of the process, the facility separates out most of the metal and glass to support recycling. Conveyors and feeders similar to those managing wood chips handle the resulting stream of RDF. There are a relatively small number of these facilities, but an extensive explanation about RDF is beyond the scope of this course.

3.3.5.3 Pulverized Coal Size

Grinding coal to a powder creates pulverized coal. With only a few exceptions it is blown directly from the grinding mill into the furnace. In order to work well, pulverized coal furnaces require the powdered fuel to meet specific particle size criteria. The size distribution of pulverized coal is normally measured with 50, 100, and 200 mesh screens. As a general rule, 90% to 95% of pulverized coal will pass through a 200 mesh screen (75µm) although with some types of coal this number can be as low as 70%. This fine size assures sufficient particle surface area that the fuel will ignite promptly and burn rapidly.

It is also necessary on most furnaces that the amount of fuel retained on a 50 mesh screen (0.3 mm) be less than 1%. These particles are too large to burn completely in the typical pulverized coal furnace. When a pulverized coal furnace produces fly ash with high carbon levels, coal particles larger than 0.2 to 0.3 mm are usually one of the primary causes. Operation and maintenance of the coal mills determines the size distribution.

3.4 FUEL PROPERTIES

3.4.1 Gas Fuels

Gas fuels are easy to burn because, unlike liquid and solid fuels, a gas mixes directly with air. Another advantage is that, with the exception of sulfur, gas fuels are usually free of contaminants that form air pollutants. So gas is usually clean burning. The most common constituents of commercially available gas fuels are methane (CH_4) and propane (C_3H_8). Small amounts of other gases are usually present in commercial gas fuels. Acetylene (C_2H_2) is a gas that is sold in small quantities, usually for use in cutting or welding applications. In some industrial facilities carbon monoxide (CO) or hydrogen (H_2) are available as a process waste or as surplus fuel; but they are used on site and not sold commercially. Both landfills and sewage treatment facilities can generate gas with significant methane content. In a number of cases, this gas is being collected and piped to a commercial use, such as electric power generation.

In the 19th and early 20th centuries, gas was manufactured locally and distributed commercially to provide illumination. The manufacturing process heated coal in the absence of air to create gas, coke and some heavy liquid hydrocarbons. The only current reminders of these early process plants are hazardous waste sites created when the liquids were discarded in on-site waste pits. While a few plants may currently be operating, coal gasification, at the present time, is primarily a research activity.

3.4.1.1 Natural Gas

Natural gas is a naturally occurring fuel that comes from wells and is transported by pipeline to the end user. Natural gas can also be transported over seas by compressing and refrigerating it to form liquefied natural gas (LNG). At one time natural gas was an unwanted byproduct of oil wells and it was flared or incinerated at the well. This practice disappeared once long distance pipelines made it feasible to transport it to market. A predicted shortage about 1970 failed to materialize and today natural gas is used wherever a pipeline makes it available. Most new electric power plants in the U.S. since about 1985 use natural gas as the primary fuel.

Natural gas, as it comes from the well, is mostly methane, but frequently contains some impurities that must be scrubbed out. Before the gas is distributed a few ppm of a mercaptan is added to give the gas an odor. Methane is odorless, but humans can detect the odor of mercaptans at extremely low concentrations. This use of mercaptans means that all commercially available natural gas has a few ppm of sulfur. The natural gas composition data shown in Table 3-9 illustrate the typical composition of natural gas from several sources. It usually consists of more than 80% methane with a wide variety of other combustible and noncombustible compounds. The specific constituents present in natural gas depend on the source and, to a lesser degree, upon the processing to remove hydrogen sulfide and other reduced sulfur compounds.

The heating value of natural gas is usually assumed to be approximately 1,000 BTU/ft^3. As indicated in Table 3-9, the heating value can vary significantly. When there is a significant amount of carbon dioxide or nitrogen (N_2) present, the heating value is reduced. If there are substantial amounts of high molecular weight organic compounds (>C_2), the heating value is increased. Accordingly, the heating values (HHVs) for natural gas can range from less than 850 BTU/ft^3 to more than 1500 BTU/ft^3.

Table 3-9. Natural Gas Composition and Characteristics
Fuel Composition, Wt. %

Fuel	*Pennsylvania*	*S. California*	*Ohio*	*Louisiana*	*Oklahoma*
CH_4	83.40	84.00	93.33	90.00	84.10
H_2	–	–	1.82	–	–
C_2H_4	–	–	0.25	–	–
C_2H_6	15.80	14.80	–	5.00	6.70
CO	–	–	0.45	–	–
CO_2	–	0.70	0.22	–	0.80
N_2	0.80	0.50	3.40	5.00	8.40
O_2	–	–	0.35	–	–
H_2S			0.18		
Total	100.00	100.00	100.00	100.00	100.00
S	–	–	0.34	–	–
H_2	23.53	23.30	23.20	22.68	20.85
C	75.25	74.72	69.12	69.26	64.84
N_2	1.22	0.76	5.76	8.06	12.90
O_2	–	1.22	1.58	–	1.41
Total	100.00	100.00	100.00	100.00	100.00
Physical Properties					
Sp. Gravity	0.636	0.636	0.567	0.600	0.630
BTU/ft^3	1,129.00	1116.00	964.00	1,002.00	974.00
BTU/lb. fuel	23,170.00	22,904.00	22,077.00	21,824.00	20,160.00

Source: DOE/EIA –0603(98)/1 Energy Information Administration

There are four general terms used to describe natural gas fuels:

- Sour gas
- Sweet gas
- Lean gas
- Wet gas

Sour gas is natural gas that has significant quantities of hydrogen sulfide and other reduced sulfur compounds. Due to the corrosion problems and health risks associated with these compounds, the hydrogen sulfide and other reduced sulfur compounds are removed before the natural gas is commercially distributed. Natural gas that is free of hydrogen sulfide and other reduced sulfur compounds is referred to as *sweet gas*.

Lean gas has a very high methane concentration implying that it will have a moderate-to-low heating value.

Wet gas contains moderate concentrations of high molecular weight organic compounds. As a result, condensation of organic vapor may result in condensed organic liquids accumulating in the transport system.

3.4.1.2 Propane and Liquefied Petroleum Gas

Propane (C_3H_8) gas changes to a liquid when compressed to about 15 psi at typical ambient temperatures. This makes it a convenient fuel that can be sold by the gallon and used as a gas. Commercial propane is typically composed of approximately 97% propane with the remainder being ethane and butane. Commercial propane has a heating value of 2,540 BTU/ft^3 and has inherently low sulfur content due to the processing steps involved in its preparation. Propane is more expensive than natural gas, so it is only used in those industrial applications where natural gas is not available but where a gas fuel is required.

Liquefied Petroleum Gas (LPG) is usually propane, with some other gases that condense to liquid form at moderate pressures. Examples of gases in commercial LPG include propane, isobutane, n-butane, pentane, and other paraffinic compounds.

3.4.1.3 Waste Biological Gases

Anaerobic biological processes (those without exposure to air) generate methane and other combustible gases. Prominent processes include animal digestive tracts, waste decomposition in closed landfills, septic systems and some sewage treatment processes. Waste gases from large landfills and from sewage treatment plants have been collected and used as fuel for engines that drive electric generators. At sites where the gas is not used it is usually necessary to flare the gas to control off- site problems such as odors and the uncontrolled accumulation of flammable gasses.

The rate of fuel gas formation in a landfill depends on a number of variables including the amount of water in the landfill, the landfill cover and degree of oxygen exclusion from the waste, waste temperature, and the composition of the buried wastes. Typically, a landfill can generate commercial amounts of fuel gas for about 20 years. Landfill gas is highly variable and can have methane contents of approximately 50% by volume.

Biogas is a mixture of methane, carbon dioxide, water, and some other organic compounds formed by the anaerobic digestion of sewage sludge. Biogas usually has a heating value of about 600 BTU/ft^3. Biogas can be used on-site at the sewage treatment plant, or it can be treated and transported via pipeline to an industrial customer.

3.4.2 Fuel Oils

3.4.2.1 Classification and Characteristics

Fuel oils are classified into several categories based on ASTM standards. A partial list of the fuel oil specifications used to classify fuel oil is summarized in Table 3-10. Note that these are limiting values and the market place may be more restrictive.

Although Table 3-10 implies a kind of continuum from light to heavy, in practice there are two general categories of fuel oil: distillate and residual. Distillate oil includes No. 1 and No. 2 and it differs radically from the heavier residual oils. The differences correspond to the distillation and refining processes.

Table 3-10. Fuel Oil Specification Ranges

Grade	*Flash Point, °C*	*Water and Sediment, (% by vol.)*	*Sulfur Content, (% by vol.)*	*Ash Content, (% by vol.)*	*Viscosity (centistokes)*	*Specific Gravity @60 °F*
	Min.	Max.	Max.	Max.	Min - Max.	Max.
No. 1	38 or legal	0.05	0.05 - 0.5		1.3 - 2.4 @ 40°C	0.850
No. 2	38 or legal	0.05	0.05 - 0.5		1.9 - 4.1 @ 40°C	0.876
No. 4	55 or legal	0.50	–	0.05 – 0.10	5.5 – 24.0 @ 40°C	
No. 5 (Light)	55 or legal	1.00	–	0.15	5.0 - 8.9 @ 100°C	
No. 5 (Hvy)	55 or legal	1.00	–	0.15	9.0 - 14.9 @ 100°C	
No. 6	60 or legal	2.00			15.0 - 50 @ 100°C	

Source, Edited from ASTM Standard D396, Standard Specification for Fuel Oils

When a refinery processes crude oil, it begins by distilling off the lighter constituents that are used to make gasoline, No. 2 oil, lubricating oil, and all the "clean" petroleum products. What is left is called "residual" or No. 6 oil. Most of contaminants in the original crude oil stay in the residual oil. Thus the residual oil generally contains higher concentrations of ash, nitrogen and sulfur which all contribute to air pollution. Therefore, distillate fuels are relatively clean burning, while the residual oils generate much higher pollutant emission levels.

Residual fuel is cheaper than distillate fuel, but it is so viscous that it requires special handling to use it. No.6 oil must be heated just to pump it, so it is stored in insulated tanks with some means of heating it. It must be heated to temperatures above about 180°F to thin it sufficiently to atomize. Failure to spray it properly can result in coke formation (the result of cooking the residual fuel to the point that it is solid carbon) in the furnace and in the burner hardware. So residual fuel is only used by electric utilities, industrial, or large commercial facilities where an operator is continuously present to monitor and maintain the combustion system. Table 3-11 summarizes some typical properties of common fuel oils

Table 3-11. Example Properties of Common Fuel Oils						
Grade	*Name*	*Color*	*API Gravity*	*Density, lb/gal*	*BTU/gallon*	*Comments*
No. 1	Kerosene	Light	38 – 45	6.675-6.950	133,000-137,000	
No. 2	Distillate	Amber	30 – 38	6.960-7.296	137,000-142,000	Home heating fuel
No. 4	Light Residual	Black	20 – 28	7.396-7.787	143,000-148,000	Fluid at ambient temp.
No. 6	Residual	Black	8 – 15	8.053-8.448	151,000-156,000	Heating required to pump and atomize

3.4.2.2 Distillate and Diesel Oil

No. 1 fuel oil is usually called kerosene. No. 2 is common heating oil. Although it can have as much as 0.5% sulfur, most No. 2 oil has sulfur levels less than 0.1%. Diesel engine fuel is made by blending No.2 oil with kerosene. The proportions vary by season – cold weather fuel has more kerosene to lower the viscosity.

In 2006, the USEPA lowered the maximum sulfur content of highway diesel fuel from around 0.05% to 0.0015% (15 ppmw). This reduction was first applied to highway diesel fuel but will eventually apply to virtually all diesel fuel. The main reason for this reduction is that sulfur fouls the catalysts that are needed for effective control of air pollution from diesel engines. Note that reciprocating diesel engines can also operate on residual oil, as do most marine diesel engines. Thus diesel engine emissions in harbor areas may be very different from highway diesel engine emissions.

3.4.2.3 Residual Oil

Residual oil is what remains after the refinery has removed all the distillate fuel from the original crude oil. This means that residual contains sulfur, nitrogen and ash (metals) in significant amounts. Residual oil is much less expensive than distillate oil. Refiners extract as much distillate product as they can from the crude and still have a marketable residual. This means they stop removing distillate when sulfur or viscosity levels of the residual reach a marketable upper limit. There is actually a small market for petroleum coke. But most residual fuel has to meet a sulfur limit of 1% or less and a viscosity that allows the fuel to be burned at temperatures of 240°F or less. Most facilities that were once permitted to burn 1.5% or 2.2% sulfur fuel have had to reduce their SO_2 emissions. Since very few oil-fired facilities have SO_2 scrubbers, their only choice is to reduce the fuel sulfur content. Therefore, residual oil is considerably lighter now than it was 20 years ago.

The main difference between No. 4 and No. 6 oil is that No. 4 oil does not have to be kept warm in order to pump it. No.4 oil is basically thinned out No. 6 oil, and a distributor can produce it by blending No. 2 and No. 6 oils.

No. 5 is a designation that is not commonly used.

Industrial boilers fire No. 6 oil, sometimes termed “Bunker C” oil, in large quantities for electric power generation and other industrial use. Its density approaches, and can exceed, the density of water. At ambient temperatures it may resemble bitumen (tar) used to make highway asphalt. However, it does not evaporate and No. 6 oil spills are very messy to clean up.

In order to fire heavy oil, the viscosity must be reduced to less than about 200 SSU (Saybolt Seconds Universal) or 45 centistokes. At or below this level an atomizer can generate a fine spray that will burn rapidly. Above these levels, the nozzle will generate a coarse spray with large droplets, which do not completely burn in the combustion zone. Burner operators use the viscosity from a fuel analysis and a special ASTM chart shown in Figure 3-4 to determine the minimum oil temperature. Any oil has a viscosity-

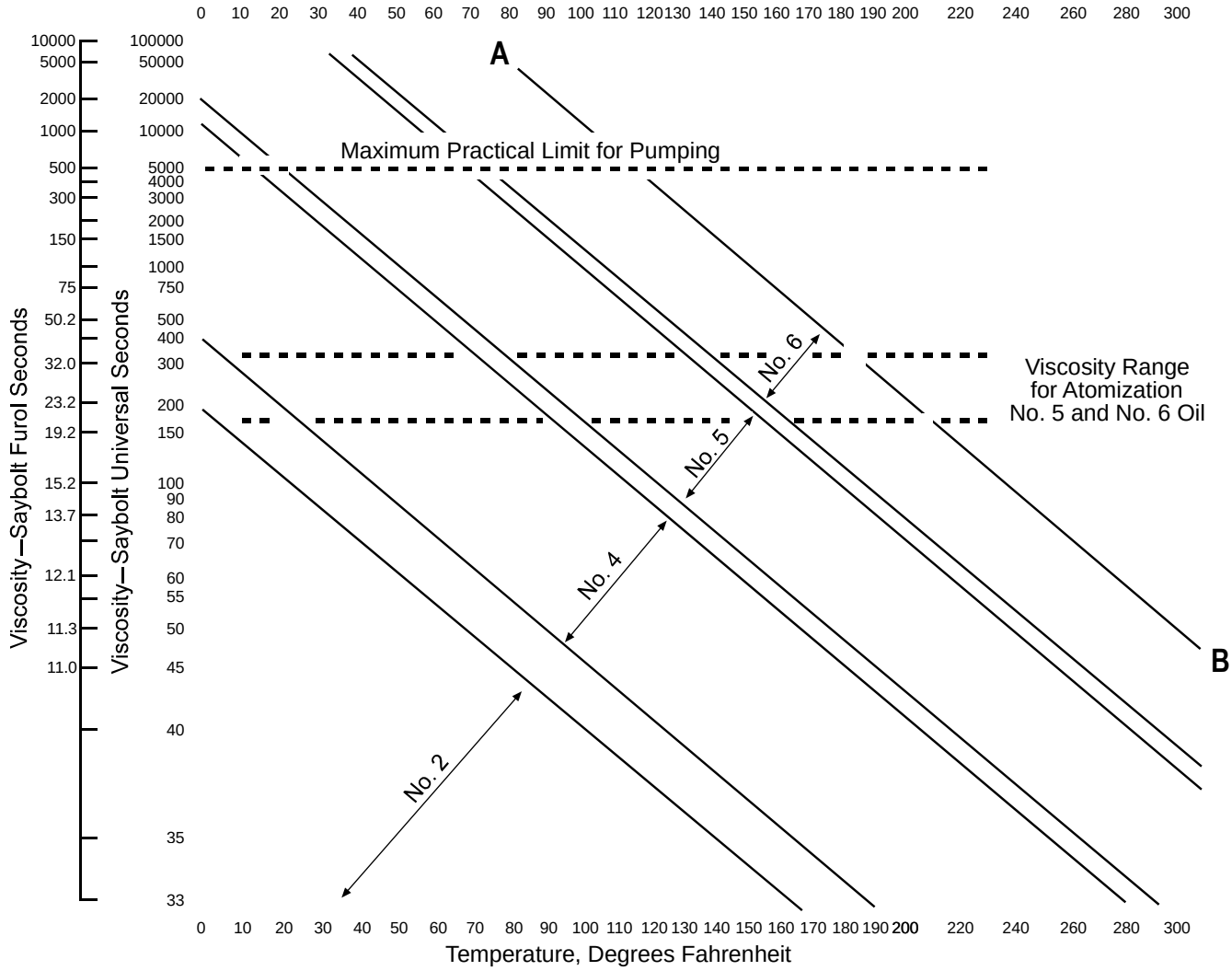


Figure 3-4. ASTM Oil Viscosity-Temperature Relationship

Source: American Society for Testing and Materials (ASTM, West Conshohocken, PA)

temperature relationship that is a straight line parallel to one of the diagonal lines in the chart. Viscosity and temperature data from the lab is plotted on the chart and then a straight line plotted down and to the right until it reaches the desired firing viscosity of approximately 150 SSU. The firing temperature can then be read on the abscissa. Note that in order to make the plot a straight line, both the vertical and horizontal scales are completely non-linear. This is the classic example of creating crooked graph paper in order to make the data fall on straight lines.

A significant aspect of No. 6 oil is the amount of vanadium and other metals in the ash. At certain temperatures, V_2O_5 is active in the catalytic oxidation of sulfur dioxide to sulfur trioxide. In boilers firing high vanadium content oil, the fraction of sulfur dioxide oxidized to sulfur trioxide can increase to levels well above those experienced in boilers firing low vanadium oil. Sulfur trioxide reacts with water at ambient temperatures to form sulfuric acid and the result is corrosion of the flue gas duct system. SO_3 concentrations of only about 10 ppm in the flue gas result in the condensation of sulfuric acid into a highly visible plume downwind of the stack. This will be discussed further in Chapter 5.

3.4.2.4 Oil Emulsions

Oil emulsions are fuel oils prepared by dispersing fine atomized oil droplets into water. Oil droplet combination (coalescence) is prevented by using a dispersing agent. There are two general uses of oil emulsions.

1- A viable liquid can be prepared from oil supplies that are too thick to be readily usable as fuel. The resulting firing characteristics are similar to a No. 6 oil. These proposed emulsions could have high sulfur, vanadium, and asphaltene levels and hence incur pollution control costs that offset their low cost.

2- Emulsions of residual oil have been used to improve combustion and reduce emissions. Water in the oil reduces flame temperature, which reduces NOx formation. Water in an oil spray can improve the atomization, which may improve combustion. But the drawback to this use of emulsions is that there are usually cheaper and simpler ways to gain the same advantages. Thus oil emulsions to date have been more of a gimmick than a true advance in combustion technology.

3.4.2.5 Coal-Water Emulsions

Finely ground (highly pulverized) coal can be mixed with water and dispersing agents to prepare an emulsion suitable for firing in oil burners. This fuel can have properties similar to No. 6 oil. The storage tanks must be designed to provide mixing to prevent any settling of the dispersed coal particles. The heating values, sulfur contents, and ash contents of the coal-water emulsion fuel depend entirely on the coal used to prepare the emulsion. Although a coal-water emulsion can be fired through pipes, valves and atomizing nozzles similar to the oil handling hardware, a number of critical differences are not easily resolved. (1) Coal ash content is at least 100 times that of oil and boilers designed for oil firing are not configured to handle such great

quantities of ash. The ash will tend to bridge over the closely spaced tubes. The furnace volume for oil firing is about half that required for coal, so the maximum load may have to be reduced by a third or more. (2) Most of the coal ash will be carried by the flue gas, meaning that a good dust collector is required to meet particulate emissions standards. Very few oil-fired boilers are built with dust collectors. (3)

The idea of coal-water emulsions received serious consideration during the oil crisis in the 1970s when there were fears of ever escalating oil prices and ongoing shortages. But coal-water emulsions hold little appeal as long as oil and natural gas are readily available and relatively inexpensive.

3.4.3 Coal

3.4.3.1 Classification and Characteristics

Coal continues to be the dominant fuel used for power generation and industrial process kilns and furnaces, and is readily available in most areas of the U.S. All coals carry significant amounts of inorganic contaminants: 5% to 25% ash, 0.5% to 5% sulfur, and 1% to 2% nitrogen. There are four distinct classes (ranks) of coal having progressively lower carbon contents and progressively higher moisture levels.

Table 3-12. ASTM (D388) Specifications for Coal (Ash and Moisture Free Basis)

Class	*Group*	*Fixed Carbon % by wt.*		*Volatile Matter % by wt.*		*Heating Value BTU/lb*		*Agglomerating Character*
Anthracite	Meta anthracite	≥98			<2			
	Anthracite	≥92	<98	≥2	<8			Nonagglomerating
	Semi anthracite	≥86	<92	≥8	<14			
Bituminous	Low Volatile Bituminous	≥78	<86	≥14	<22			
	Med. Volatile Bituminous	≥69	<78	≥22	<31			
	High Volatile A Bituminous		<69	≥31		≥14000		Commonly
	High Volatile B Bituminous					≥13000	<14000	Agglomerating
	High Volatile C Bituminous					≥11500	<13000	
						≥10500	<11500	
Subbituminous	Subbituminous A					≥10500	<11500	
	Subbituminous B					≥9500	<10500	
	Subbituminous C					≥8300	<9500	Nonagglomerating
Lignite	Lignite A					≥6300	<8300	
	Lignite B						<6300	Nonagglomerating

Source: DOE/EIA –0603(98)/1 Energy Information Administration

Table 3-13. Properties of Example Coals				
Analyses (dry basis), % by wt.	*Anthracite*	*Bituminous Pittsburgh Seam*	*Subbituminous Spring Creek*	*Lignite North Dakota*
Proximate Analysis, % by wt				
Volatile Matter	5.91	38.11	32.71	29.03
Moisture	7.70	5.20	24.10	33.30
Fixed Carbon	76.70	48.06	38.86	30.22
Ash	9.69	8.63	4.33	7.40
Ultimate Analysis, % by wt				
Hydrogen	1.90	5.10	5.00	4.50
Carbon	83.70	74.00	70.30	63.30
Sulfur	0.70	2.30	0.35	1.10
Nitrogen	0.90	1.60	0.96	1.00
Oxygen	2.30	7.90	17.69	19.00
Ash	10.50	9.10	5.70	11.10
Heating Value				
BTU/lb, as received	11,890	12,540	9,190	7,090
Ash Analysis, % by wt				
SiO_2	51.00	50.58	32.61	29.80
Fe_2O_3	3.50	17.16	7.53	9.00
TiO_2	2.40	1.10	1.57	0.40
Al_2O_3	34.00	24.62	13.38	10.00
CaO	0.60	1.13	15.12	19.00
MgO	0.30	0.62	4.26	5.00
Na_2O	0.74	0.39	7.41	5.80
P_2O_5	–	0.39	0.44	–
K_2O	2.65	1.99	0.87	0.49
SO_3	1.38	1.11	14.56	20.85
Ash Fusibility Temp, °F, Reducing Conditions				
Initial Deformation	–	2220	2180	2030
Softening	–	2470	2320	2170
Fluid	–	2750+	2370	2300
Ash Fusibility Temp, °F, Oxidizing Conditions				
Initial Deformation	–	2560	2180	2160
Softening	–	2650	2320	2220
Fluid	–	2750+	2700	2300

Source: Steam, Its Generation and Use, The Babcock and Wilcox Company, Barberton, OH, 41st Edition, 2005, page 9-10

Beginning with anthracite, which is almost pure carbon, they are:

- Anthracite
- Bituminous
- Subbituminous
- Lignite

Coal is categorized in more detail in accordance with the ASTM specification D388 summarized in Table 3-12. This classification system is based fixed carbon levels or heating value from proximate analyses. Older anthracite and bituminous coals are categorized based on fixed carbon and while coals with less than 69% fixed carbon are categorized based on their heating value (HHV on a mineral free basis).

Examples of coal ultimate and proximate analyses for the four categories of coal are provided in Table 3-13. These data are intended only to provide a general indication of the properties of each type of coal. Within each category of coal, there is considerable variability in the properties. Even coal supplied from a specific mine also can have considerable variability over time due to spatial differences in the coal deposit. Coal is inherently a non-homogeneous material.

Anthracite is a hard, brittle coal mined primarily in central Pennsylvania and is slow burning in most combustion processes due to its low volatile content. Meta-anthracite, the most aged form of anthracite coal, burns so slowly it is sometimes blended with other coals with higher volatile contents. It can have very low moisture levels of less than 3% and is generally low in sulfur. The low sulfur content and its clean burning characteristics make it the premium coal for residential furnaces. The heating value of anthracite is moderately high ranging from 12,000 to 13,500 BTU/lb. (as received).

Bituminous coals have high heating values and moderate to high volatile levels. They burn well when pulverized and are used extensively in utility power stations in the Midwest, south, and east. Bituminous coals are well suited for the production of metallurgical coke because the coal becomes sticky and cohesive when heated in the absence of air. In fact, the ability to form the sticky bituminous material during coke formation was the basis for naming this type of coal as “bituminous.” The formation of sticky, partially swollen material during combustion can cause problems when bituminous coals are burned in some types of stoker furnaces.

Many of the bituminous coals can have moderate-to-high sulfur levels resulting in high emissions of sulfur dioxide. Some bituminous coals also have moderate-to-high mercury levels. The emission of mercury from large combustion sources is an issue of increasing concern.

Unlike some bituminous coals, the subbituminous coals do not swell appreciably during heating. The subbituminous coals have high moisture levels and can be extremely vulnerable to spontaneous combustion in coal storage piles. They have more ash than bituminous and anthracite coals, but generally has low sulfur levels and reasonable heating values. Accordingly, they have been substituted for bituminous

coals in some sources to reduce SO_2 emissions. However, subbituminous coals are entirely non-coking.

Lignite is the lowest rank coal that sometimes has recognizable plant debris; therefore, it has a high moisture level, up to 30% by weight, and is vulnerable to spontaneous combustion in coal storage piles. Even when the fuel appears to be dry, the moisture levels can be quite high. This type of coal also has a high volatile content. Due primarily to the low heating value, it may not be economical to ship lignite fuel a long distance.

Three main regions of the country produce coal: the Appalachian, interior, and western regions. Figure 3-5 illustrates the geographic distribution of coal reserves throughout the U.S.

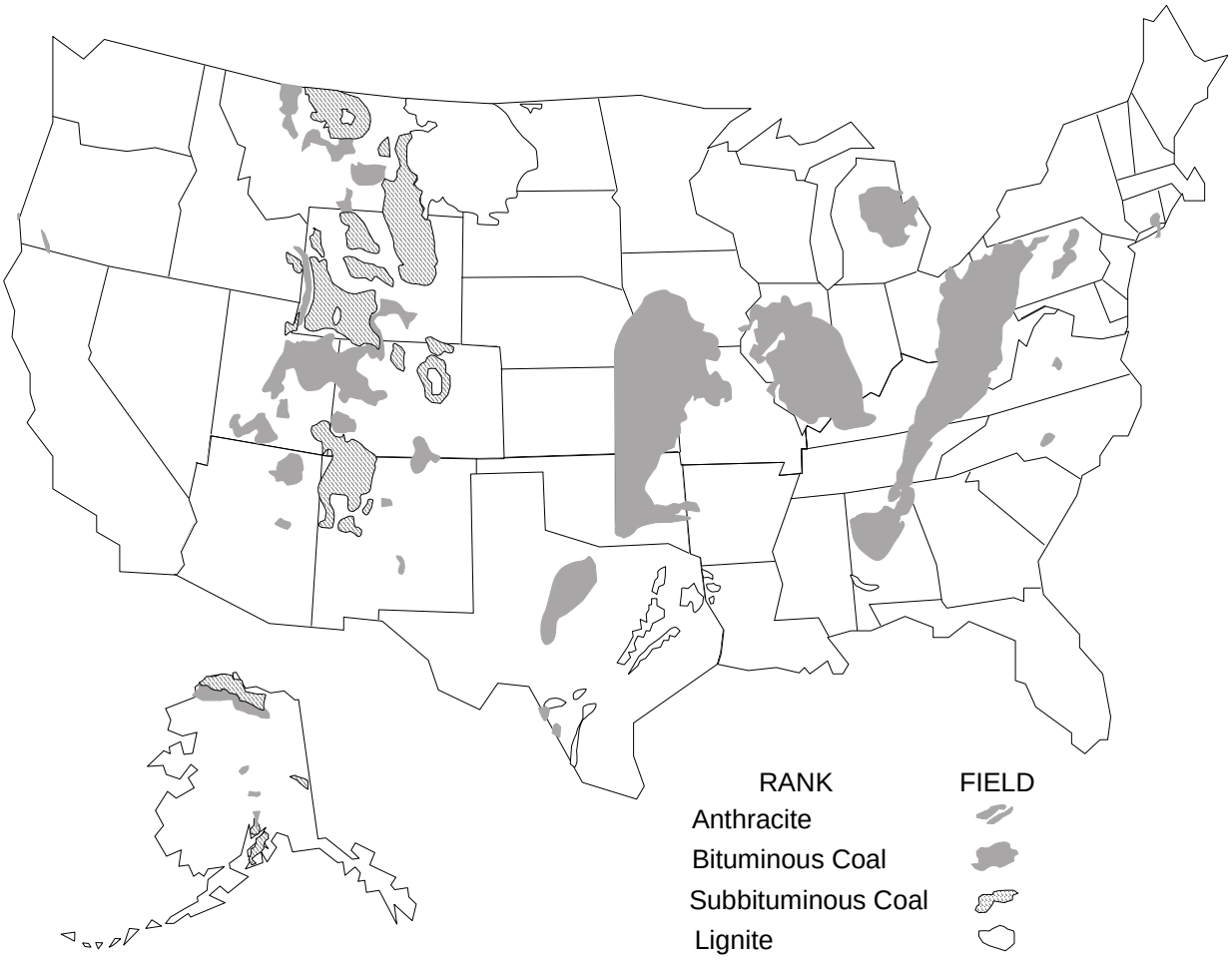


Figure 3-5. Geographic Distribution of Coal Reserves
Source: DOE, IEA

As this figure indicates, anthracite is available primarily in eastern Pennsylvania. Bituminous and subbituminous coals are largely available in numerous coal seams

present in western Pennsylvania, West Virginia, Kentucky, Ohio, and Illinois. Subbituminous coals are available throughout the Midwest, including Wyoming and Colorado. Lignite is available in portions of the Dakotas and Montana.

Due to the cost associated with shipping coal, most plants use coal supplies that are relatively close. Accordingly, most bituminous coal combustion occurs at plants in the Midwest, East, and South, while western boilers and industrial combustion processes use primarily subbituminous and lignite coals. There are also some bituminous coal supplies in the West as indicated in Figure 3-5.

The low sulfur content of subbituminous and lignite coals have become increasingly attractive to some utility boiler operators in the Midwest and East. In some cases, these coals are economically attractive because they allow compliance with SO_2 emission requirements without the cost of scrubbers or alternative SO_2 control techniques.

3.4.3.2 Coal Properties Related to Combustion

Operators must consider all of the properties of the coal supplies being considered when considering fuel changes for SO_2 compliance or other purposes. There are a number of physical and chemical properties of coal that can make their use impossible in some types of boilers. These properties include, but are not limited to the following:

- Agglomerating/caking tendencies
- Ash softening and fusion temperatures
- Coal size distribution
- Grindability and friability
- Mercury content

These characteristics are described briefly in the following subsections and include the ASTM testing procedures used to quantify the levels of the coal characteristics.

Agglomerating/Caking Tendencies

The agglomerating/caking tendencies of coal can be especially important with respect to some types of bituminous coal-fired in stoker boilers.

The agglomerating/swelling characteristics of coal can be categorized by the free swell index, also known as the “Coke Button”. This value is determined in accordance with ASTM procedures D720. This test involves burning a one-gram sample of coal in a covered crucible under a specific time temperature profile. The free swell scale ranges from a value of 0 (free burning) to 9 (severe swelling). Coals with free swell indices less than approximately 5 are usually not subject to the various stoker-firing problems potentially caused by caking coals. These are termed “free burning” coals. In these types of coal, the coal particles burn separately and do not fuse together during heating. When the free swell index is greater than 5, there is

some vulnerability to combustion problems due to the fusing of coal particles that chokes off air flow through the grate.

Ash Softening and Fusion Temperatures

The ash softening and fusion temperatures indicate the tendency of coal ash to melt or become sticky in the combustion chamber. Most coal-fired boilers are designed to handle solid (dry) ash that can be easily removed from the boiler. However, some coal ashes will soften and liquefy at the operating temperature in some regions of the boiler. When this type of fuel is burned, the boiler cleaning and ash handling system are challenged and the boiler may have to reduce load or shut down for cleaning. A boiler designed with a "wet bottom" is intended to handle the coals that form molten ash.

ASTM Procedure D1857-68 defines three temperatures that can be used to evaluate ash behavior in the combustion furnace:

- Initial deformation temperature
- Softening temperature
- Fluid temperature

The initial deformation temperature is the value at which a cone of coal ash first begins to deform due to softening. The softening temperature is defined as the point at which the cone has deformed to a hemispherical lump. The fluid temperature is defined as the temperature at which the ash forms a thin molten puddle.

The ash fusion temperature is the result of complex inorganic ash chemistry. For blended coal supplies, the ash fusion temperature of the blended coal is difficult to predict from the ash fusion temperatures of the individual coal supplies. In fact, two coals – each having a low ash fusion temperature – can conceivably yield a blended coal with a high ash fusion temperature. The converse is also true. Due to the complexity of the ash chemistry, it is appropriate to test the blended samples rather than attempting to calculate the values from the separate results for each coal supply.

Stoker Fuel Size Distributions

The coal size distribution can affect the operation of stoker-fired boilers. Excessive coal fines can accumulate in piles close to the coal distributor. Oversize particles can be thrown completely across the boiler and accumulate on the rear walls. In either case, the size distribution problems create a fuel-air maldistribution that contributes to increased air pollutant emissions.

Coal Size Terminology

A variety of "common use" terms have been applied to coal sizing. These are defined for each major category of coal. The size terms for bituminous coal are provided in Table 3-14. (Different terms exist for anthracite, subbituminous, and lignite coals.)

Table 3-14. Common Use Size Distribution Terms for Bituminous Coal		
Coal Category	*Size Description*	*Size Characteristics*
Bituminous	Run-of-mine	No size segregation
	Run-of-mine 8 inch	Lumps greater than 8 inches broken
	Lump	Larger than 5 inches
	Egg	Smaller than 5 inches and larger than 2 inches
	Nut	Smaller than 2 inches and larger than 1.25 inches
	Stoker	Coal smaller than 1.25 inches and larger than 0.75 inches
	Slack	Coal smaller than 0.75 inches

Source: DOE/EIA –0603(98)/1 Energy Information Administration

Grindability and Friability

Coal that is hard to grind can reduce the throughput of coal pulverizers and thereby limit the capacity of a pulverized coal-fired boiler. The ability to grind coal is measured using the Hardgrove grindability value (ASTM D4090). In this procedure, a 50-gram sample of 16 x 30 mesh coal is ground for a standard time period. The amount of coal less than 200 mesh after grinding is used to calculate the grindability. The 200-mesh weight fraction is then used to calculate the Hardgrove value.

The friability of coal is measured to determine the vulnerability of coal to produce excessive quantities of fine coal particles during coal mining, processing, shipping, and firing. The friability is measured using either a “drop-shatter” test or a tumbler test. Coal that is highly friable is vulnerable to the formation of fines as the fuel is transported and fed into the boiler. Friability does not matter when it is fed to a pulverized coal furnace, but it can cause excess fines to be fed to a stoker.

3.4.3.3 Contaminants, Air Pollution, Cleaning

Mercury content

Mercury is a volatile metal that is released into the exhaust gases during combustion. It forms elemental mercury, or mercuric oxide (HgO), or mercuric chloride (Hg_2Cl_2) depending on temperature and the presence of oxygen and chlorine. Unless there is specific control equipment to capture it, most of the mercury will penetrate air pollution control systems such as fabric filters, electrostatic precipitators, and flue gas desulfurization systems. Once released into the environment, mercury accumulates in fish as methyl mercury, moves up the food chain and becomes a threat to human health and welfare.

Mercury is neither created nor destroyed during combustion and it is not collected efficiently by standard pollution control equipment. Accordingly, one way to minimize mercury emissions is simply to select fuels with low mercury contents.

While data are limited regarding mercury levels, there is some general information regarding the levels of mercury in U.S. coals. A summary of typical mercury levels is provided in Table 3-15.

Note there can be significant variability in the coal mercury levels within a given region and within a given coal mine. The data in Table 3-15 provides only a general indication of the regional variability in mercury levels. While the amount of mercury in coal is small, electric utility plants use so much coal that the mercury emissions can be several pounds daily.

Table 3-15. Mercury Content in Coal

State	*Coal Rank*	*Higher Heating Value, Btu/lb.*	*Mean Mercury Concentration, ppm (w/w)*	*Median Mercury Concentration, ppm (w/w)*	*Mercury Content Variance, ppm (w/w)*
Alabama	Bituminous	12,575	0.22	0.18	0.028
Alaska	Subbituminous	7,756	0.06	0.05	0.002
Arizona	Subbituminous	10,834	0.04	0.05	0.000
Arkansas	Lignite	6,220	0.33	0.24	0.075
Colorado	Bituminous	11,250	0.06	0.03	0.005
Colorado	Subbituminous	9,527	0.06	0.05	0.003
Illinois	Bituminous	11,605	0.09	0.06	0.002
Indiana	Bituminous	11,386	0.10	0.08	0.006
Iowa	Bituminous	99,937	0.16	0.14	0.010
Kansas	Bituminous	12,014	0.17	0.14	0.019
Kentucky	Bituminous	12,595	0.16	0.11	0.024
Louisiana	Lignite	7,955	0.12	0.12	0.000
Maryland	Bituminous	12,786	0.33	0.18	0.160
Missouri	Bituminous	10,839	0.17	0.15	0.016
Montana	Lignite	6,701	0.13	0.10	0.017
Montana	Subbituminous	8,124	0.08	0.06	0.003
Montana	Bituminous	6,790	0.23	0.23	0.003
New Mexico	Subbituminous	9,297	0.06	0.04	0.005
North Dakota	Lignite	6,265	0.14	0.11	0.017
Ohio	Bituminous	11,948	0.20	0.17	0.022
Oklahoma	Bituminous	13,135	0.23	0.11	0.084
Pennsylvania	Bituminous	12,759	0.27	0.20	0.069
Tennessee	Bituminous	13,364	0.15	0.10	0.024
Texas	Lignite	7,628	0.17	0.14	0.018
Utah	Bituminous	10,061	0.09	0.05	0.011
Virginia		13,580	0.11	0.07	0.009

Source: DOE/EIA –0603(98)/1 Energy Information Administration

3.4.3.4 Coal Cleaning and Sulfur Levels

Ash

Mineral matter in coal can be either inherently part of the organic coal, or separate in the form of layers within or adjacent to the coal seam. To some extent the amount of mineral matter in coal can be controlled by careful mining procedures that minimize the amount of overburden that is accidentally (or carelessly) included with the coal that is shipped to market. Coal cleaning can remove some of this incidental mineral matter. There are no economical ways to remove ash that is chemically bound with the organic coal.

Sulfur

Sulfur is present in coal in three different chemical forms: (1) pyritic sulfur, (2) organic sulfur, and (3) sulfates. The fraction of the sulfur that is present as pyritic sulfur is important in some boiler applications because this can contribute to clinkering and slagging in the boiler. The pyritic content of cement kiln feed is also closely associated with the sulfur dioxide emissions from the kiln. As the kiln feed is heated, pyritic sulfur emits sulfur dioxide that is then vented into the atmosphere.

Some pyritic sulfur is present in large particles that can be partially removed during physical coal cleaning because pyrites are denser than coal.

ASTM procedure D 2492 is used to chemically analyze the sulfur-bearing materials within the coal. This speciation of the sulfur bearing materials is performed only when coal cleaning is being evaluated or when there are operating problems potentially associated with the sulfur forms in the coal.

Coal Cleaning

Much of the ash in coal is rock and dirt from overburden or layers within the coal deposit. When contaminants are not chemically combined with the coal, physical processes can potentially remove them. Coal cleaning is usually performed at or close to the mine to reduce the ash and sulfur content of the fuel. This reduces the fuel transportation costs and decreases the sulfur dioxide emissions resulting from the combustion of the coal.

Early in the 20th century coal was cleaned by manually picking rock from the coal as it moved slowly up a conveyor. Today there are two main techniques used to clean coal: (1) a washing technique that uses the difference in densities of organic fuel particles and ash or sulfur particles, and (2) a froth flotation technique that uses the difference in surface characteristics of organic fuel particles and the ash or sulfur-containing particles. Coal cleaning can usually reduce the quantity of ash in the coal by 25% to 50% and the quantity of sulfur by 5% to 25%. However, some fuel loss will occur if coal cleaning is very aggressive.

Coal washing can also increase the moisture content of the fuel. However, drying the coal using good drainage techniques or centrifuges can minimize moisture content.

3.5 OTHER SOLID FUELS

3.5.1 Fossil Solid Fuels

Peat

Peat is a highly variable fuel with a heating value as low as 3,000 BTU/lb. and a moisture level as high as 70%. The color of the fuel can also vary from yellow to brownish black. The sulfur content of peat is usually less than 1% (dry basis), while the ash content can vary from 2% to 70% by weight (dry basis). Due primarily to its very low heating value, peat is rarely used for the types of boilers and manufacturing processes that are within the scope of this course.

Coke

Coke is a solid, carbonaceous residue that remains after bituminous coal and other similar coal fuels are heated in the low oxygen environment. Coke usually has a very low volatile content and fixed carbon levels approaching 90% by weight. Coke heating values are usually above 14,000 BTU/lb.

Most coke is produced and used by the steel industry. However coke can and is used in combustion processes such as cement kilns, cement kiln precalciners, industrial heaters, and industrial dryers: Coke falls into three classifications:

- Metallurgical coke
- Petroleum coke
- Coke breeze

Metallurgical coal has ash characteristics compatible with steel composition and it is used to make metallurgical coke. A coke plant is built and operated as part of the steel mill that it serves.

Petroleum coke is a solid residue that remains after crude oil is heated in either the delayed coked or fluid coking processes. Petroleum coke has volatile matter levels of less than 12% by weight and fixed carbon levels that vary from 70% to 95% by weight. The sulfur levels in petroleum coke can range from 2.5% to 8% by weight, while ash contents of petroleum coke are lower, usually below 3%. The heating value is usually 14,100 to 15,600 BTU/lb, slightly above the levels usually associated with coal.

Coke breeze is physically degraded coke particles that form, in part, due to the relatively high friability characteristics of coke materials. As much as 40% (by weight) of coke breeze material will measure 1/8 inch diameter, or less. The ash levels of coke breeze are usually higher than those of standard coke fuels.

Another form of coke is used in a combustion process not covered in this course; charcoal briquettes. They are typically made from wood and/or coal and are used in backyard barbeques.

3.5.2 Wood

A variety of wood materials are used for fuels in utility and industrial boilers, and some manufacturing process combustion systems. The most significant variables affecting wood firing characteristics are moisture content and the physical form of the wood. Wet wood does not burn easily and a stoker furnace must dry the wood before combustion starts. Wood forms fed to furnaces range from shredded or chipped wood to sawdust to sander dust. The form and moisture content determine how the fuel is fed and the design of the combustion system.

Wood fuels derive from the following general types of source:

- Green chips and bark from logging or lumber mill waste
- Construction, demolition and mixed waste that is usually shredded in a hog mill
- Dry chipped or shredded wood waste from a manufacturing plant
- Sander dust from a manufacturing plant.

Green Wood

Green wood chips can come from clean up operations at a logging site or they are generated at a mill from trimmings and bark. Green wood typically has a moisture content in the range of 50% to 60%, which results in a heating value in the range of 4,000 to 5,000 BTU/lb. The main inorganic contaminant is likely to be sand or dirt clinging to the bark. Green wood can be either chipped or shredded. A chipper uses less power and the blades can easily be kept sharp if the wood is free of metal and rock. As illustrated in Figure 3-6, chipped wood is often accompanied by small wood sawdust or similar material that is generated simultaneously.

Figure 3-6. Wood Chips

If logs are stored in salt water, the wood can acquire salt contents of 0.5% to 2% by weight. During combustion, all of the sodium and chlorine are liberated and emitted as a sodium oxide (Na_2O) fume and hydrochloric acid (HCl).

Mixed Wood Waste

Wood is frequently the largest component of construction and demolition waste. If it can be separated from most of the inorganic material it may be relatively dry and is thus an excellent fuel. Mixed wood waste is usually broken up in some kind of hammer mill (wood hog) that is not damaged by nails, door hinges and other light hardware that would dull the blades of a chipper. Hogged wood is uneven fragments that can be limited to less than 4" to 6" in length. If mixed wood waste contains small amounts of pressure treated or painted wood, there will not be a significant effect on air emissions. Pressure treated lumber used for exterior construction can have moderate-to-high levels of arsenic and chromium. If substantial amounts of treated wood are burned there could be a measurable increase in emission of metals from the additives in the paints and coatings.

Dry Wood Waste

Dry wood from a facility such as a furniture factory has heating values in the range of 8,000 to 10,000 BTU/lb. Waste wood materials from fiberboard operations can have higher heating values due to the presence of dried phenol-formaldehyde and urea binders – values can be in the range of 12,000 to 14,000 BTU/lb. Nitrogen levels in this type of wood fuel are low, with the possible exception of fiberboard scraps that can have nitrogen levels of 0.5% to 1% by weight due to the presence of small quantities of nitrogen-containing binders.

Sawdust and Sander Dust

When fine sawdust or sander dust are collected during the production of dimensional lumber or furniture they can be fired in suspension similar to pulverized coal. Sawdust and sander dust usually originate from the dimensional lumber that has been kiln dried. Accordingly, these fuels have a low moisture content of less than approximately 10% by weight and a high heating value of more than 8,000 BTU/lb.

Some of the general characteristics of wood fuels are summarized in Table 3-16. There are substantial differences in the characteristics of hardwood and softwood fuels and, within each of these two major categories, there are substantial differences from one species to another.

Table 3-16. Wood Properties (Dry Basis)

Analyses (dry basis), % by wt	*Jack Pine*	*Birch*	*Maple*	*Western Hemlock*
Proximate Analysis, % by wt				
Ash	2.1	2.0	4.3	2.5
Volatile Matter	74.3	78.5	76.1	72.0
Fixed Carbon	23.6	19.2	19.6	25.5
Ultimate Analysis, % by wt				
Carbon	54.3	57.4	50.4	53.6
Hydrogen	5.9	6.7	5.9	5.8
Sulfur	0	0	0	0
Nitrogen	0.1	0.3	0.5	0.2
Ash	2.0	1.8	4.1	2.5
Oxygen	38.6	33.8	39.1	37.9
Heating Value				
Btu/lb.	8930	8870	8190	8885
Ash Analysis, % by wt				
$Si0_2$	16.0	3.0	9.9	10.0
Al_2O_3	6.3	0	3.8	2.1
Fe_2O_3	5.0	2.9	1.7	1.3
CaO	51.6	58.2	55.5	53.6
$CaCO_3$	4.9	13.0	1.4	9.7
MgO	5.5	4.2	19.4	13.1
MnO	1.6	4.6	1.0	1.2
P_2O_5	2.8	2.9	1.1	2.1
K_2O	4.1	6.6	5.8	4.6

Table 3-16. Wood Properties (Dry Basis) cont.				
Analyses (dry basis), % by wt	*Jack Pine*	*Birch*	*Maple*	*Western Hemlock*
Mn_2O	3.1	1.3	2.2	1.1
TiO_2	0.2	trace	trace	trace
SO_3	2.6	3.2	1.4	1.4
Ash Fusibility Temp, °F				
Initial	2450	2710	2650	2760
Softening	2750	2720	2820	2770
Fluid	2760	2730	2830	2780
Weight				
lb/ft^3 (bone dry)	29	37 to 44	31 to 42	26 to 29

Source: Babcock & Wilcox, Steam 40th Edition, Page 8-18.

It is apparent that all wood fuels have a high volatile content, low ash content, low sulfur content, and low nitrogen content. The nitrogen content of wood is considerably lower than the levels usually present in coal. Accordingly, the NOx emissions from combustion systems burning wood are lower than those firing coal.

3.5.3 Biomass Fuels

Biomass fuel refers to crops specifically grown for fuel purposes as well as to agricultural wastes used as fuel. At the present time there are a number of wood-fired facilities that rely on trees cut specifically for fuel as well as on wood waste. There are also facilities like sugar cane mills that extract the sugar from the cane and then burn the waste (bagasse) to produce energy to run the plant. Ethanol and diesel fuel can be produced from corn or from some agricultural wastes.

Bagasse is a biomass fuel that has been used extensively over the last 30 years. This is fiber and associated plant material remaining after the sucrose and glucose has been removed from sugar cane. Bagasse fuels can have moisture levels above 50% by weight. Ash content can be as high as 2.5%, primarily due to the presence of small soil particles that are on the surface of the sugar cane after harvesting. A proximate and ultimate analysis of a typical bagasse fuel is provided in Table 3-17.

Table 3-17. Bagasse Properties	
Analyses (as-fired), % by wt	*Value*
Proximate	
Moisture	52.0
Volatile Matter	40.2
Fixed Carbon	6.1
Ash	1.7
Analyses (as-fired), % by wt	*Value*
Ultimate	
Hydrogen, H_2	2.8
Carbon, C	23.4
Sulfur, S	trace to 0.6
Nitrogen, N_2	0.1
Oxygen, O_2	20.0
Moisture, H_2O	52.0
Ash	1.7
Heating Value	
Btu/lb.	4,000
kJ/kg	9,304

Studies have been conducted on the potential to grow and use fuels such as hybrid poplars, hybrid willows, silver maples, switch grass, rice straw, bagasse, poplar, and general vegetation. With the exception of those facilities already operating, most of these concepts must wait for substantially higher fuel market prices before they are economically attractive.

If one ignores economic considerations for the moment, biomass fuel has certain attractive features. (1) Biomass fuel is renewable. Use of biomass fuel reduces our dependence on finite (but substantial) supplies of fossil fuels. (2) Biomass fuels do not increase the amount of carbon in the global carbon cycle, so their use does not contribute to the increase in atmospheric CO_2 and global warming. Energy crops are being actively investigated and developed by the U.S. Department of Energy's Biofuels Feedstock Development Program (BFDP).

3.5.4 Solid Wastes

The vast majority of our municipal wastes are buried in landfills. However a number of municipalities have constructed waste-to-energy plants where waste is burned as fuel to generate electric power and/or steam heat.

Municipal and medical wastes are also burned in incinerators where there is no energy recovery, but this is a diminishing population. Most incinerators built prior to

about 1980 have been shut down by air pollution concerns and new facilities need energy recovery in order to compete economically with landfills.

Municipal waste can include anything that a person could conceivably place in a trash can or put out on the curb. So there is no simple way to summarize what is or is not present. In communities where recycling is successful, municipal waste will include less glass, paper and metal than is present in the overall waste stream. Municipal and medical waste incinerators can inadvertently receive and process a variety of wastes that are undesirable. These inappropriate materials can be classified into two groups: (1) waste materials that could generate toxic emissions and (2) waste materials that could damage the combustion equipment. A partial list of these materials includes the following:

1. Waste that could emit toxic materials:

    a. Asbestos-containing insulation

    b. Batteries containing mercury

2. Wastes that could damage combustion equipment:

    a. Containers with more than two or three pounds of liquid fuel or solvent

    b. Compressed gasses such as Medical oxygen or acetylene cylinders

    c. Ammunition

    d. Coils of steel cable

In a well-designed and operated furnace, most hazardous wastes will be burned up and any potential emissions controlled. Asbestos is not flammable and the procedures for managing it do not allow for it to be commingled with municipal waste. Mercury will slip through the air pollution control equipment unless there are specific controls to capture mercury. Containers of gas or liquid fuel can explode in an incinerator. If there is enough fuel, the explosion will damage the furnace. Steel cable can get tangled in either the feeder mechanism or the ash handling hardware.

Table 3-18 lists some general categories of waste and typical properties. Non-hazardous wastes are regulated at the State level, so precise definitions are not attempted. While all of these waste streams have components with fuel value, they also have components which can be recycled or which have no fuel value.

Table 3-18. Classifications and Properties of Municipal and Medical Wastes		
Description	*Heating Value BTU/lb.*	*Example materials*
Municipal Solid Waste	4,000 to 6,000	Mixtures of highly combustible waste, such as paper, cardboard, wood, animal and vegetable wastes from restaurants, hospitals, and markets. Typically contains 20% - 50% moisture and 15% to 30% non-combustible solids.
Construction and Demolition Debris	varies	Any non-regulated waste from construction & demolition work including wood, roofing, siding, sheet rock, plaster, plumbing, wiring, fixtures, broken pavement, dirt etc.
Industrial Waste	varies	Items such as rubber, plastics, wood waste, packaging, etc. from industrial operations, boiler ashes, etc. BTU values must be determined for the individual materials to be destroyed.
Medical Waste, Black Bag	7,000 to 10,000	A mixture of general hospital waste containing non-regulated waste. Includes paper, plastics (both chlorinated and non-chlorinated), and cardboard. Waste is typically from the hospital's food service, administration, patient rooms, operating rooms, and laboratories.
Medical Waste, Red Bag	8,500	Regulated wastes – usually associated with infectious hazards. Includes waste saturated with blood or body fluids. Includes sharps – needles and glassware. May include wastes generated by pharmaceutical firms, research and diagnostic laboratories, and other health care facilities.

The heating values of municipal waste will vary from approximately 1,000 BTU/lb. to approximately 8,500 BTU/lb. This variation is due primarily to variation in moisture content. There can be considerable seasonal variability in the waste characteristics burned in a municipal incinerator and wet weather will increase the moisture content. In localities that do not recycle yard waste, grass clippings and wet leaves will have a major impact on combustor operation.

Medical waste composition is somewhat similar to municipal waste except that it usually has a fairly low moisture content. It also contains more packaging waste, which generally has a high heating value. As indicated in Table 3-19, medical waste components can have heating values that range from less than 100 BTU/lb for high metal or moisture-containing materials to more than 20,000 BTU/lb for wastes containing mainly plastics.

Table 3-19. Characteristics of Medical Wastes			
Category	*Bulk density as-fired, lb/ft^3*	*Moisture Content of component, % by wt*	*Heat value as-fired, BTU/lb.*
Human Anatomical	50-75	70-90	800-3,600
Plastics	5-144	0-1	13,900-20,000
Swabs, Absorbants	5-62	0-30	5,600-12,000
Alcohol Disinfectants	48-62	0-0.2	11,000-14,000

Table 3-19. Characteristics of Medical Wastes (cont.)			
Category	*Bulk density as-fired, lb/ft^3*	*Moisture Content of component weight, % by wt*	*Heat value as-fired, BTU/lb.*
Animal Infected Anatomical	30-80	60-90	900-6,400
Glass	175-225	0	0
Beddings, shavings, paper, fecal matter	20-45	10-50	4,000-8,100
Gauze, pads, swabs, garments, paper, cellulose	5-62	0-30	5,600-12,000
Plastics, PVC, syringes	5-144	0-1	9,600-20,000
Sharps, needles	45-50	0-1	60
Fluids, residuals	62-63	80-100	0-2,000

Medical wastes can have high levels of chlorine due to the consumption of polyvinyl chloride (PVC) plastics. The concentrations of metals such as cadmium, arsenic, mercury, and lead can also be high.

Small hospital incinerators are rapidly being retired and medical waste is going to large regional incinerators or into the municipal waste stream. So in the near future, medical waste will only be a distinct fuel at a few facilities.

3.6 CONCLUSION

This chapter is an overview of fuels, how they are characterized, methods of burning them and some of the implications for air pollution. Additional information is available in the references. Subsequent chapters of this text will draw on the information presented here in presenting methods of combustion analysis and air pollution control.

Review Exercises

1. Which fuel is produced in the greatest amount, in terms of energy, in the U.S.?
   a. Oil
   b. Natural gas
   c. Nuclear
   d. Coal

2. Ultimate analysis of a fuel would provide which of the following?
   a. Data required by an agent purchasing fuel for a specific plant
   b. Amount of moisture absorbed by coal during rail shipment
   c. Chemical composition
   d. Ash characteristics

3. Obtaining a representative sample for lab analysis becomes more challenging in which sequence?
   a. Natural gas, coal, municipal waste
   b. Wood waste, oil, coal
   c. Natural gas, coal, oil
   d. None of the above

4. Use of the lower heating value rather than the higher heating value will _____.
   a exclude the heat of condensation from the BTU/lb value.
   b. reduce the figure for BTU/lb.
   c. have a greater effect for natural gas than for coal.
   d. All of the above.

5. The difference between residual oil and distillate oil is _____.
   a. distillate oil evaporates completely when heated and residual will not
   b. residual oil contains higher levels of inorganic contaminants than distillate
   c. residual oil must be heated to fire it while distillate is fired at ambient temperature
   d. All of the above

6. Municipal solid wastes _____.
   a. are usually fairly dry and thus burn easily
   b. may be composed of 30% non combustible material
   c. never include containers of fuel or waste classified as hazardous.
   d. are uniformly mixed so it is easy to obtain a representative sample for analysis.

7. Medical wastes will _____.
   a. sometimes burn intensely because of the amount of plastic and packaging material
   b. always burn poorly because of the amount of wet anatomical remains
   c. be safe to handle because all sharps are kept separated in special containers
   d. never include ordinary non-infectious waste

8. Coke is a fuel that is _____.
   a. used primarily in metal manufacturing such as steel making
   b. is manufactured by driving all the volatile material out of coal
   c. is composed almost entirely of carbon
   d. All of the above

9. Inorganic material in coal _____.
   a. is composed mostly of hazardous and toxic metals
   b. is composed mostly silicon and metal oxides
   c. may include high concentrations of mercury
   d. cannot be determined from laboratory analysis

10. A combustion source will normally buy fuel that _____.
   a. is marginally compatible with the installed hardware
   b. is least expensive and allowed in the operating permit
   c. has sulfur content higher than that listed in the facility's operating permit
   d. has a high water content to reduce combustion temperatures

Review Answers

1. d. Coal

2. c. Chemical composition

3. a. Natural gas, coal, municipal waste.

4. d. All of the above

5. d. All of the above

6. b. may be composed of 30% non combustible material

7. a. probably burn intensely because of the amount of plastic and packaging material

8. d. All of the above.

9. b. is mostly silica and metal oxides

10. b. is least expensive and allowed in the operating permit

References

[1] U.S. Department of Energy, Energy Information Administration, Annual Energy Review 2010, available at www.eia.doe.gov/oiaf/aeo/index.html. The DOE is an excellent source of information about the properties, availability and usage of fuels in this country.

[2] Meyers, Robert A., Editor. *Handbook of Energy Technology and Economics*, (John Wiley & Sons, Inc., 1983). The book has major sections on all types of fossil fuels as well as renewable sources like wind, solar and geothermal power.

[3] North American Manufacturing. *North American Combustion Handbook*, (North American Manufacturing Company, Cleveland, OH, 1952). This is a good basic reference for gas and oil properties and utilization.

[4] Schmidt, Paul F. *Fuel Oil Manual*, Fourth Edition, (Industrial Press Inc., New York, 1985). The book provides descriptions of test methods and a broad discussion of oil properties in relation to oil use, but does not list ASTM test method numbers.

[5] Yen, T. F. *The Role of Trace Metals in Petroleum*, (Ann Arbor Science, Ann Arbor, Michigan, 1982). The book provides some basic data on typical metal levels, as well as chemical detail relevant to refining oil to control trace metal content.

[6] Schmidt, Richard A. *Coal in America: An Encyclopedia of* Reserves, Production and Use, (Coal Week, McGraw-Hill Publishing, 1979). All you ever wanted to know about coal.

[7] American Society for Testing and Materials (ASTM, West Conshohocken, PA), www.astm.org. Essentially all the test procedures used by laboratories to analyze fuel samples are adopted and published by ASTM.

Chapter 4: Fundamentals of Combustion

LESSON GOAL

Demonstrate an understanding of the fundamentals of combustion; including the role of excess air and the quantitative relationship between mass flow and heat release through successful completion of the chapter review exercises.

STUDENT OBJECTIVES

When you have mastered the material in this chapter, you should be able to:

1. Describe basic combustion chemistry and list the products of combustion.
2. Use the Law of Conservation of Energy to determine firing rate from fuel flow or visa versa.
3. Use the Law of Conservation of Mass and the definition of excess air to relate exhaust flow rate to the gas flow rate when the air-fuel equivalence ratio is unity.
4. Define the terms *stoichiometric air-fuel ratio, F-factor,* and *excess air*.
5. Calculate the combustor-firing rate (mmBTU/hr) for a combustion source using measured data for exhaust gas flow rate and O_2 concentration.
6. Convert gas volume at a known temperature and pressure to the volume at standard conditions.
7. Calculate the combustor firing rate for a source fired with a fuel for which there is a known F_w-factor using stack test data.
8. Calculate the excess air correction factor and the percent excess air from measured O_2 data.
9. Calculate combustor residence time from measured furnace volume and the measured exhaust flow rate.
10. Calculate the approximate maximum average temperature in the combustion chamber of a thermal oxidizer using an exhaust O_2 measurement.

11. Calculate what fraction of fuel energy goes up the stack using temperature and O_2 data.
12. List the major and minor elements of energy lost up the stack and discuss the energy balance for a boiler.

Chapter 4: Fundamentals of Combustion

4.1 INTRODUCTION

Combustion is a complex science. A typical furnace flame starts with turbulent fluid mechanics that is then combined with heat transfer, mass transfer and chemical reactions. The design of combustion systems frequently includes a substantial understanding of all these sciences. However, it is possible to perform a great deal of useful analysis with relatively simple tools. This chapter will discuss the complex aspects of combustion in general terms and present several analytical tools that are useful due to their simplicity. Most of the analytical techniques are based on the basic laws of conservation of mass and energy.

This chapter will discuss the basic physical and chemical rules that govern relationships between combustion parameters. These rules will be simplified wherever possible so that the calculations can be performed on a hand calculator with minimal need for complex data reduction. The chapter begins with a general description of a typical furnace flame, the principles of fluid mechanics and heat transfer, and the chemical reactions that result. This chapter will further discuss the complex aspects of combustion in general terms and present many analytical tools used in combustion source evaluation.

4.1.1 Chemical Balance

Conservation of mass requires that the mass of fuel and air equal the mass of exhaust products. We can illustrate this with the simple chemical equation for the combustion of methane. There are the same number of atoms on each side of the equation.

$$\underset{\text{(fuel)}}{CH_4} + \underset{\text{(air)}}{2O_2} \rightarrow \text{HEAT} + \underset{\text{(exhaust gas)}}{CO_2 + 2H_2O} \qquad (4\text{-}1)$$

Methane yields an equation with a simple chemical balance, but a similarly balanced equation can be written for any hydrocarbon fuel where the relative amounts of carbon and hydrogen are known. The relative amounts of fuel and air define the stoichiometric ratio and when they are balanced, as in equation 4-1, the stoichiometric ratio equals one. Equation 4-1 can be used to illustrate several concepts:

- Since the combustion products are CO_2 and water, combustion in its cleanest form is non-polluting. Most stationary sources come very close to 100% conversion of fuel to CO_2 and H_2O.

- We can burn many hazardous organic substances (wastes) to non-polluting end products for the same reason. Contaminants in the fuel (waste in this case) are the potential pollutants.

- Combustion forms water, so the flue gases will carry a lot of water vapor. The effects are felt when water condenses in emission monitoring equipment and in the methods of calculating emission rates. It also generates confusion about the composition of a visible plume.

- The mass balance of an equation shows that the amount of oxygen, and hence the amount of air required, is determined by the amount of fuel burned. So in real systems the air flow rate must be controlled to match fuel flow rate.

Three elements important to real combustion are missing in this simple equation.

- Air is composed of about 79% nitrogen (N_2), so there is a lot of N_2 that enters the combustion with the O_2 and is released with the flue gas. This has a huge effect on the basic size of a combustion system, but in practice is only important when dealing with oxygen enriched systems. However, one should keep in mind that the mass ratio of air to fuel is usually more than 10:1. Fuel is a very small part of the mass flow through the system.

- Real systems don't operate at a stoichiometric ratio = 1.00. A little extra air is required for all combustion, so there is extra O_2 (and N_2) on both sides of the equation. How much extra air, how we control it and how we measure it are important subjects we will discuss later.

- Most fuel has contaminants (ash, sulfur, nitrogen, etc.) that may or may not participate in the combustion, but which will appear in the flue gas as air pollutants.

4.1.2 Heat Input Rate – Conservation of Energy

Energy must be conserved in a combustion device. Chemical energy in the fuel is released during combustion and appears as heat. Most of the heat is then transferred from the exhaust gases to the product (steam, warm air, etc.). Fuel is fired into any combustion source at a rate sufficient to maintain load; whether load is defined as megawatts to maintain the voltage in a power grid or heat to maintain the temperature of a building. Fuel flow varies from a minimum up to a maximum design firing rate. (Note: The terms "firing rate" and "heat input rate" will be used interchangeably.) A combustion source has a design capacity, which can be expressed in various forms such as kilowatts for a power plant, pounds of steam per hour for a boiler or

horsepower for an engine. Underlying any of these design capacity terms is a heat input or firing rate – normally expressed as millions of BTU per hour (mmBTU/hr). There is a direct relationship between firing rate and horsepower, megawatts or whatever the published dimension of the source. In this course a combustion source will be characterized by the size of its designed heat input rate expressed in mmBTU/hr.

A new source will achieve its design capacity (megawatts, horsepower, steam flow rate, etc) at or slightly below its design firing rate. With age and deterioration, the source may have to increase its firing rate in order to achieve the design capacity. This loss in efficiency can, in severe cases, amount to 10% or more.

The design heat input rate appears on the permit of most significant combustion sources. This firing rate is important because it determines which regulations apply. For example, sources smaller than 250 mmBTU/hr have different rules than larger sources. The design firing rate is always listed in the specifications of a new source, but it may be harder to locate for an old existing source. There can be several definitions for a source such as: "normal maximum", "maximum continuous rated" (MCR) or "emergency maximum" that refer either to firing rate or to overall capacity. Not to add confusion, but older sources, boilers in particular, can be uprated or derated in such a way as to yield a design heat input different from the original. Thus the design heat input for permit purposes can be a judgment call.

All furnaces are heat transfer devices so the basic design parameter is heat flux – normally measured (in the U.S.) in BTU/hr or million BTU/hr (mmBTU/hr). The capacity of the furnace or boiler to transfer heat is not changed if the fuel changes from liquid to gas or to a solid. So one should think of the size of a combustion device in terms of its heat input or firing rate in BTU/hr or, more commonly, in mmBTU/hr. From the firing rate one can derive the fuel use in units such as:

- cubic feet per hour (gas fuels)
- gallons/hour (oil)
- tons/hr (coal, wood or waste)

Equation 4-2 is the relation between the fuel energy (HHV or heating value), fuel flow rate and firing rate. One can write similar equations for gas or liquid fuel.

$$\text{Fuel energy (BTU/lb)} * \text{Fuel mass flow (lb/hr)} = \text{Firing rate (BTU/hr)} \qquad (4\text{-}2)$$

Example 4-1.

Determine the oil flow rate to a boiler operating at 85 mmBTU/hr. The typical heating value of residual oil is 150,000 BTU/gallon.

Solution:

$$\frac{85 * 10^6 \text{ BTU/hr}}{150{,}000 \text{ BTU/gal}} = 567 \text{ gal/hr (9.4 gal/min)}$$

One advantage of working with firing rate (mmBTU/hr) rather than fuel flow rate is that it reduces confusion when dealing with a facility that fires multiple fuels. Other advantages will appear later when we discuss exhaust flow rates and emissions measurements. Note that the BTU basis – higher or lower heating value must either be specified or implicitly understood.

4.1.3 Fuel and Air Flow – Conservation of Mass

Combustion requires fuel and air – the exhaust is the sum as indicated in Equation 4-3.

$$\text{Fuel mass flow} + \text{Air mass flow} = \text{Exhaust gas mass flow} \qquad (4\text{-}3)$$

With rare exception, the mass of air required for combustion is 10 to 15 times the fuel flow. In other words, the exhaust flow is only a little larger than the inlet air flow on virtually all combustors. The only exceptions are when firing low grade gas fuels composed primarily of N_2 or CO_2 and in combustion systems that use pure oxygen rather than air.

As noted earlier, the amount of fuel fed to a combustor is governed by systems load demand. On nearly all regulated combustion devices the load, and hence the fuel flow, varies with time. Fuel flow varies over the range defined by the minimum practical firing rate and the design (maximum) firing rate. The amount of air required is directly proportional to the fuel flow, so it also varies with time as it tracks the fuel flow. In practice it is possible to leave the air at a fixed level at or above that required for the maximum firing rate; but a properly operated source will have the air flow track the fuel flow as closely as possible.

4.1.4 Excess Air

The chemical balance, illustrated in Equation 4-1, is a quantitative link between the amount of air required and the amount of fuel used in a combustor. The amount of air chemically required to burn the fuel is frequently called the *stoichiometric* air flow. Alternatively, when the fuel and air flow are chemically or stoichiometrically balanced, we say that the *equivalence ratio* is equal to one. The equivalence ratio is defined as "the actual air-fuel ratio divided by theoretical or stoichiometric air-fuel ratio." (Caution: Different references may use either air-fuel or fuel-air ratio when presenting the stoichiometric ratio.)

Real combustion systems operate with more air than the stoichiometric air requirement in order to avoid the emissions, such as CO, that result from incomplete combustion. Products of incomplete combustion result when some of the fuel does

not mix with enough air. If one could achieve a completely uniform air-fuel mixture in the combustion zone, very little excess air would be required. But perfect mixing is impossible and the overall air flow must be high enough to assure complete combustion in the most poorly mixed region of the flame. Excess air, as expressed in Equation 4-4, is that fraction of the total air flow that is not chemically required for combustion.

$$\text{Total air flow} = \text{Stoichiometric air} + \text{Excess air} \qquad (4\text{-}4)$$

Excess air is normally expressed as a percent of the stoichiometric flow and can be any value from near zero to several hundred percent.
Excess air is arguably the most important operating variable in most combustion systems. Part of the reason is illustrated in Figure 4-1, which shows the typical relationship between excess air and emissions. Products of incomplete combustion (smoke, CO and VOC) are minimal until the air flow drops below some critical level, then they increase sharply. The "knee" in this curve defines the minimum practical excess air level. NOx behaves differently; it usually decreases linearly with decreasing excess air. This different behavior means that emission control efforts always deal with a trade-off between NOx and PIC. Lower NOx means more PIC and visa versa. Figure 4-1 illustrates this relationship.

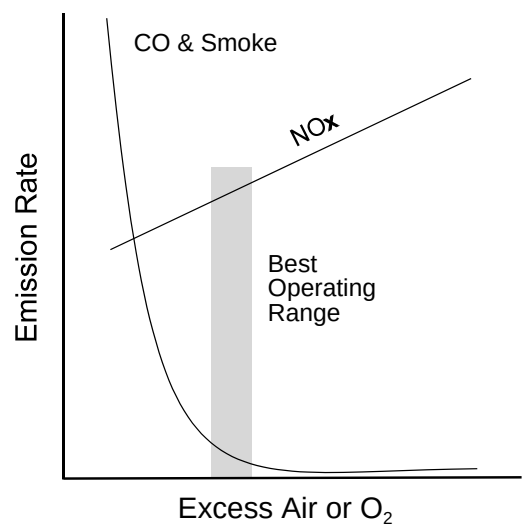


Figure 4-1. NOx and CO Emissions vs. Excess Air

The amount of excess air required by a combustion system to avoid PIC emissions depends on the design, load and other factors. As a general rule, the better the system, the less excess air is required to prevent smoke and/or incomplete combustion – the knee in the curve occurs at a lower excess air level. Table 4-1 lists some typical excess air ranges and flue gas oxygen levels for common combustion systems.

Table 4-1. Typical Minimum Excess Air Levels		
Type of Combustion	*Excess Air*	*% Oxygen*
Suspension firing: gas, oil, pulverized coal	5% - 15%	1% - 3%
Cyclone (crushed coal)	10% - 15%	2% - 3%
Stoker grate: coal, wood, solid waste	30% - 75%	5% - 9%
Fluidized bed	5% - 150%	1% -13%
Combustion Turbine	250%	15%
Lean burn reciprocating engine	>5%	>1%

Oxygen and excess air levels shown here refer to the exit of the combustion zone and may be lower than those measured at the stack. The first four systems listed in Table 4-1 are operator controlled; that is, the operator can adjust the excess air level. Systems that can operate at lower levels than those listed here, without generating excessive smoke or CO, are doing very well. Those operating at substantially higher levels probably have room for improvement.

Operation at the minimum practical excess air is desirable for several reasons:

- Lower air flow means a lower stack flow rate – less hot gas going up the stack, which means improved thermal efficiency;
- NOx emissions are lower at lower excess air levels;
- Maximum load on some boilers is limited by the size of the air fans, so reducing the excess air requirement increases the maximum load.

So two objectives of good combustion performance – and hence low emissions – are to:

- design and maintain a system which is capable of low excess air levels, and
- continuously operate that system very close to the minimum practical air flow.

Typical data for engines and combustion turbines is also shown in Table 4-1, but the operator usually has no control over excess air in these systems. Excess air level is built into the engine or turbine fuel injection system and adjustments over a very limited range are done at the factory or on site by the manufacturer's technicians.

4.1.5 Water Vapor in Exhaust Gas

Combustion of the hydrogen in hydrocarbon fuels generates water vapor. The amount of water vapor is quite substantial - when firing oil the amount (mass) of water vapor produced is greater than the amount (mass) of oil-fired. With natural gas the mass of water produced is more than double the mass of gas-fired. Firing a wet fuel such as wood also adds to the water vapor in the exhaust gas. The typical volumetric amounts of water vapor in the exhaust gas from some typical combustion sources are:

- Natural gas 20% by vol.
- Oil 10% by vol.
- Coal 6% by vol.
- Green wood 18% by vol.

The presence of all this water affects the combustion system design as well as combustion diagnostics and air emissions. One effect, discussed in Chapter 3, is that the higher heating value (HHV) of the fuel depends on how much water vapor is in the exhaust gas. HHV is used both in combustion system design and in emission rate calculations.

When the water condenses it produces several affects. As long as the exhaust gas temperature remains above the water dew point, the water appears in vapor form. But condensation occurs locally on cool surfaces and when the gas is cooled in emission sampling systems. Table 4-2 lists several water vapor concentrations and their corresponding dew point temperatures.

Table 4-2. Water Saturation Temperature vs. Concentration

Temperature °F	*Volume %*	*Weight %*
32	0.6	0.4
60	1.7	1.1
80	3.4	2.1
100	6.5	4.1
120	11.5	7.5
140	19.7	13.2

This shows that at typical ambient temperatures, air (or exhaust gas) can only hold about 2% moisture by volume; higher concentrations will condense. With a few exceptions real system stack gas temperatures are always above 250°F and water vapor in the flue gas does not condense until the gas leaves the stack and begins to mix with the atmosphere. One of the exceptions is flue gas sampling systems used to

measure air emissions. Most of these systems cool the flue gas sample to room temperature in order to analyze it, which means these systems include a condenser to remove liquid water that would disable the instruments. So they analyze a dry sample that has 10% to 20% less volume than the original wet sample. The concentration of the air pollutants in the remaining dry sample gas is higher and this difference makes the resulting data incompatible with measurements of exhaust velocity and exhaust flow volume. Chapter 7 provides a more detailed discussion of exhaust sampling.

Exhaust gas moisture also affects flame temperature. The specific heat of water vapor is about 0.50 BTU/lb/°F, which is roughly twice that of air and of dry, exhaust gas. As a result, water vapor variation can have a subtle but profound effect on combustion. Briefly stated, it takes a lot more energy to raise the temperature of wet flue gas than for dry flue gas. Thus flame temperatures are lower when there is a lot of water vapor present. This is particularly significant when dealing with NOx emissions, as discussed in Chapters 5 and 6.

4.2 COMBUSTION MASS FLOWS, STOICHIOMETRY

A lot of information can be derived about a combustion source from measurements of the exhaust gases in the stack (from a stack test). A principal objective of this section is to demonstrate the following statement:

Using measured data for exhaust gas flow rate and O_2 concentration, the combustor firing rate (mmBTU/hr of heat input) can be accurately calculated for most sources.

Note that only two measured parameters are required and there is no reference to other source data. In most cases, the kind of fuel a source is firing does not need to be known. The calculation can be done on a hand calculator with only a few steps. The exceptions to this statement are:

- If the source is firing a wet fuel like green wood or municipal solid waste, a measurement of exhaust gas moisture is also required.

- If the source is a process, such as a cement kiln that adds CO_2 or H_2O to the exhaust gases, the interpretation of the stack data is more complex.

There are at least two good reasons why a person dealing with air emissions would want to be able to use stack test data to determine the source-firing rate.

1- The source firing rate may be unknown or in question based on data from source operations.

2- Comparison of firing rates determined from (a) source data and (b) stack data is a powerful quality control check of emissions data determined during a stack test.

Conservation of mass is the primary basis for this section, but we will also make use of some properties of fuels. Previous versions of this course and many academic authors have used voluminous equations to reach results; however, this course cuts through the heavy derivations and focuses on simpler approaches that lead to a better understanding of the results.

4.2.1 Stoichiometric Air Flow

The air flow that must be supplied to a combustion system is governed by two parameters: (1) the firing rate, or heat input rate, and (2) the amount of excess air necessary to assure complete combustion and to prevent smoke. First, consider the stoichiometric air flow, or the amount chemically required for complete combustion. For example, use a simple fuel, pure methane, to illustrate the derivation process.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Equation 4-1 shows that one molecule of methane requires two molecules of oxygen to burn completely and form one molecule of carbon dioxide and two molecules of water. Counting molecules gives the volume of gases involved – one molecule of methane produces three molecules of combustion products. In order to relate the mass or the weight of these quantities we need to know the atomic and molecular weights of the constituents. These values are listed in Table 4-3.

Table 4-3. Typical Atomic and Molecular Weights

Constituent	*Weight*	*Constituent*	*Weight*
C	12.011	CO_2	44.01
H	1.008	H_2O	18.016
O	16.00	CH_4	16.042
N	14.007	S	32.06

The mass of the constituents relative to the mass of methane derive from the ratio of molecular weights to methane as follows:

44.01/16.042 = 2.74 lb CO_2 produced per lb CH_4
2*18.016/16.042 = 2.246 lb H_2O produced per lb CH_4
64.00/16.042 = 3.99 lb O_2 consumed per lb CH_4

This gives the relative mass of each combustion product but does not tell us the total amount of exhaust gas. Actual combustion takes place in air that is mostly nitrogen. So there is actually a large amount of nitrogen that simply passes through the combustion process without chemical participation. The approximate composition of air is listed approximately in Table 4-4.

Table 4-4. Composition of Air			
Compound	*Actual Vol.*	*Approx. Vol.*	*Approx Wt.*
N_2	78.08	79.1	76.9
O_2	20.95	20.9	23.1
Argon	0.93	0	0
Other	1.0	0	0

Here the "other" category is mostly argon with small amounts of CO_2 and other gases. The ratio of nitrogen to oxygen shows us the mass of nitrogen relative to oxygen:

76.9/23.1 = 3.33 lb N_2 per lb O_2 (mass ratio)

79.1/20.9 = 3.78 ft^3 N_2 per ft^3 O_2 (volume or mole ratio)

Hence the amount of nitrogen present during stoichiometric combustion of methane is

3.33 (lb N_2 per lb O_2) * 3.99 (lb O_2 / lb CH_4) = 13.28 lb N_2 per lb CH_4

This gives all the components of the exhaust gas from stoichiometric combustion of one pound of methane:

2.74 lb CO_2
2.246 lb H_2O
13.28 lb N_2
- - - - - - - - - - -
18.27 lb exhaust gas (E.G.) per lb CH_4

This is the basis of the standard accounting procedure used to relate mass flow of air to fuel mass flow. This procedure can be performed for a fuel of any composition; although the calculations will be more involved than for methane.

However, this derivation can be carried two steps further and reach a much more useful result. The heating value for pure methane is 23,875 BTU/lb. If the mass of exhaust gas is divided by the heating value,

18.27 (lb E.G./lb CH_4) / 23875 (BTU/lb) = 765 (lb E.G./mmBTU)

the result will be the weight of stoichiometric exhaust gas generated when one mmBTU of methane is burned. This weight in turn can be converted to a volume by multiplying it by the density of flue gas.

765 (lb E.G./mmBTU) * 385 (std ft^3 E.G./lb-mole E.G.) / 29 (lb E.G./lb-mole E.G.) = 10156 ft^3/mmBTU

Where: 29 is the typical molecular weight of flue gas (lb/lb-mole)
385 is the number of cubic feet in a pound mole (ft^3/lb-mole)

The result is the volume of exhaust gas generated by burning 1.0 mmBTU of methane with no excess air. This is a useful form because it relates a commonly measured parameter, flue gas volume, to a key source parameter – firing rate. It is a number that was derived using the conservation of mass, in the form of a balanced chemical reaction, and the composition of the fuel. No other parameters were used; it is independent of source design and operating parameters.

This parameter, standard cubic feet of gas per million BTU (std ft^3/mmBTU or scf/10^6 BTU), can be derived from any fuel. In fact, it has been calculated for many samples of different fuels and the results published. The relationship between stoichiometric stack flow and firing rate is called, in EPA parlance, the *F-factor*. F-factors are useful for several reasons.

- The F-factor is the key that links exhaust flow to firing rate.
- F-factors generally are fairly constant for a given fuel. In some cases they are nearly constant for different fuels.
- Default F-factors published by the EPA may be as good or better than those derived from individual fuel analysis.

The availability of reliable F-factors means that one can do a calculation to relate stack gas volumetric flow and firing rate without having to obtain a fuel analysis or go through lengthy calculations. In short, the F-factor is a key component of a very useful tool for analyzing combustor performance.

Table 4-5 lists values tabulated in 40 CFR 60 Appendix A, Method 19.

Table 4-5. "F-Factors" for Various Fuels (scf/mmBTU)

Fuel Types	F_d *- dry*	F_w *- wet*	F_c *- carbon*
Anthracite coal	10100	10540	1970
Bituminous coal	9780	10640	1800
Lignite	9860	11950	1910
Wood	9240	------	1830
Oil	9190	10320	1420
Natural gas	8710	10610	1040

Source: 40CFR60 Appendix A, Method 19

In the preceding example for methane gas, it was determined that the total exhaust flow, including water vapor, which corresponds to F_w, is the wet F-factor. The wet F-factor,

F_w, is the total volume of flue gas (standard cubic feet) generated when one million BTU of heat is released by combustion with no excess air.

A similar derivation can be used to exclude water vapor to determine the amount of dry exhaust gas. F_d, the dry F-factor is the volume of dry flue gas (standard cubic feet) generated when one million BTU of heat is released by combustion with no excess air. Formulas for calculating F_d and F_w from a fuel analysis are as follows.

$$F_d = \frac{10^6}{HHV} \times \; 3.64\,(\%H) + 1.53\,(\%C) + 0.57\,(\%S) + 0.14\,(\%N) - 0.46\,(\%O) \qquad (4\text{-}5)$$

$$F_w = \frac{10^6}{HHV} \times \; 5.56\,(\%H) + 1.53\,(\%C) + 0.57\,(\%S) + 0.14\,(\%N) - 0.46\,(\%0) + 0.21\,(\%H_2O \qquad (4\text{-}6)$$

Where: %H, %C, %S, %N, and %O are concentrations (% by weight) from an ultimate analysis of fuel and HHV is the higher heating value in BTU/lb.

In order to calculate F_w, the analysis for the fuel "as fired" that includes the water in the fuel must be used. F_d can be calculated either from an "as fired" analysis or a dry fuel analysis provided the matching HHV is used.

Table 4-5 shows a third column, F_c, which is the volume of carbon dioxide generated when a million BTU of energy is released. In order to use this factor in most calculations, the CO_2 concentration as well as the total flue gas flow rate is needed.

Before starting an example of how to use an F-factor, an explanation of the F-factor concept is in order. One usually thinks of measuring combustion energy by measuring the amount of fuel consumed. But combustion requires both fuel and O_2 from combustion air. The F-factor looks at the other side of the combustion equation and measures how much air is consumed to release the energy. Interestingly enough, the amount of flue gas generated (which is directly related to and only slightly larger than the amount of air consumed) is remarkably predictable and nearly constant for various fuels. In short, if how much oxygen was consumed is known, there is a very good basis from which to determine the amount of heat released. Equation 4-7 expresses the relationship between the stoichiometric gas volume and firing rate.

$$\text{E.G. Stoich. Flow}\left(\frac{\text{std ft}^3}{\text{hr}}\right) = \text{Firing Rate}\left(\frac{\text{mmBTU}}{\text{hr}}\right) \times F_w\left(\frac{\text{std ft}^3}{\text{mmBTU}}\right) \qquad (4\text{-}7)$$

And: F_w is taken from Table 4-5 or is derived from a fuel analysis.

Wet F-factors show the total flue gas volume, while dry F-factors show the volume of flue gas after all the water vapor is removed. Note that the wet F-factors are nearly

constant for coal, oil and gas. Wet fuels, such as lignite and wood, generate more water vapor that increases the amount of exhaust gas. Since neither type of F-factor varies much, default values such as those in Table 4-5 may be preferable to F-factors calculated from a single fuel analysis; especially where there is significant uncertainty in the lab results. Given that F_w is a readily available "constant", Equation 4-7 shows the direct relationship between firing rate and exhaust flow.

In order to relate the actual exhaust flow to firing rate, one must account for excess air – which is discussed in subsequent paragraphs. But assuming the stoichiometric exhaust flow is known, the amount if there were zero excess air, it is easy to calculate the firing rate.

Example 4-2.

Given that the stoichiometric exhaust flow is 45,000 standard cubic feet per minute (scfm) on a source fired with oil and gas, what is the combustor firing rate?

Solution:

If the relative amounts of oil and gas being fired are known, it is safe to choose a middle value for F_w and the error will be small. The F_w-factors for oil and gas are 10,320 and 10,610 respectively, so, for this example, pick the rounded-up average of 10,500.

$$45{,}000\ (ft^3/min) * 60\ (min/hr) / 10{,}500\ (ft^3/mmBTU) = 257\ (mmBTU/hr)$$

Obviously we could just as easily have started with the firing rate and determined the stoichiometric stack flow.

4.2.2 Excess Air

Under normal operation the air flow to most combustion sources provides stoichiometric air plus some *excess air*. Any operation with less than stoichiometric air assures incomplete combustion – meaning that some partly oxidized components of the fuel such as CO, will be present in the exhaust gas. A wood stove with the dampers closed to bank the fire for the night is a good example of an operation with less than stoichiometric air. Adding excess air assures there is enough air for complete combustion, although PIC can still be generated if the fuel and air do not mix completely in the combustion zone. In this section we will discuss how excess air is measured, and how it is used diagnostically.

4.2.2.1 Excess Air Management

In most stationary sources, the air flow to the combustor is controlled, in part, by measuring the excess air and maintaining a fixed excess air level. In fact, controlling excess air exactly is now an integral part of the air pollution control systems used in

automobiles as well as many stationary sources. Theoretically, one could determine the excess air level in a system by measuring the fuel flow, calculating the air required for combustion and then subtracting this from the measured air flow. Fortunately, there is a far simpler and more precise method, and that is to measure the oxygen concentration (% O_2) in the flue gas. Air enters the combustion zone with 20.9% O_2 concentration. So whatever amount of O_2 remains in the exhaust gas, by definition, represents the excess air. Using instruments developed since about 1970, O_2 concentration in exhaust gas can be measured accurately, reliably and inexpensively. Note that when calculating air emissions it is standard practice to use O_2 measured in a dry gas sample (% by vol., dry basis).

There is a simple relationship between excess air and flue gas oxygen concentration, given by Equation 4-8.

$$\%\,\text{Excess Air} = \frac{\%\,O_2}{20.9 - \%\,O_2} \times 100 \qquad (4\text{-}8)$$

This is more of a definition of excess air than a rigorously derived formula, but it is the form that pervades all the current air pollution data reduction methods. % O_2 (by vol., dry basis) is the amount of oxygen remaining after combustion. 20.9 – %O_2 is the initial minus the final amount of air, which, by conservation of mass, must be the amount of air consumed in the flame. So the excess air formula is simply the ratio of the amount of oxygen remaining divided by the amount consumed.

This formula is not exactly the form that results if one started with a balanced chemical equation and went through a rigorous derivation. An assumption implicit in Equation 4-8 is that the combustion air volume is the same as the flue gas volume – which is only approximately correct. The exact formula for excess air includes fuel composition as well as % O_2. Equation 4-8 is simple, it does not depend on fuel composition and it is widely accepted. However, note that 20.9% is the dry volume concentration of O_2 in the atmosphere, so O_2 should be measured dry. In most sampling systems the gas sample is extracted and cooled before it enters the instrument, yielding a dry measurement. If O_2 is measured wet (hot flue gas with no condensation or using a dilution type sampling system), the O_2 value must be corrected upward by the ratio of wet to dry flue gas volumes before it is used in standard data reduction formulas.

Equation 4-8, the relationship between excess air and %O_2, is represented in graph form in Figure 4-2. This figure also shows a series of curves relating CO_2 to excess air for three different fuels. While CO_2 can be used to determine excess air, one needs a fuel analysis to determine the specific relationship.

[CO_2 was commonly used in the past to determine relative excess air level and it is still used in some cases today. It was used in preference to O_2 because exhaust gas was analyzed with an Orsat device – a laboratory apparatus that determined

composition by sequentially absorbing CO_2, O_2 and CO in chemical solutions and measuring the associated change in gas volume. CO_2 was the first gas analyzed, so it was easier to measure than O_2 for routine determination of excess air. The Orsat is a cumbersome and, except in the hands of a skilled technician, a highly unreliable device. Modern instruments developed since about 1970 render the Orsat apparatus archaic, although EPA Method 3b still calls for it.]

If one has a fuel analysis, O_2 and CO_2 become duplicate measurements. On any given source, one can determine one from the other. Figure 4-2 provides one way to do this; although we have provided CO_2 curves for only three specific fuels. The relationship between CO_2 and O_2 is codified by the EPA in 40 CFR 60, Appendix A, Method 3B. In this case, it is used as a data quality control check when measured data for both O_2 and CO_2 are available for a specific test. This will be covered in great detail in Chapter 7.

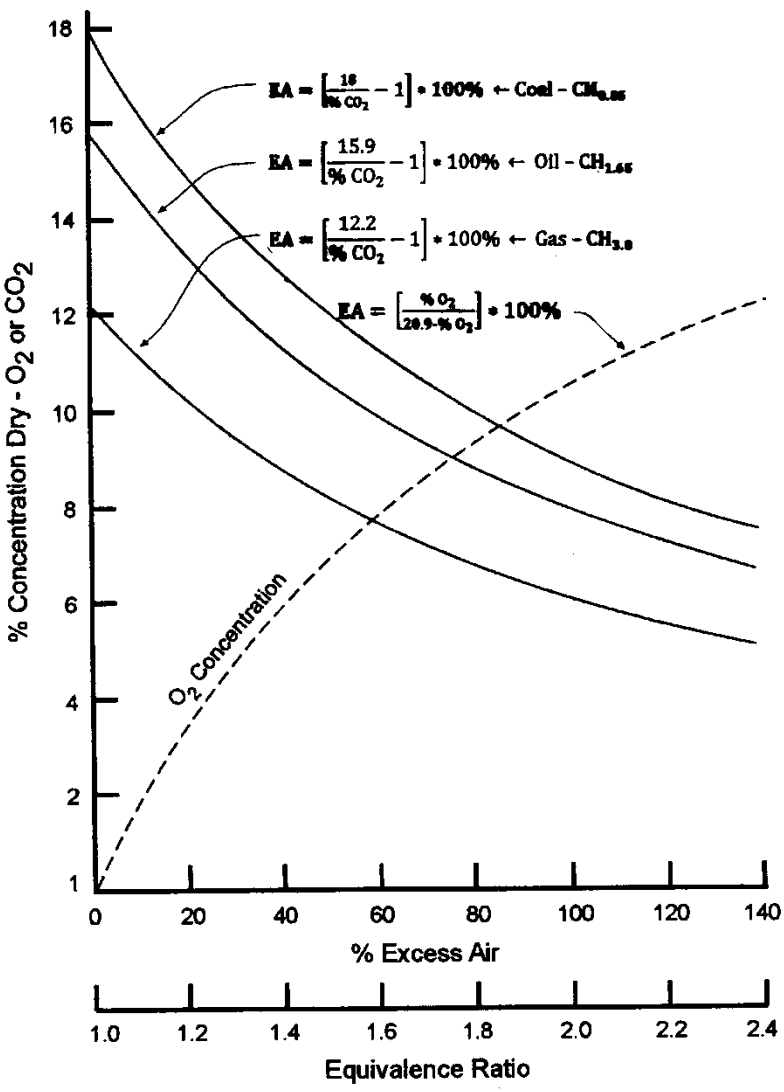


Figure 4-2. Excess Air versus O_2 and CO_2

Equation 4-8 can be manipulated algebraically to define another commonly used term, the *excess air correction factor that* is also called the *air-fuel equivalence ratio*. If 100% is added to the excess air, the result is the amount of air relative to the stoichiometric amount. In other words, zero excess air corresponds to 100% of the stoichiometric requirement; 15% excess air would be 115% of stoichiometric air flow rate.
The excess air correction factor is defined as:

$$\mathbf{ER = Equivalence\ Ratio = (1 + EA)}$$

$$\mathbf{ER = EA\ Correction\ Factor\ = \frac{20.9}{20.9 - \%O_2}} \qquad \mathbf{(4\text{-}9)}$$

The lower abscissa in Figure 4-2 shows this term. The total exhaust flow including excess air is simply the stoichiometric flow times the excess air correction factor that gives Equation 4-10.

$$\text{Exhaust Flow = Stoich. Flow } \times \left(\frac{20.9}{20.9 - \%\ O_2} \right) \qquad (4\text{-}10)$$

Used in combination with Equation 4-7 this provides the relationship between exhaust flow, firing rate and exhaust O_2 concentration.

$$\text{Firing Rate } \left(\frac{\text{mmBTU}}{\text{hr}} \right) = \frac{\text{Exhaust Flow } \left(\frac{\text{ft}^3}{\text{hr}} \right) \times \frac{20.9 - O_2}{20.9}}{F_w \left(\frac{\text{ft}^3}{\text{mmBTU}} \right)} \qquad (4\text{-}11)$$

Given any two variables, the third can be calculated. Thus, a source-firing rate can be calculated from data that is normally measured during a stack emissions test – stack flow rate and O_2. Conversely one can determine the stack flow rate (and thus fan size, dust collector size, etc.) if the firing rate is known together with a reasonable estimate of the excess air level.

Example 4-3.

Stack test measurements showing 20,000 scfm total exhaust flow and 4.0% O_2. Calculate the source-firing rate during the test.

Solution:

Calculate the stoichiometric flow rate using Equation 4-10.

$$20{,}000 \left(\frac{\text{std ft}^3}{\text{min}} \right) \times \frac{20.9 - 4.0}{20.9} = 16{,}172 \left(\frac{\text{std ft}^3}{\text{min}} \right)$$

Then use equation 4-7 to calculate the firing rate.

$$16{,}172\left(\frac{\text{std ft}^3}{\text{min}}\right)\times\frac{60\ \ \text{min}/\text{hr}}{10{,}500\ \ \text{std ft}^3/\text{mmBTU}}=92.4\left(\frac{\text{mmBTU}}{\text{hr}}\right)$$

Where: The generic value of 10,500 (std ft^3/mmBTU) was used for F_w.

One can eqaully well use equation 4-11 to calculate flow in a single step. Comparing this calculated firing rate to the reported firing rate is an effective tool for checking the quality of reported emissions data or to verify the source operating load during an emissions test.

Oxygen measurement is quite simple, but there are some caveats. O_2 instruments are used either as part of the operating system or to support emissions measurements. Boiler operators put their gas sampling point as close to the combustion zone as practical, while instruments used in conjunction with emission monitors are further downstream, usually in the stack. Two factors deserve note. First, O_2 (or any other flue gas constituent) may not be uniformly distributed in a large duct, so a single probe can give a value different from a multi-probe or multi-point average. This problem is prevalent on large boilers with multiple burners and large ducts. Multiple probes or a traverse of the duct may be required to obtain an approximate average.

Second, an O_2 instrument does not distinguish between O_2 coming out of the combustion zone and O_2 introduced by air leaks. An O_2 measurement just shows the net amount at that location. As a general rule the excess air increases as the flue gases move farther from the combustion zone because of air leakage. So an O_2 measurement tells the amount of excess air at the measurement location - values at two locations will be different depending on the amount air leakage and the degree of stratification. In regard to emission measurements, it is critically important that excess air (O_2 or CO_2) be measured at the same location, and preferably with the same probe, used to measure the emission species. By doing this, the amount of air dilution is determined at the emission sampling point and not some other unrelated position.

4.2.3 Water Vapor

Water vapor in exhaust gases originates from hydrogen in the fuel, from water in the fuel, or from water in the combustion air. All fuels, except nearly pure carbon, generate more water in the flue gas than typical ambient saturation levels, so condensation and liquid water are always an issue when sampling or handling exhaust gas. Normally the water vapor content is measured during any emissions sampling program, but the amount of moisture can also be estimated from the fuel properties. Estimated water vapor contents can be compared to measured data as part of a quality control program.

4.2.3.1 Water from Fuel Hydrogen

The amount of water vapor generated by burning the hydrogen in the fuel can be derived starting with a balanced chemical reaction like Equation 4-1. For example, combustion of a fuel with average composition of CH_y gives the following reaction.

$$CH_y + (1+y/4)(O_2 + 3.78N_2) \rightarrow CO_2 + y/2\ H_2O + (1 + y/4)*3.78*N_2$$

The right side shows y/2 molecules of water vapor. Working some algebra yields the volume percent of water vapor from fuel hydrogen in the stoichiometric exhaust gas:

$$V_{w^1} = \frac{y/2}{4.78 + 1.45 \times y} \times 100 \qquad (4\text{-}12)$$

Here the fuel composition has been normalized to one atom of carbon. The hydrogen content 'y' can be calculated from the weight percent carbon and hydrogen in a fuel analysis using the following relationship:

$$y = 12 * (\%H) / (\%C)$$

Where: 12 is the atomic weight of carbon.

Many fuels have $y \approx 2$, which results in a stoichiometric water vapor content of about 13% by volume. In real systems there is excess air present, which reduces or dilutes the water vapor concentration – meaning that water vapor from fuel hydrogen will always be lower than given by Equation 4-12. Dividing V_w from Equation 4-12 by the excess air correction factor (Eqn 4-9) gives the concentration of fuel hydrogen water vapor in the actual flue gas.

$$V_w \text{ actual exhaust concentration } = V_{w^1} \times \left(\frac{20.9 - \%\,O_2}{20.9} \right)$$

4.2.3.2 Water from Fuel Moisture

The other major source of water vapor in the exhaust gas is moisture in the fuel. Fuels like wood and municipal waste can be more than 50% water as fired, so they add a lot of water vapor to the flue gas. The concentration of water vapor (from fuel moisture) in the exhaust gas can be calculated, but it depends on the fuel heating value as well as the amount of moisture in the fuel. For wood or municipal waste, the approximate volume of water in the flue gas resulting from water in the fuel is given by the formula:

$$\% \text{ Flue Gas Water Vapor} = 25 \times \left(\frac{w}{100 - 0.75\,w} \right) \qquad (4\text{-}13)$$

Where: w = % moisture in the fuel as fired

This give the water vapor at zero excess air. So to get the concentration in the diluted flue gas, divide by the excess air correction factor.

For example, 50% moisture in wood fuel will generate about 20% moisture in the flue gas before air dilution. The moisture from hydrogen in the fuel will add about 13% more bringing the total to roughly 33%. However, any source fired with wet wood will operate with at least 50% excess air, and that reduces the water vapor concentration in the exhaust gas to less than 22%.

Drying operations or sources like cement kilns add water to the flue gas from the process, so the exhaust gas moisture is higher than the amount generated by the fuel. In order to estimate the flue gas moisture content from these sources, one needs information about the process as a basis for a mass balance.

This section has presented the basic concepts behind the amount of water vapor in combustion exhaust gas. A rigorous presentation has not been attempted because that is seldom useful in practice. The properties of wet fuels fluctuate enough to frustrate attempts to perform accurate mass balances. In general, the main need for flue gas water vapor information is to set up the emissions test and to reduce the data after the test. However, there are cases where one needs to estimate water vapor content where measured data is not available or is in question.

4.2.4 Calculating Gas Volume and Density

Analysts who deal with emissions, stack flows and combustion frequently encounter gas volume calculations. Most of the required calculations are based on the Ideal Gas Law - written as

$$PV = nRT$$

Where: P is pressure in lb/ft^2
V is volume in ft^3, n is number of moles and
V/n = 385 ft^3/mole for gas at 68°F (528°R)
R is the universal gas constant = 1545 ft-lb/(lb-mole °R)
T is temperature in degrees Rankin

While this law is not frequently used in this form, from this rule, one can readily derive the pressure-volume-temperature relationships that are commonly used.

Anyone who deals with exhaust flow data will, from time to time, have to adjust a flow rate for changes in temperature and/or pressure. This is a simple calculation that is easily

misunderstood. The basic rule is that *gas volume is proportional to temperature and inversely proportional to pressure*. Heating the gas makes it expand. Compressing it (reducing its volume) raises the pressure. Beyond that the only thing to remember is that both temperature and pressure must be in absolute units – where 0° is -460°F (-273°C) and zero pressure is a perfect vacuum. So temperature is measured in °R (°F + 460) or °K (°C + 273) and pressure in inches of mercury or psia (psi absolute). Expressed in a formula, gas volume changes obey the rule:

$$V_1 = V_2 \times (T_1/T_2) \times (P_2/P_1) \qquad (4\text{-}14)$$

Although this relationship can be used for any temperatures and pressures, it is most commonly used to correct an actual gas volume (i.e., at stack temperature and pressure) to standard conditions. Standard pressure is normally the average atmospheric pressure at sea level which is 29.92 inches Hg = 760 mm Hg = 14.7 psia. Standard temperature varies from one discipline to the next. EPA methods and the air pollution community use 68°F = 528°R = 293°K = 20°C. Note that the F-factors all refer to gas volumes at standard conditions.

Measurements of temperature and pressure are not the focus of this course, but deserve brief comment. When measuring gas flow rate, the pressure is the static pressure of the gas in the stack or duct. Stack pressure, where emission measurements are normally made, is usually very close to atmospheric (barometric) pressure outside the stack. But occasionally measurements are made upstream of a fan or an emissions control device with an associated pressure change. Stack thermal draft or very high velocity can slightly lower the pressure at the sampling location Thus the pressure relative to atmosphere (draft) in the duct should be recorded and used to determine the absolute pressure where ever the flow is measured. Thus the sample point static pressure is the sum of the atmospheric pressure and the draft:

$$P_s = P_{bar} + \Delta P_{draft} / 13.6$$

Where: P_s = Sample point static pressure in inches Hg
P_{bar} = Barometric pressure outside the duct in inches Hg
ΔP_{draft} = Duct or stack draft in inches of water
13.6 is the difference in density between mercury and water.

In most cases correcting P_s for stack draft has a very small affect on the reported emissions.

Example 4-4. Correcting gas volume.

Stack flow is measured at 8,000 ft^3/min at a temperature of 310°F, a barometric pressure of 28.67 inches Hg, and a stack draft of –0.45 inches w.g. Determine the flow rate in standard cfm (std ft^3/min).

Solution:

First determine the absolute static pressure of the stack flow.

$$P_s = 28.67 - 0.45/13.6 = 28.64 \text{ inches Hg}$$

Second, use Equation 4-14 where the stack flow is condition No. 1 and standard conditions are condition No. 2.

$$V_{std} = 8000\text{acfm} * [528°\text{R}/(460 + 310)°\text{R}] * [28.64 \text{ inHg}/29.92 \text{ inHg}] = 5251 \text{ scfm}$$

Flue gas density changes with pressure and temperature in the opposite direction from pressure – as volume increases, pressure decreases. For the most part, numeric values for density are only needed at standard conditions. The formula for gas density at standard conditions is

$$\rho(\text{lb/std ft}^3) = \text{MW}(\text{lb/lb-mole}) / 385 \text{ (std ft}^3\text{/lb-mole)} \qquad (4\text{-}15)$$

Where: MW is the molecular weight of the gas.

The molecular weight of dry air is 29.0. This can easily be derived from the ratio of the weight of the constituents using the composition of the atmosphere (Table 4-4) and the molecular weight of the constituents (Table 4-3).

$$\text{MW}_{\text{dry air}} = (78.08*28 + 20.95*32 + 0.93*40)/(78.08 + 20.95 + 0.93) = 28.96$$

Where: 40 is the molecular weight of argon

The molecular weight of flue gas is generally close to air, 29.0, and this is usually a safe assumption when the composition is unknown. The weights of the two combustion constituents, CO_2 and H_2O are respectively heavier and lighter than air, so their combination frequently averages to about 29. The exception is flue gas with high moisture content, in which case the average molecular weight is lower, which reduces the gas density. EPA Method 3 for molecular weight, allows the use of the value 30.0 as a default for dry gas molecular weight when the source is burning coal oil or gas.

The density of exhaust gas can be calculated with Equation 4-15 using the gas composition and the weighted average of the molecular weights of individual species in the same way the density of air was calculated.

Example 4-5.

The exhaust gas from a coal-fired combustion source has measured concentrations of water vapor = 8% by vol. and O_2 = 5% by vol. What is the approximate density of the exhaust at standard temperature and pressure?

Solution:

An approximate composition of gas is needed. The curves in Figure 4-2 can be used to infer CO_2 concentration for a coal-fired source. 5% O_2 means 31% excess air, which means the CO_2 must have been about 14%. Most of the balance of the gas was nitrogen, so:

$$\%N_2 = 100 - 8 - 5 - 14 = 73\%$$

Now use the weighted average of the molecular weights to find the average molecular weight:

$$MW_{avg} = [73*28 + 14*44 + 5*32 + 8*18]/100 = 29.6$$

[This is identical to the equation for the molecular weight (MW_d) of dry flue gas presented in EPA Method 2.]

Use Equation 4-15 to determine density:

$$\rho = 29.6 \text{ (lb/lb-mole)} / 385 \text{ (std ft}^3 \text{ / lb-mole)} = 0.077 \text{ (lb/ std ft}^3\text{)}$$

When flue gas moisture content is known, the relationship between wet and dry flue gas is given by an equation presented in EPA Method 2,

$$MW_s = (1-B_{ws}) * MW_d + 18 * B_{ws}$$

Where: MW_s is molecular weight of (stack) exhaust gas
B_{ws} is the proportion by volume of water in the gas
MW_d is molecular weight of dry exhaust gas

4.3 ENTHALPY OF COMBUSTION AND HEATING VALUES

Enthalpy is the engineering term for the sensible energy content of a substance and is usually expressed as BTU/lb. Fuel combustion releases stored chemical energy and then transforms it into the enthalpy of the exhaust gases. As these gases transfer heat to their surroundings, they cool and their enthalpy drops. In a boiler, the heat is transferred to water or steam thereby increasing the enthalpy of the water or steam. Tracking the energy flow in a combustion device can be a useful exercise. This chapter will show how evaluation of energy flows can be useful in combustion source diagnostics.

4.3.1 Flame Structure – Primary and Dilution Zones

Fire is a very simple, but familiar concept. However, the physical and chemical phenomenon involved is complex and engineering modeling of combustors always requires major simplifying assumptions. A detailed discussion will not be attempted here, but some basic concepts are essential to subsequent sections of this chapter.

Combustion can occur at any temperature, as evidenced by spontaneous combustion which starts at room temperature and progresses to the point of creating flames. The chemical reactions are slow at low temperatures, but if the heat is not dissipated, the fuel can get hot enough to burst into flame. As a general rule, flames involve high temperatures – typically 2500°F and higher. Cooler fires can exist, but they usually require some special design effort to make them stable. Whenever a flame temperature gets too low, the flame usually becomes unstable and goes out. Most of the combustion reactions take place very rapidly in an initial flame zone that is highly visible; the exception is a natural gas flame that is barely visible. As the gases move beyond the initial flame zone, they cool rapidly, but some residual combustion takes place until the temperature drops below 1400°–2000°F.

Below about 1400°F chemical reactions are too slow to support any flame. Stated more succinctly, flames are usually hot or not at all. Cool combustion is a special situation not encountered in most combustors. [Catalytic reactors are a different concept that does not require a traditional flame.]

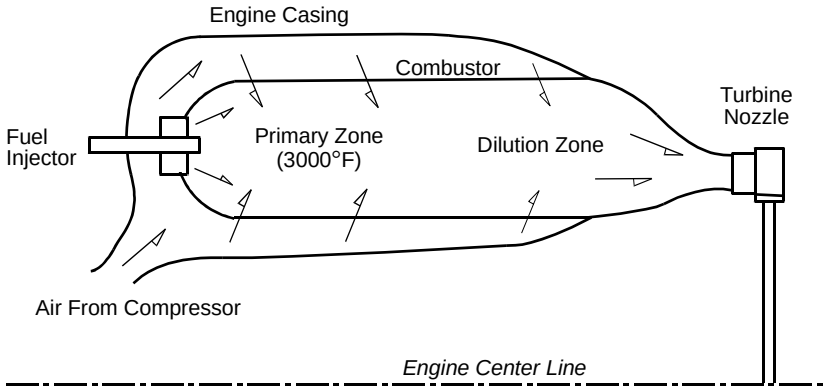


Figure 4-3. Gas Turbine Combustor

A review of two typical combustion systems will be conducted to illustrate some concepts of flame structure. Figures 4-3 and 4-4 show two combustion systems – one for a combustion turbine and the other a typical furnace. The gas turbine combustor depicted in Figure 4-3 consists of a stainless steel "can" with a bunch of holes and a fuel injector at one end. Air from the compressor flows through the holes into the combustion zone and the hot combustion gases then flow through the turbine. The turbine inlet temperature, depending on the engine design and the power level, is

anywhere from about 1200°F to 2400°F – which is less than the temperature of a satisfactory flame. So the combustor is designed with a primary zone next to the fuel injector that operates well above 2500°F. The primary zone provides a hot stable flame. Downstream of the primary zone additional "dilution" air is added to cool the gases to an acceptable turbine inlet temperature. So the combustor has a hot stable fire with a moderate exhaust temperature. The holes in the combustor are all carefully tailored to provide just the right amount of air in the right place to make the combustor work well and generate an appropriate temperature profile at the turbine inlet. A gas turbine combustor operates nearly adiabatically where most of the heat radiated from the flame is carried back into the combustor by the dilution air that flows around the combustor.

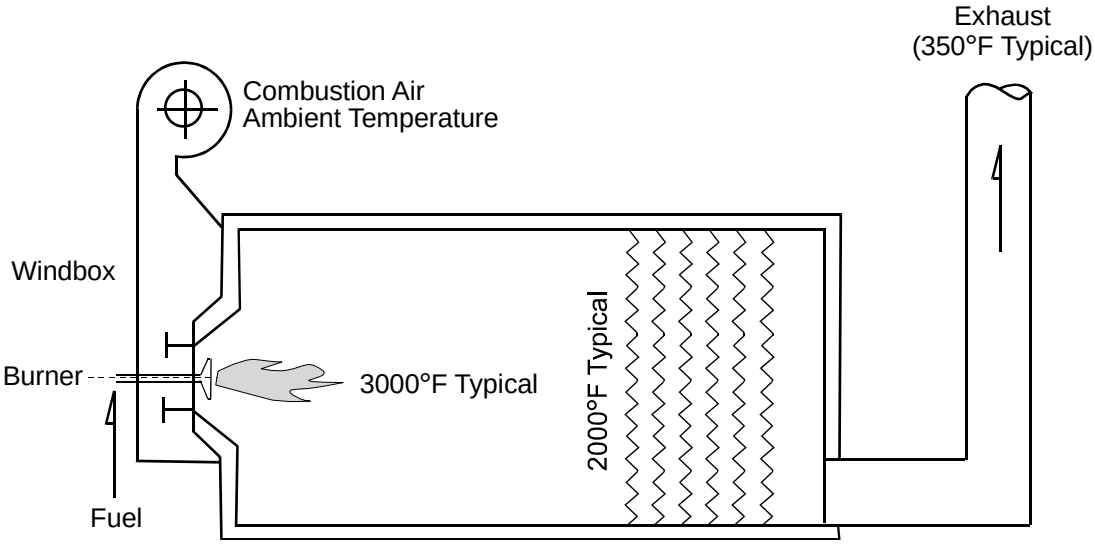


Figure 4-4. Boiler Combustor

Figure 4-4 is a basic furnace or boiler. It is similar to the turbine combustor in the sense that the burner generates a hot stable fire and the furnace exit is much cooler – typically 2000°F. A major difference is that the combustion gases cool off by radiating heat to the furnace walls, not by dilution with additional cold air. Another difference is that a furnace operates at atmospheric pressure rather than several hundred psi and the residence time in the furnace is one to three seconds versus 15 milliseconds in the turbine combustor. Both boiler and turbine combustors rely on a hot primary fire to achieve complete combustion and maintain stable operation.

A brief conceptual discussion can relate physical and chemical processes to flame characteristics. In most commercial combustion systems the fuel mixes with the air in the flame, as opposed to being mixed prior to ignition. So the rate of combustion is governed by the slower of two mechanisms: mixing and chemical reaction. The fuel and air have to be mixed down to the molecular level, because all carbon and hydrogen molecules must come in contact with oxygen molecules before a chemical reaction can occur. The chemical reaction rate is very fast at typical flame temperatures. So most combustion rates are limited by mixing – meaning the size and character of the flame are controlled by how well the fuel is mixed with the air.

And the mixing, in turn, is controlled by the design of the burner that injects the fuel and air into the flame zone. The chemical differences in fuel hydrocarbons usually do not make much difference [provided they are not predominantly halogens such as carbon tetrachloride which absorb energy]. Designing burners for different fuels means dealing with the physical properties that control the quality of a liquid fuel spray, the size of pulverized fuel particles, or other mixing related parameters.

In combustors with slow or imperfect mixing, chemical reaction rates can become a significant operating limitation. As discussed in the next section, temperatures drop rapidly after the combustion gases leave the flame zone. If mixing is incomplete and the temperature drops far enough, the chemical reaction rates slow to the point that PIC are left over. So it is generally true that combustion is either fast or incomplete. A closely related concept is that flames either burn hot or they go out – they are either on or off, not half way. This leads to the next section on flame temperatures.

4.3.2 Combustion Temperature Levels

How hot is the flame in a typical combustor? The answer depends on the burner design, the location in the flame and perhaps on whether it is instantaneous or time averaged. Set aside "low NOx" combustors for the moment and consider only traditional burner flames. In these flames the fuel and air are mixing in the flame as opposed to being premixed and then ignited in the combustion zone. Most combustor flames reach peak temperatures in the vicinity of 4000°F at some point in the flame. By following a fuel particle through the flame, one might note the temperature will rise rapidly to a peak level as the fuel mixes with air and burns. But this peak temperature level is very short lived for two reasons: (1) the hot gases continue mixing with excess air in the combustion zone which cools them and (2) radiative heat transfer is intense and the gases begin cooling the instant the chemical energy is released. The points where the fuel reaches stoichiometric proportions with air are the hottest and, if the flame is steady, will be fixed regions in the flame. Regions downstream of this point will be cooler. While an attempt to map out flame zone temperatures will not be made at this time, an upper limit for the peak flame temperature can be established.

4.3.2.1 Stoichiometric Flame Temperature

If combustion occurs in a closed furnace with very well insulated walls (and the inside refractory can withstand the temperature) there will be very little heat transfer from the flame to its surroundings. The resulting temperature will approach the "adiabatic" temperature. This temperature can be determined from a simple energy balance. First consider the case of stoichiometric air flow. The hottest possible adiabatic flame temperature is reached when there is no excess air to dilute or cool the flame. This is the highest temperature that can occur anywhere or anytime during combustion. A basic energy balance results when the exhaust gases absorb all the energy released by fuel combustion.

Fuel energy released = Enthalpy of the exhaust gas (E.G.)

$$Q\,[\text{Btu}] = V\,[\text{scf}] * \frac{29}{385}\left[\frac{\text{lb}}{\text{scf}}\right] * C_p\left[\frac{\text{Btu}}{\text{lb}\ ^\circ\text{F}}\right] * \Delta T\left[^\circ\text{F}\right] \qquad (4\text{-}16)$$

Where:
- Q = Fuel energy released
- V = E.G. volume at standard conditions
- Cp = E.G. specific heat
- ΔT = E.G. temperature rise

Set Q = 10^6 BTU and solve for ΔT:

$$\Delta T \quad ^\circ\text{F} = \frac{Q}{V \times C_p} \times \frac{385}{29} \qquad (4\text{-}17)$$

This is one equation with three unknown variable – ΔT, Q and V. C_p, the specific heat of exhaust gas, is a number that is tabulated and can be taken from a table. Q and V are coupled, as shown earlier, by chemical balance using the fuel analysis. When Q is 10^6 BTU, the associated volume of flue gas will be equal to the F-factor, F_w. This is almost correct, except that the F-factors are derived using the higher heating value (HHV) of the fuel. The sensible energy balance expressed in Equations 4-16 and 4-17 does not include the heat of vaporization for water vapor. So we need to use an adjusted F-factor, F_w` that is based on the lower heating value (LHV). So we define

$$F_w` = F_w * \text{HHV/LHV}$$

Now use F_w from Table 4-5 and heating values from Table 3-4 and set V = F_w`. Using these substitutions and the typical values of F_w = 10,320, HHV = 19,000, LHV = 17,800 and C_p = 0.30 in Equation 4-17, the result is ΔT = 4017°F

In other words, the theoretical maximum possible combustion temperature for a typical fuel is roughly the initial temperature plus 4000°F. The value for specific cases varies considerably because the value of C_p is not constant at high temperatures and it is strongly dependent on the amount of water vapor in the combustion gases. Knowing an exact value for the adiabatic flame temperature is seldom useful, but it is valuable to know (1) the form of Equation 4-17 and (2) the fact that the adiabatic temperature rise for most flames is in the vicinity 4000°F.

4.3.2.2 Adiabatic Temperature with Excess Gas

The adiabatic flame temperature, as derived in Equation 4-17, is for stoichiometric combustion because V was obtained from a table of F-factors that, by definition, are stoichiometric volumes. The same derivation could be used for a flame with excess air or excess gas, in which case V would be larger than the F_w -factor value.

Increasing the amount of combustion gas, without increasing the amount of energy released, spreads the energy to more gas and lowers the adiabatic flame temperature. For example, if we increased the amount of combustion gas by 25%, the temperature rise would be reduced approximately to

$$\Delta T_2 \approx \Delta T_1/1.25 = 0.8 * \Delta T_1 = 3360°F$$

"Approximately" is used here because changes in the value of specific heat would modify this result. One could use Equation 4-17 with applicable values of V and C_p to get a more accurate value, but the basic concept is that temperature rise is inversely proportional to the amount of gas involved in combustion.

Extra gas in a combustor can be either air or recirculated exhaust gas. Flue gas recirculation (FGR) is a NOx control technology that will be discussed in Chapter 6. Here we will consider the effect of extra (excess) air. Nearly all combustion systems operate with some excess air and its effect on average flame temperature is easily predicted. We simply multiply the volume, $V = F_w`$, in Equation 4-17 by the excess air correction factor from Equation 4-9.

$$\Delta T = \frac{10^6}{Fw` \times C_p} \times \frac{20.9 - \% O_2}{20.9} \times \frac{385}{29} \qquad (4\text{-}18)$$

If typical values of F_w = 10,500 and C_p = 0.30 were inserted into this equation, the results would appear as plotted in Figure 4-5. The line left of the peak represents incomplete combustion and is estimated. The actual peak temperature is uncertain because C_p is not well defined when the gas begins to ionize. Figure 4-5 is not exact because a fixed value for C_p was assumed; however, that is not correct, especially at typical flame temperatures.

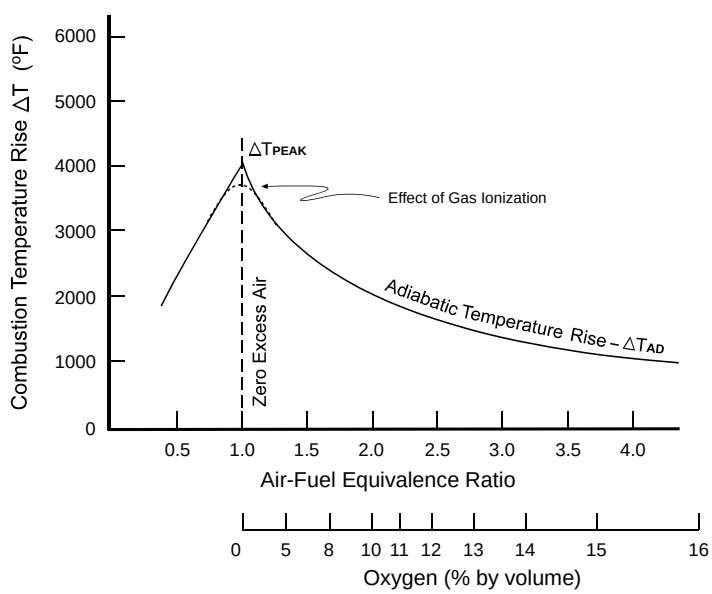


Figure 4-5. Adiabatic Temperature vs. Excess Air

In general the adiabatic flame temperature is inversely proportional to the amount of gas present, provided there is at least the stoichiometric oxygen requirement. Figure 4-5 shows graphically the dependence of adiabatic flame temperature rise on excess air. This relationship is not just theoretical; it applies to real systems with low heat losses such as the exit of a thermal oxidizer or the exit of a gas turbine combustor. This relationship can also be applied on a microscopic scale to give the upper limit of the temperature in some region of the flame with a known air-fuel ratio. As seen in Section 4.3.2.3, the temperature in various regions of the flame can be very different from the average flame temperature and from the combustor exit temperature.

While the calculation of peak flame temperature tends to be an esoteric exercise, there can be many benefits in determining the temperature of thermal oxidizers and some other devices.

Example 4-6. Thermal Oxidizer Temperature

Stack tests are performed on a gas-fired thermal oxidizer such as that shown in Figure 2-16. Contaminated air enters the incinerator from an oven at 250°F. The measured stack oxygen concentration measured during the emission tests is 14.0%. What was the maximum possible average temperature in the combustion chamber?

Solution: There are two approaches:

1. A temperature of about 1350°F is the approximate temperature rise for an adiabatic combustion system operating at 14% O_2 (see Figure 4-5). Adding the inlet temperature gives us: 1350°F + 250°F = 1600°F as the maximum combustion chamber temperature. The actual temperature would have been slightly lower due to heat loss to the surroundings.

2. Use Equation 4-18 to calculate the temperature rise. A specific value for C_p can be determined, as is done in the following section, but for now use a general value of C_p = 0.30. The adjusted F-factor, using values for natural gas from Table 4-5 and Table 3-4 is:

$$F_w` = 10610 * 22{,}200/20{,}000 = 11{,}777 \text{ (std ft}^3\text{/mmBTU)}$$

Inserting these numbers in Equation 4-18 gives:

$$\Delta T = \frac{10^6}{11{,}777 \times 0.30} \times \frac{20.9 - 14.0}{20.9} \times \frac{385}{29} = 1240^{o}F$$

Adding the inlet temperature gives the final temperature:

$$T_{max} = 250° + 1{,}240° = 1{,}490°F$$

The two approaches yield different results because Figure 4-5 is based on oil fuel and approach No. 2 used data specific to natural gas. If exhaust gas composition were used to determine a more exact value of $C_{p,}$ there would be a third answer. However, quibbling about the exact value belies the object of the example, which is that: *the average exhaust gas O_2 concentration and the maximum possible average combustion zone temperature are linked and you can determine one from the other.* This is useful in checking the quality of emissions test data for some sources. If the maximum temperature computed from the O_2 concentration is significantly lower than the reported actual temperature, it means there is an error in either the O_2 measurement or in the temperature measurement. Of course a measurement error could seriously compromise some or all of the test data.

Note that in this example there could have been a heat exchanger in the system and the calculation is still valid. However, calculating temperature from oxygen concentration does require an airtight system that does not take in atmospheric air between the combustion chamber and the measuring point.

4.3.2.3 Local versus Average Temperature

Figures 4-3 and 4-4 illustrate that temperatures are not uniform in most combustors, even if there is little heat loss from the flame. The average combustor exit temperature is lower than the peak combustion temperature for two reasons: (1) radiative heat loss from the flame, and (2) the fact that fuel mixes with air in the flame. To understand the second reason, consider a small parcel of fuel (a tiny drop of oil or a puff of gas) and follow its progress in Figure 4-5. The fuel enters the combustor on the left side as pure fuel mixed with zero air. As it mixes with air it progresses to the right, eventually reaching the excess air level at the combustor exit conditions – the average exhaust air-fuel equivalence ratio which is greater than 1.0. The temperature of this fuel parcel rises as it burns, but the temperature can never exceed the adiabatic temperature line. However, since its equivalence ratio will have to pass through 1.0 at some time, the temperature at that time can reach the peak level, about 4000°F above the air inlet temperature. So when fuel mixes with air during combustion (diffusion flame), all the fuel can potentially pass through the adiabatic peak temperature as it burns. This concept is explored further when we discuss NOx formation. However, the purpose of this discussion here is simply to show that flames can have very high local temperatures even if the exit temperature or even the overall average flame temperature is relatively low.

If the fuel and all the air are premixed, then ignited in the combustor, none of the fuel passes through the point when equivalence ratio equals 1.0 (provided there is some excess air) and none of the flame can reach the corresponding peak temperature. In a premixed system the flame temperature can never be higher than the point on the temperature curve that corresponds with the air-fuel equivalence ratio at the combustor exhaust. So a premixed flame will not have the hot spots that characterize a diffusion flame.

Figure 4-5 shows us the upper limit of the average exit temperature for any type of combustor. The higher the excess air level, the lower the average exit temperature. In a system where the fuel and air are completely premixed the maximum flame

temperature and maximum exhaust temperature are one and the same. If the combustor injects fuel into the combustion zone, so there is mixing in the flame, then local peak temperatures can go as high as the adiabatic temperature at the air-fuel equivalence ratio equals 1.0, which is somewhere around 4000°F above the inlet temperature.

4.3.3 Energy Content of the Flue Gas

Energy from combustion is transferred initially to the combustion gases (also called exhaust gas or flue gas) and then to the walls and surfaces of the furnace. The total energy released equals the amount transferred to the surroundings plus the amount carried by the flue gas exiting the stack. The energy in the flue gas is made up of three components: (1) the sensible energy that is proportional to the temperature of the gas, (2) the latent heat of vaporization of the water vapor, and (3) energy in unburned fuel – products of incomplete combustion.

$$Q_{EG} = Q_{LH} + Q_S + Q_{PIC}$$

Where:
Q_{EG} = total flue gas energy content
Q_{LH} = flue gas latent heat
Q_S = flue gas sensible heat
Q_{PIC} = energy in the products of incomplete combustion

Q_{EG} and Q_{LH} will be discussed here, while Q_{PIC}, which is usually small to negligible, will be discussed in Chapter 5.

4.3.3.1 Latent Heat

Latent heat energy in the exhaust gas is contained in the water vapor from fuel moisture and hydrogen combustion. Latent heat energy is only released if the vapor is condensed to liquid water. This means that latent heat is not usable energy in most systems. If energy input were measured using the lower heating value of the fuel (LHV), then latent heat energy would be excluded from consideration. However, since we normally characterize fuels by their HHV rather than by their LHV, we have no choice but to account for the latent heat in any energy balance. The amount of latent heat is about 1000 BTU per pound of water vapor. That is the energy that would be available if we cooled the gas to about ambient temperature and condensed most of the vapor into liquid water. Written in an equation, the latent heat flow is:

$$Q_{LH}\left(\frac{BTU}{hr}\right) = W_{EG}\left(\frac{lb}{hr}\right) \times \left(\frac{\%\,H_2O}{100}\right) \times \left(\frac{18}{29}\right) \times 1000\left(\frac{BTU}{lb}\right) \qquad (4\text{-}19)$$

Where:
- Q_{LH} = flue gas latent heat, BTU/hr
- W_{EG} = flue gas mass flow rate, lb/hr
- $\%H_2O$ = concentration of water vapor in the E.G., % by volume
- 18 = molecular weight of water, lb H_2O/lb-mole H_2O
- 29 = molecular weight of E.G., lb E.G./lb-mole E.G.
- 18/29 = factor to convert water fraction from a volume to a mass basis

Knowing the absolute value of the latent heat flow is useful in some situations, but knowing the heat loss relative to total firing rate (Q_{Tot}) is usually more informative. If Equation 4-19 is divided by the firing rate given by Equation 4-11, the result is:

$$\frac{Q_{LH}}{Q_{Tot}} = \frac{\%\,H_2O}{100} \times \frac{20.9}{20.9 - \%\,O_2} \times \frac{F_w}{1000} \times \frac{18}{385} \qquad (4\text{-}20)$$

Note that the exhaust flow rate cancels out and the fraction of total energy carried by uncondensed water vapor depends primarily on two variables – % H_2O and % O_2. In fact, if we put in a typical value of 10,500 for F_w (valid for coal, oil or natural gas), the result is:

$$\frac{Q_{LH}}{Q_{Tot}} = \frac{\%\,H_2O}{100} \times \frac{20.9}{20.9 - \%\,O_2} \times 0.49 \qquad (4\text{-}21)$$

This simple approximate equation gives values well within typical measurement accuracy for most fuels. This equation also yields low values for wet fuels such as green wood, municipal waste or lignite.

Example 4-7. Energy in uncondensed water vapor

What is the energy carried by uncondensed water in the stack of a gas-fired source where the exhaust flow has 4.5% O_2 and 17% water vapor by volume?

Solution:

$$\frac{Q_{LH}}{Q_{Tot}} = \frac{17}{100} \times \frac{20.9}{20.9 - 4.5} \times 0.49 = 0.106$$

10.6% of the fuel energy (based on higher heating value) is in the form of uncondensed water vapor. Note that this amount of energy will be carried out the stack unless the gas can be cooled enough to condense the water. While some

residential furnaces and water heaters capture most of this energy with near ambient stack temperatures, very few industrial or commercial facilities do so.

The equations presented here are useful to a person using stack test data. The latent heat content could have been formulated from just a fuel analysis. Normally, fixed or standard values are assigned to the latent heat stack losses for predictable fuels such as natural gas, oil and most coals. Table 4-6 lists three fuels and the approximate amount of latent heat energy derived from fuel hydrogen in the exhaust.

Table 4-6. Approximate Exhaust Latent Heat Energy

Fuel	*C/H Ratio*	*HHV (BTU/lb)*	Q_{LH}/Q_T
Natural Gas	$CH_{3.8}$	23,000	0.094
Heavy Oil	$CH_{1.7}$	18,500	0.060
Bitumin. Coal	$CH_{0.8}$	13,500	0.042

Fuel moisture also adds water to the exhaust gas and this affect is not included in the last column of Table 4-6.

4.3.3.2 Sensible Energy

The sensible energy carried by the flue gas is proportional to temperature difference between flue gas and ambient air, and can be expressed as:

$$Q_S \text{ (BTU/hr)} = W_{EG} \text{ (lb/hr)} * C_p \text{ (BTU/lb/°F)} * \Delta T \text{ (°F)} \qquad (4\text{-}22)$$

Where: Q_S = flue gas sensible heat, BTU/hr
W_{EG} = E.G.mass flow rate, lb/hr
C_p = E.G. specific heat, BTU/lb/°F
ΔT = temperature difference between flue gas and ambient air, °F

Gases just beyond the combustion zone are hot and carry most of the combustion energy. By the time they reach the stack they have cooled and carry relatively little energy. Divide Equation 4-22 by Equation 4-11, and the fraction of the total fired energy is present as sensible energy.

$$\frac{Q_S}{Q_{Tot}} = \Delta T \times \frac{20.9}{20.9 - \%\,O_2} \times \frac{C_p \times F_w}{10^6} \times \frac{MW_{FG}}{385} \qquad (4\text{-}23)$$

where: MW_{FG} is the molecular weight of exhaust gas
[$MW_{FG}/385$ is the gas density in lb/ft^3]
F_w is the wet F-factor (Table 4-5)

Here, as in the case for latent heat, there are two significant variables and several constants. If the following values are used for the constants that are typical of a coal-, oil- or gas-fired boiler stack: $C_p = 0.30$; $F_w = 10{,}500$; and $MW_{FG} = 29$, then Equation 4-23 reduces to:

$$\frac{Q_S}{Q_T} = \frac{\Delta T}{4200} \times \frac{20.9}{20.9 - \%\,O_2} \tag{4-24}$$

Equations 4-23 and 4-24 show that the sensible heat carried by the exhaust gas increases when either the temperature or the O_2 increase. This is logical because increases in either temperature or flow rate should increase the energy. Equation 4-24 suggests that when the temperature rise reaches 4200°F at $O_2 = 0$, then $Q_S = Q_T$ and all the combustion energy is converted to sensible energy. In other words, the implied adiabatic flame temperature is 4200°F. The reason this number differs from the 4000°F we derived earlier is that Equation 4-24 did not reckon with some of the heat being absorbed by water vapor. Note that Equations 4-23 and 4-24 are not intended for use at temperatures approaching typical flame temperatures.

Example 4-8. Exhaust sensible heat

Boiler stack measurements show T = 375°F and O_2 = 3.3% on a day when the ambient temperature is 50°F. What fraction of the fuel energy is wasted in the form of hot gas going out the stack?

Solution:

$$\frac{Q_S}{Q_{Tot}} = \frac{375 - 50}{4200} \times \frac{20.9}{20.9 - 3.3} = 0.092$$

In this example about 9.2% of the fuel energy is in the form of hot gas going out the stack.

The equations derived here for latent and sensible heat contents show that a considerable amount of information can be derived from a few simple measurements. In many combustion sources, the fuel energy is either used or it goes up the stack. Thus if we know the amount of energy carried up the stack, we know what fraction was used. Therefore, we can infer the thermal efficiency of many sources just by measuring stack temperature and O_2 concentration. The subject of source efficiency is explored further in Chapter 7.

4.3.3.3 Specific Heat

Reference has been made to specific heat several times during the preceding pages, usually designated by C_p, which stands for specific heat at constant pressure. The scale for specific heat is defined simultaneously with the definition for a BTU or

calorie. Water is defined to have a specific heat of 1.00 BTU/(lb-°F). The specific heat for other materials is derived by comparing them to water.

The specific heat of exhaust gas depends on both composition and temperature. Table 4-7 gives values for several gases at several temperatures. These are values at the stated temperature. One can also find tables that give average specific heat values over a range of temperatures.

Table 4-7. Specific Heat [BTU/(lb-°F) or kcal/(kg-°C)]

Temperature	*Air*	*CO_2*	*Water Vapor*
68°F	0.242	0.200	0.445
212	0.244	0.218	0.452
500	0.249	0.245	0.470
1100	0.260	0.285	0.526
2200	0.278	0.315	0.622
3000	0.297	0.325	0.673
3800	0.303	0.330	0.709

One of the first observations about the values in Table 4-7 is that the values for water vapor are approximately double the values for air and CO_2. So exhaust gases with large amounts of water vapor will have significantly higher specific heat than dry gas. It is frequently necessary to estimate the approximate water content of exhaust gas in order to make reasonably accurate energy balances.

Many energy related calculations for combustion sources deal with exhaust gases at or below about 1500°F. A second observation is that in this temperature range C_p for dry gas is about 0.25 and C_p for water vapor is about 0.5. These approximations can be used for most calculations without inducing substantial errors.

Example 4-9.

What is the specific heat of a combustion source exhaust gas with 18% H_2O and a stack temperature of 475°F?

Solution:

$$0.18 * 0.47 + (1 - 0.18) * 0.25 = 0.290 \text{ BTU/(lb-°F)}$$

The specific heat of the exhaust gas from most sources fired with fossil fuels falls in the range of 0.26 to 0.29. However, it can go considerably higher for the exhaust from sources fired with very wet fuel such as many bio-fuels or municipal waste.

This means that when wet fuel is introduced, the combustion zone temperature will be lower and the exhaust will carry more energy up the stack than when firing dry fuel.

4.4 COMBUSTOR SIZE AND RESIDENCE TIME

4.4.1 Combustor Size

The size of any combustion device is directly related to the design firing rate, although different types of combustion devices are not necessarily comparable. The combustor volume required depends on several factors.

- Combustor volume is roughly proportional to the fuel firing rate or heat input rate (BTU/hr).
- Combustor volume is inversely proportional to the operating pressure. For example, engines have smaller chambers than atmospheric pressure furnaces.
- Combustor volume depends on the fuel mixing/combustion rate. For example, pulverized coal furnaces are bigger than oil-fired furnaces that are usually bigger than gas-fired furnaces.

Combustion intensity or thermal loading is defined as the heat release per unit volume and is generally measured in units of BTU/hr per cubic foot of combustor volume (BTU/(hr-ft^3). Boilers and furnaces generally are designed with thermal loadings in the range of 50,000 to 150,000 BTU/(hr-ft^3). Combustion turbines, operating at 10 atmospheres or more of pressure, have design heat release rates more than ten times as high.

Example 4-10. Furnace Thermal Loading

What is the thermal loading of a furnace with firebox dimensions of 7 ft x 8 ft x 25 ft, fired at design maximum rate of 120 mmBTU/hr?

Solution:

The furnace volume is: 7 * 8 * 25 = 1400 ft^3
Thermal loading is 120(10^6)/1400 = 85,700 BTU/(hr-ft^3)

Knowing the thermal loading of a combustor relative to other similar combustors can give an indication of the flexibility to modify it. A furnace with a low thermal loading is more amenable to up-rating than a furnace that is highly loaded. A furnace with high thermal loading will usually be less amenable to low NOx technologies that stage the combustion and increase the volume of the flame.

4.4.2 Residence Time

Regulations for certain types of incinerators specify a minimum combustion residence time. This is based on the philosophy that the wastes, if given long enough at a high enough temperature, will be destroyed. In practice, residence time is not usually a critical parameter governing performance, but the concept provides regulatory reassurance.

Combustor residence time is the average time it takes fuel to transit the combustion zone. If fuel is injected at t = 0, the resulting exhaust products depart the combustion zone at $t = t_{res}$. Residence time is defined and calculated as the furnace volume (ft^3) divided by the gas flow, in actual ft^3/second.

$$t_{res} = \text{Furnace volume } (ft^3)/\text{Actual gas flow } (ft^3/\text{second}) \qquad (4\text{-}25)$$

Example 4-11. Residence Time.

Determine the residence time of a thermal oxidizer with an exhaust flow of 2600 std ft^3/min and an operating temperature of 1450°F in a 350ft^3 chamber.

Solution:

First, determine the gas flow at actual ft^3 per second.

$$\text{Actual flow} = 2600 * \{(1450+460)/528\}/60 = 157 \text{ acf/sec}$$

Now use Equation 4-25

$$\text{Residence time} = 350/157 = 2.2 \text{ seconds}$$

Residence time is directly linked to thermal loading because the gas flow rate is proportional to the firing rate via the F-factor. Specifying a minimum residence time assures that the firing rate or flow rate through the device does not exceed a specified (permitted) value for the size of the device. Of course residence time alone is not sufficient to assure good combustion performance or the complete destruction of wastes. This issue is covered in more detail in Chapter 6.

4.5 CONCLUSION

Combustion is such a complex process that combustor design continues to rely heavily on “cut and try” methods rather than modeling using computers. However, the combustion process obeys the basic laws of conservation of mass and energy. Using these basic rules, it is possible to develop several simple tools that can be used for inspection and diagnosis of typical combustion systems.

Combustion diagnostics has always relied heavily on the analysis of the exhaust gases. In recent years, interest in air emissions has elevated the science of exhaust gas analysis. Using a few exhaust or stack measurements and some very simple calculations, we can determine the source firing rate in addition to the emissions. The amount of energy going up the stack can be determined, and that, in many cases, is enough to accurately determine the thermal efficiency of the source. In short, stack data can usually be used to determine the useful load of the source, which provides a means to check the quality of measured emissions data.

This chapter has discussed the basic physical or chemical rules used to generate relationships between combustion parameters. These rules are simplified where possible so that the calculations can be performed on hand calculators with minimal need for complex data reduction.

Review Exercises

1. Calculate the approximate density of the exhaust gas from an oil-fired boiler at standard temperature and pressure if the water vapor content is 10% by volume and O_2 = 3.3% (dry measurement).
   a. 0.074
   b. 0.076
   c. 0.078
   d. 0.083

2. What is the maximum possible average temperature in the combustion chamber of a gas fired thermal oxidizer, when the contaminated air temperature = 150ºF, and the exhaust gas O_2 = 14.3% dry volume. (Use the calculation method and assume an average specific heat of 0.30 BTU/lb-°F.)
   a. 1,260°F
   b. 1,180°F
   c. 1,340°F
   d. 1,470°F

3. What fraction of fuel energy for a coal-fired boiler goes up the stack in the form of hot gas?

   When: Stack temperature, T = 400ºF
   Exhaust gas O_2 = 5%
   Ambient Temperature = 75ºF

   a. 8.7%
   b. 10.2%
   c. 11.7%
   d. 15.1%

4. Determine the oil flow rate to a boiler.

   Where: Firing rate = 90 mmBTU/hr.
   Heating Value of Oil = 125,000 BTU/gal.

   a. 12 gal/min
   b. 720 gal/min
   c. 8 gal/min
   d. 15 gal/min

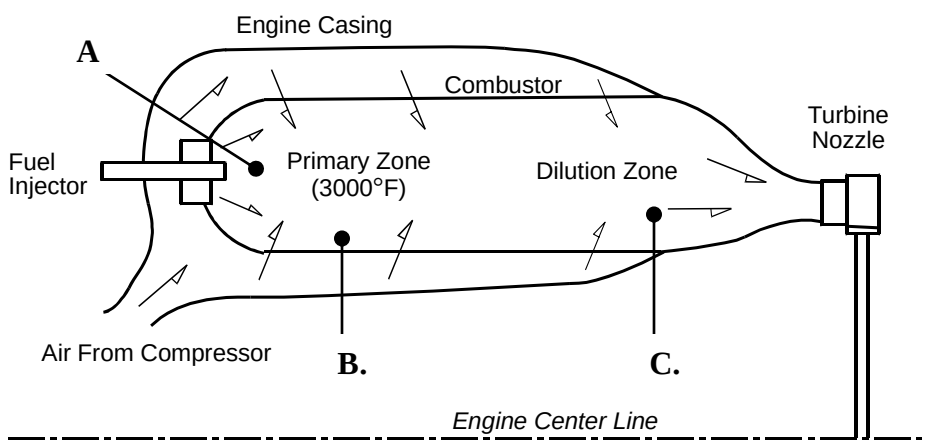
5. Determine the flow rate from a combustion source stack in standard cfm (scfm).

When: Actual (measured) flow rate = 7,000 ft^3/min
Temperature = 310ºF
Standard Temperature = 68ºF
Atmospheric pressure = 28.00 inches Hg
Stack draft at the test location = -0.05 inches w.g.

a. 4,490 ft^3/min or scfm
b. 4,600 ft^3/min or scfm
c. 6,100 ft^3/min or scfm
d. 10,210 ft^3/min or scfm

6. Which of the following correctly characterizes the relationship between wet and dry flue gases?
a. More energy is required to raise the temperature of wet flue gas than dry flue gas.
b. More energy is required to raise the temperature of dry flue gas than wet flue gas.
c. Flame temperatures are generally lower when there is very little water vapor present.
d. The specific heat of water vapor is roughly half the value of that for dry exhaust gas.

7. Where is the primary mixing zone located in the following illustration?
a. Location A
b. Location B
c. Location C
d. Turbine



8. The size of any combustion device is usually directly related to its design firing rate. The design combustor volume will also depend on which of the following?
a. Fuel moisture
b. Stoichiometric flame temperature
c. Operating pressure
d. Stack height and temperature

9. Which of the following definitions best describes *enthalpy*?
   a. The amount of air chemically required to burn fuel.
   b. An engineering term for the sensible and latent energy content of a substance.
   c. A process in which water vapor is extracted from fuel moisture by hydrogen combustion.
   d. The relationship between stoichiometric stack flow and firing rate.

10. Which of the following accurately describes *latent heat*?
   a. Latent heat is energy produced in the exhaust gas used to power industrial processes.
   b. Latent heat is approximately 5000 BTU/lb. of water vapor.
   c. Latent heat is usually designated C_p, which stands for specific heat at a constant pressure.
   d. Latent heat is not usable energy in most combustion systems.

Review Answers

1. Determine the dry gas composition. Use Figure 4-2 and 3.3% O_2 to obtain about 13.5% CO_2. Obtain the nitrogen content by difference: 100 – 3.3% - 13.5% = 83.2% N_2. The molecular weight of the dry exhaust gas is 0.832*28 + 0.033*32 + 0.132*44 = 30.3. Determine the molecular weight of the wet (total) exhaust gas as 30.3*0.9 + 18*0.10 = 29.1. The density of this gas is 29.1/385 = 0.076 lb/ft^3

   b. 0.076

2. Note that assuming a F_w value for natural gas of 10,610 [sfc/10^6 Btu] from table 4-5: F_w' = F_w*HHV/LHV=10,610*22,200/20,000 = 11,777[sfc/10^6 Btu]. Then use equation 4-18 to determine the maximum possible temperature rise from the exhaust gas O_2 content: $\Delta T = (10^6/(11{,}777*0.30))*((20.9-14.3)/20.9)*385/29 = 1{,}187°F$. The adiabatic (maximum average) temperature is the sum of $\Delta T + T_{inlet}$ = 1,187+150=1,337 °F

   c. 1,340°F

3. Equation 4-24 gives a simple approximate formula for the fraction of heat input lost in the form of hot gas leaving the stack: Q_S/Q_T = (400-75)/4200 * 20.9/(20.9-5) = 0.102.

   b. 10.2%

4. Dividing the firing rate by the energy content of a gallon of fuel gives:
   90 (mmBTU/hr)/0.125 (BTU/gal) = 720 gal/hr.
   Dividing this by 60 minutes per hour gives 12 gal/min.

   a. 12 gal/min

5. Use equation 4-14 to correct the gas volume from stack (2) to standard (1) conditions:
   V_1 = 7000 * [(68+460)/(310 +460)] * (28.00 – 0.05/13.6)/29.92 = 4491 std ft^3/min.

   a. 4490 ft^3/min or scfm

6. a. More energy is required to raise the temperature of wet flue gas than dry flue gas.

7. a. Location A

8. c. Operating pressure

9. b. An engineering term for the sensible and latent energy content of a substance.

10. d. Latent heat is not usable energy in most combustion systems.

References

1. Buschmann, J. C., and Larsson, A. C. *Worldwide Experience with Selective Catalytic Reduction.* Presented to the Institute of Clean Air Companies (ICAC) Forum '98, Durham, NC, March 18-20, 1998.

2. Clean Coal Technology. *Control of Nitrogen Oxide Emissions: Selective Catalytic Reduction (SRC)*. Topical Report Number 9. July 1997.

3. Donnelly, J.R., and Brown, B. *JOY/Kawasaki Selective Catalytic Reduction De-NO_X Technology.* Presented at the 82nd Annual Meeting of the Air & Waste Management Association, Anaheim, CA, June 25-30, 1989.

4. Durilla, M., Chen, J. M., and Speronello, B. K. *Composite SCR Catalysts for NOx Reduction*. Paper prepared by Engelhard, Inc. 1990.

5. Kokkinos, A., Cichanowicz, J.E., Eskinaze, D., Stallings, J., and Offen, G. *NOx Controls for Utility Boilers: Highlights of the EPRI July 1992 Workshop.* Air Waste Management Association, November 1992, pp. 1498-1505.

6. Sharreef, G.S., Stone, D.K., Ferry, K.R., Johnson, K.L., and Locke, K.S.. *Selective Catalytic Reduction NOx Control for Small Natural Gas-Fired Prime Movers*. Paper 92-136.06. Presented at the 85th Annual Meeting of the Air and Waste Management Association, Kansas City, MO. June 21-26, 1992.

7. Tonn, D. P., and Uysal, T. A. *2200MW SCR Installation on New Coal-Fired Project.* Presented to the Institute of Clean Air Companies (ICAC) Forum, Durham, NC, March 18-20, 1998.

8. U.S. Environmental Protection Agency. *Alternative Control Techniques Document: NOx Emissions from Cement Manufacturing*. EPA-453/R-94-004. March 1994.

9. U.S. Environmental Protection Agency. *Alternative Control Techniques Document: NOx Emissions from Glass Manufacturing.* EPA-453/R-94-037. March 1994.

10. U.S. Environmental Protection Agency. *Alternative Control Techniques Document: NOx Emissions from Process Heaters (Revised).* EPA-453/R-93-034. March 1994.

11. U.S. Environmental Protection Agency, *Code of Federal Regulations, 40CFR60 Appendix A – Test Methods*, available at www.epa.gov/ttn/emc

Chapter 5: Air Pollution Formation

LESSON GOAL

Demonstrate an understanding of how various gaseous, liquid, solid, and emulsion fuels are used in combustion sources through successful completion of the chapter review exercises.

STUDENT OBJECTIVES

When you have mastered the material in this chapter, you should be able to:

1. Describe the relationship between various fuel contaminants and the related emissions.
2. List the potential air pollutants resulting from incomplete combustion.
3. Calculate the maximum emission rate of most air pollutants from an ultimate fuel analysis.
4. Describe the formation of sulfuric acid and the resulting air pollution impacts.
5. Discuss the effects of SO_3 on the emissions from a boiler fired on No. 6 oil.
6. Describe the formation mechanisms for small (<1μm) and large (>2μm) particles in the combustion process.
7. Describe why fine combustion particulate has a chemical composition different than that of the fuel ash.
8. Discuss the effects of atomization on emissions from a No. 6 oil-fired boiler.
9. Describe how the grinding and size distribution of pulverized coal particles affects the amount of carbon in fly ash (carbon carry over).
10. Describe how and why black smoke is formed.
11. Describe the two primary NOx formation mechanisms.
12. Discuss the typical effect of excess air on NOx emissions and the trade off with products of incomplete combustion (PIC).
13. Describe the key elements necessary for complete combustion.
14. Describe the formation and control of dioxins and furans.
15. Describe how opacity is affected by the size distribution of particles in a plume.

Chapter 5: Air Pollution Formation

5.1 INTRODUCTION

Combustion sources emit a number of different pollutants that can be divided into three categories:

- *Products of Incomplete Combustion (PIC)*: black smoke/soot, CO, organic compounds, and in some cases particulate matter.

- *Pollutants resulting from inorganic contaminants in the fuel:* SOx, particulates, HCl, etc.

- *NOx*: nitrogen oxides from atmospheric N_2 and O_2 breaking down in the combustion zone and reacting

The emission rates of some of these pollutants are regulated because excess emissions could threaten ambient air quality. Note that there are air pollutants such as ozone which are not emitted from combustion sources, but which are formed in the atmosphere from combustion pollutants. For example, NOx is regulated in order to control ozone. A less clear cut example is $PM_{2.5}$ some of which is emitted directly and some of which is formed from SO_x, NO_x, or other gas phase species. Future rules may regulate various combustion emissions in order to address $PM_{2.5}$ and/or to preserve visibility in scenic areas.

The first several sections of this chapter address the first two categories of emissions listed above. The last category, NOx, occupies the largest section of the chapter. NOx is a pollutant of considerable concern, because of its relationship to ozone formation, and because the amount of NOx formed during combustion is substantially influenced by the design and operation of the combustor.

The purpose of this chapter is to explore air pollutant formation in combustion sources, while air emission control will be reviewed in the next chapter. For most pollutants this is a logical separation of topics. However, NOx formation and control are closely linked when combustion controls are used. This is addressed in part by providing a modest overlap in these two chapters in the area of NOx emissions.

5.1.1 Actual Emission Rates

The basic chemistry of pollutant formation combined with a mass balance provides a relatively simple basis for predicting emission rates of some pollutants. Unfortunately, this approach is too imprecise to be useful for predicting emissions of NOx, any product of incomplete combustion, and several other pollutants. These emission rate predictions must be based on data from actual sources. The *EPA Compilation of Emission Factors (AP-42)* is the most comprehensive compilation of data currently available. While it is produced and continually updated by the EPA, the Federal Government does not take responsibility for the accuracy or applicability of the data. When a facility underestimates emissions from a specific source it cannot attribute the mistake to the generic data in AP-42.

5.1.2 Potential Emission Rates

Conservation of mass tells us that w*hat goes into a combustor must come out* with the exhaust gases. All the inorganic species in the fuel come out in some form of pollutant, usually as gases or particulates. In addition, all combustion sources emit NO and NO_2, however the amount will vary. The sum of these two gases is termed NOx. Table 5-1 lists the contaminants of two common fuels (No. 6 oil and coal) and the resulting pollutants. Most sources burn fuel almost completely, but any of them can emit excessive products of incomplete combustion (PIC) if poorly designed or improperly operated. Boiler sources do not normally emit PIC in significant quantities; however, NOx control strategies tend to degrade combustion performance, leading to a trade off between NOx and PIC. Combustion turbines and reciprocating engines normally emit small, but potentially significant, amounts of PIC, and here too, the PIC emissions may be affected by NOx controls.

Table 5-1. Emissions Originating in the Fuel

Fuel Constituent	*Fuel Concentration*		*Pollutant Concentration*		*Primary Method of Control*
	No. 6 Oil	*Coal*	*Species*	*Conversion*	
Sulfur[1]	0.5 – 2%	1 – 4%	SO_2	99%	Low sulfur fuel
			H_2SO_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_nH_m	98%	85%	C, CO, HC	0 – small	Combustion tuning

Notes: [1] SO_4 in the fuel does not convert to SO_2 or sulfuric acid.
[2] Only organic nitrogen contributes to NOx formation.

The column labeled "Conversion" refers to the fraction of the contaminant that, based on conservation of mass, typically leaves the combustion zone as an air pollutant. Ash, for instance, can settle to the bottom of the furnace where it can be shoveled out and this portion is not a potential air pollutant. If we assume 100% conversion, the calculation of maximum potential emissions using fuel analysis and a mass balance is straight forward. All combustion source emissions can be expressed in units of pounds per million BTU (lb/mmBTU). Divide the amount of contaminant in the fuel (expressed as lb contaminant/lb fuel), by the fuel heating value expressed as (mmBTU/lb fuel), the result is (lb contaminant/mmBTU). One pound of contaminant can convert to more than a pound of pollutant if the contaminant is oxidized or combines with other species. So there is a need to specify the amount of pollutant generated by each lb of contaminant in order to determine the potential emissions in units of (lb/mmBTU). The general formula for converting fuel analysis to maximum potential emissions is:

$$\frac{\text{lb}}{\text{mmBTU}} = \frac{\%\,\text{contaminant}/100}{\text{HHV}\left(\dfrac{\text{BTU}}{\text{lb}}\right)/10^6} \times \frac{\text{lb pollutant}}{\text{lb contaminant}} \tag{5-1}$$

When the pollutant is a gas, the ratio of pollutant to fuel constituent is the ratio of molecular weights. When particulate is formed from fuel ash, the ratio of pollutant to fuel ash is unity because the fuel ash measured in the laboratory is generated in essentially the same manner as particulate is formed in a furnace.

Example 5-1.

Determine the potential SO_2 emission rate for 3% sulfur coal with HHV = 12,000 BTU/lb.

Solution:

In the case of sulfur oxidizing to SO_2 ($S + O_2 \rightarrow SO_2$) the conversion number is the ratio of molecular weights of SO_2 and S, which is 64/32 = 2 (lb of SO_2 / lb of S). So the potential SO_2 emissions from 3% S coal is:

$$\frac{0.03\left(\dfrac{\text{lb S}}{\text{lb coal}}\right)}{0.012\left(\dfrac{\text{mmBTU}}{\text{lb coal}}\right)} \times \frac{64}{32} = 5\left(\text{lb of } SO_2 \big/ \text{mmBTU}\right) \tag{5-2}$$

So 3% sulfur coal will generate, at most, 5 lb/mmBTU of SO_2 emissions. Actual emissions will be lower if any of the SO_2 is collected, combined or absorbed with other species in the combustor.

One can do a similar calculation to determine the potential emissions of any inorganic contaminant in the fuel. This sets an upper limit on the potential emissions – 100% conversion and all the contaminant is emitted. The trouble is that the conversion to air emissions is less than 100% for nearly all the common contaminants except sulfur and chloride. So while this simple mass balance sets a useful upper limit, knowing both the conversion rate and the furnace collection/absorption rate aids in determining a more useful emissions estimate from the fuel analysis.

Before discussing the individual pollutant species, note that fuels like natural gas burn relatively clean because they contain no inorganic contaminants and hence produce none of the resulting pollutants. In addition, relatively clean flue gas benefits air pollution control components such as the catalysts used to control NOx and CO. The only significant pollutants from natural, gas-fired sources are NOx and CO, and the formation of these species can usually be controlled to very low levels both in the combustion process and with catalytic control devices.

This reduced pollution formation potential is true to a lesser extent for No. 2 oil-fired sources. One exception is that ordinary No. 2 oil can contain up to 0.5% sulfur resulting in significant SO_2 emissions and potential degradation of catalyst-based control devices. No. 2 oil, being a liquid, is also not as amenable as natural gas to low NOx combustion concepts that rely on mixing fuel and air prior to combustion.

5.2 ACID GASES: SULFUR OXIDES AND HCl

5.2.1 Sulfur Oxides

Most fuels contain at least a trace of sulfur and many waste fuels contain significant amounts of chloride. These inorganic contaminants convert mostly to SO_2 and HCl gases in the combustion zone. The potential emissions can be calculated from a fuel analysis as described in the preceding section.

5.2.1.1 SO_2

As a general rule, unless a source has a SO_2 collector (usually a scrubber), virtually all the sulfur in the fuel goes up the stack in the form of SO_2 (sulfur dioxide gas). For example, a 1% sulfur oil will generate about 1.1 lb/mmBTU emissions of SO_2. So it is common practice to control SO_2 emissions by placing a limitation on fuel sulfur content, which is easier to monitor than SO_2 emissions. SO_2 remains a gas at ambient conditions after it leaves the stack but it is water soluble. Once it leaves the stack it dissolves into rain or fog droplets and can then easily adsorb onto dry surfaces.

5.2.1.2 SO_3 and Sulfuric Acid

A small fraction (less than 5%) of the sulfur in the fuel will be oxidized to SO_3 in the combustion zone or somewhere upstream of any emissions sampling. SO_3 is a gas at high temperature, but it is highly hygroscopic. As it cools below about 600°F, it will combine with water to form sulfuric acid.

$$SO_3 + H_2O \rightarrow H_2SO_4$$

As the exhaust gas cools further, the acid continues to attract water, so that at ambient conditions it is present as dilute sulfuric acid. Figure 5-1 is a schematic progression of sulfur from fuel to sulfuric acid.

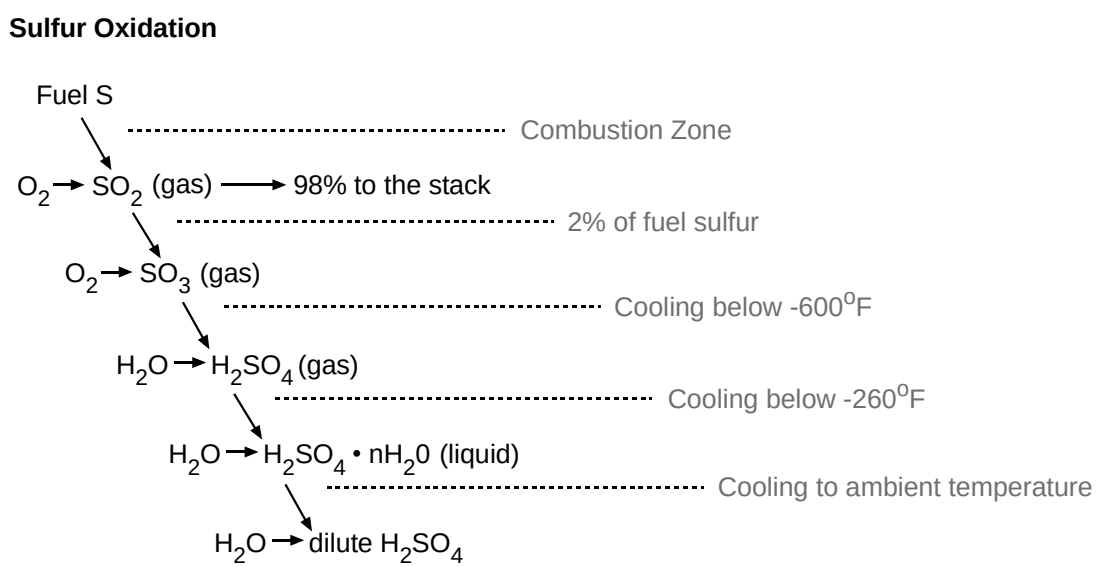


Figure 5-1. Fuel Sulfur Conversion to Pollutants

SO_3 and H_2SO_4 are different chemicals, but in the context of a combustion source, they are effectively the same thing. Once SO_3 is formed it will appear as sulfuric acid (diluted more or less) when it is emitted – unless it reacts with something to form a salt. In this text the term "sulfuric acid" includes hydrated and non-hydrated forms.

Example 5-2. Conversion of fuel sulfur to SO_3

It is estimated that 2% of the sulfur in oil that contains 1.5% sulfur will be converted to SO_3, the precursor to sulfuric acid. What will the flue gas concentration be, expressed in units of ppm corrected to 3% O_2? Residual oil has a higher heating value of about 18,500 BTU/lb.

Solution. The following three-step calculation is one of several approaches.

a. Determine the emission rate in units of lb/mmBTU. Divide the fuel sulfur content by the fuel heating value, correct the weight for the oxidation of sulfur to SO_3 and for the % sulfur conversion.

$$\frac{0.015\left(\frac{\text{lb S}}{\text{lb oil}}\right)}{0.0185\left(\frac{\text{mmBTU}}{\text{lb oil}}\right)} \times \frac{80}{32}\left(\frac{\text{lb } SO_3}{\text{lb S}}\right) \times 2\% = 0.0405\left(\frac{\text{lb } SO_3}{\text{mmBTU}}\right)$$

b. Convert this to ppm by volume, which requires using the F-factor and the density of SO_3 gas. Use a generic F-factor of 10,500 ft^3/mmBTU.

$$\frac{0.0405\left(\frac{\text{lb } SO_3}{\text{mmBTU}}\right)}{10{,}500\left(\frac{ft^3 \text{ fluegas}}{\text{mmBTU}}\right)} \times \frac{385}{80}\left(\frac{ft^3\ SO_3}{\text{lb } SO_3}\right) = 18.6 \quad 10^{-6} \quad = 18.6 \text{ ppm } SO_3$$

where 80/385 is the density of SO_3 gas in lb/ft^3

c. The f-factor gives a volume with zero excess air. The goal is to dilute this concentration with enough air to achieve 3% O_2. Use the excess air correction factor as follows

$$18.6 \text{ ppm} \times \frac{20.9\% - 3\%}{20.9\%} = 15.8 \text{ ppm } SO_3 \text{ @ } 3\%\ O_2$$

The amount of fuel sulfur converted in a combustion source to sulfuric acid is always small and the actual amount of acid emitted is difficult to predict using analytical methods. Simple chemical equilibrium models are not adequate primarily because of the catalytic influences of other inorganic fuel contaminants. For example, vanadium pentoxide (V_2O_5) is a catalyst that is used commercially to make sulfuric acid from SO_2. Vanadium is a principal ash constituent of residual oil so any source fired on residual oil is coated internally with dust and deposits containing various vanadium compounds. The amount or extent of these deposits varies with time and the extent of boiler cleaning activity. Catalytic activity depends on temperature and a typical utility boiler has surfaces at temperatures ranging from 250°F to 1200°F. So predicting the amount of SO_2 that will be oxidized is not analytically practical. On sources fired with coal or other solid fuels, the ash may contain substantial amounts of calcium or other chemically basic species. Ash with a high pH will tend to combine with sulfuric acid, neutralizing it to form solid sulfate salt. Given all these variables, simple prediction of sulfuric acid emissions has to be based on experience or actual measurements. Figure 5-2 is one set of data showing how fuel sulfur and exhaust gas oxygen affect the emissions of sulfuric acid.

Flue gas levels of sulfuric acid (sometimes termed SO_3) are generally less than 25 ppm. While the numbers are small, these emissions can have disproportionate impacts. Ambient impacts are usually most serious in areas close to the source, most notably in a plume down wash area. Sulfuric acid has a much stronger odor and is more reactive than SO_2 so even though there is much more SO_2 than acid, it is the acid that is noticeable and has the primary health impact. Note that most of the SO_2 is eventually converted to sulfuric acid at some point downwind of the stack. So, in terms of regional impacts, it may make little difference how much of the fuel sulfur is emitted in the form of sulfuric acid.

Estimate of SO_3 in Combustion Gas

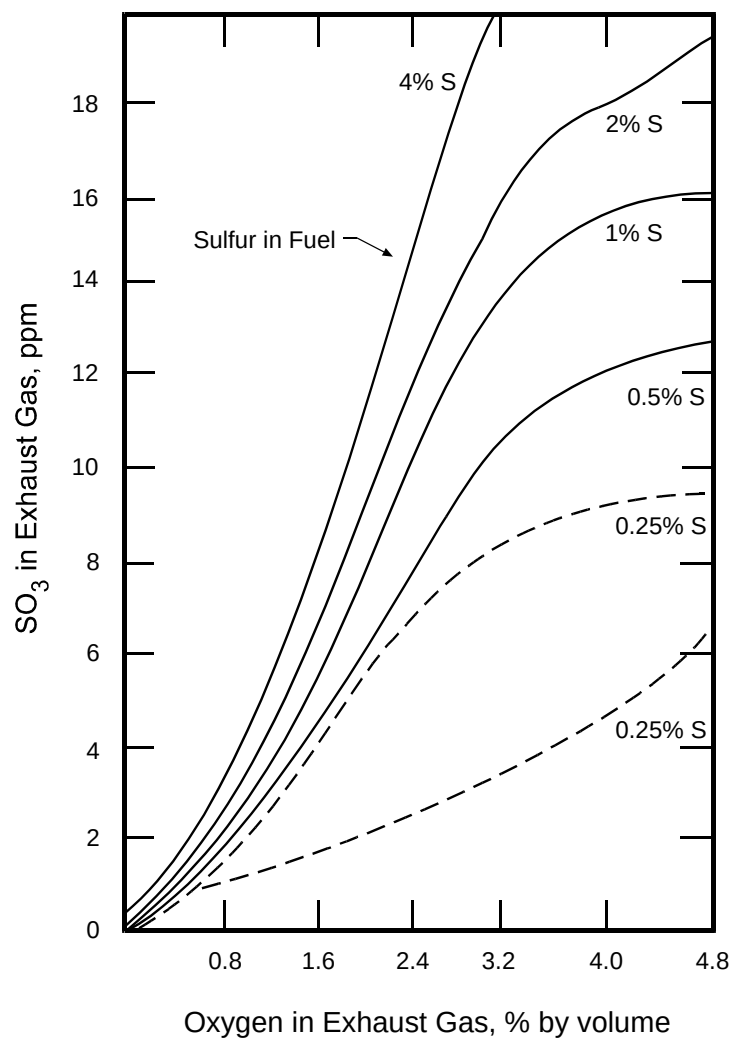


Figure 5-2. Conversion of Fuel Sulfur to SO_3

Adapted from data in the Handbook of Energy Systems engineering, Leslie C. Wilbur, Wiley-Interscience, 1985

Sulfuric acid formed upstream of the stack has two significant effects. First, if the stack concentration of SO_3 is above 5-10 ppm, it usually generates a visible plume. This is an ephemeral plume that varies in appearance depending on time of day and weather conditions. SO_3 emissions produce a classic condensation plume, usually thin or invisible at the stack exit, it growing larger and denser as it moves down wind. The plume is usually bluish white, but if the sun is low it can be reddish brown. The plume visibility (Method 9 opacity) is heavily influenced by background haze or clouds. On utility sources it can be heavy in the morning, during and after a load increase, then disappear by noon. The pollutants are usually invisible to an in-stack opacity monitor because most of the condensation occurs after the exhaust leaves the stack. So sulfuric acid can be the cause of high plume opacity readings that are hard to measure, hard to predict, and hard to control.

Second, if SO_3 condenses on any surfaces before leaving the stack (which will happen on any surface below about 260°F) it causes corrosive damage. However, the temperature at which acid condenses depends on the concentration. Figure 5-3 is the theoretical dew-point/temperature curve. In practice, the condensation temperature falls between 250°F and 280°F for typical coal- and oil-fired combustion sources. This temperature range is the main reason that designed stack temperature on most sources are seldom much below 300°F. Corrosion-generated holes in ducts tend to grow larger because the cooling effect of air leaks accelerates acid condensation and therefore accelerates corrosion. Damage to a dust collector will also eventually degrade its performance, leading to higher particulate emissions.

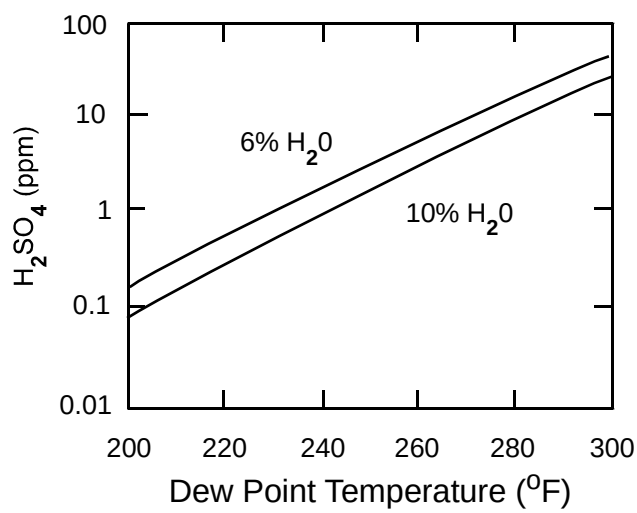


Figure 5-3. Sulfuric Acid Dew Point

Acid condensed on the surface of a duct generates deposits of fly ash, acid and metal corrosion products. These corrosion deposits eventually flake off, blow out the stack and can cause nuisance particulate fallout adjacent to the stack. The particles are large enough to fall out close to the stack rather than being carried long distances in the plume. The fallout material is easily washed away, but usually not before the acid has permanently stained the surface of a car, boat or sidewalk. The material rarely

shows up in a Method 5 particulate test, making it impossible to regulate in a quantitative manner. But it has been enough of a problem at some locations that the plant routinely paid for car washes, or even installed a car wash for its employees. So a small amount of sulfuric acid in the exhaust can create significant environmental problems even though it is the SO_2 emission impacts have been the main driving force behind sulfur related regulations.

5.2.1.3 Ash Retention of Sulfur Oxides

Sulfur oxides, particularly SO_3, react with the particulate matter derived from the fuel ash. Some types of coal have a sufficiently basic ash that it absorbs nearly all the acid produced during combustion. In these cases, emissions consist entirely of SO_2 with little or no acid emissions. The result is fly ash with significant amounts of sulfate salts, such as sodium sulfate or calcium sulfate. Some of the SO_2 may also react with fuel ash to form sulfate. Absorption of sulfur oxides by fuel ash usually accounts for less than 10% of the fuel sulfur. However, there are sources that deliberately add basic compounds to the combustion zone resulting in the conversion of most of the fuel sulfur to solids that can be removed by the dust collector. Note that sulfate, whether in the form of sulfuric acid or a sulfate salt, can add significantly to the amount of particulate in the exhaust gas.

5.2.2 Hydrochloric Acid

Much of the chloride in fuel will convert to HCl (hydrochloric acid) in the combustion zone. One may generally assume that all of the organic chlorides will be converted to HCl. Compounds like NaCl (sodium chloride) may pass through the combustion zone unchanged. In theory, a fuel that is low in hydrogen (coke or anthracite coal) can suppress HCl formation and drive the chloride to form Cl_2 (chlorine gas). However, in practice, there are not many sources that fire low hydrogen fuels with significant amounts of chloride. Cement kilns can fire low hydrogen fuels like pulverized coke, but when they burn hazardous wastes with significant chlorides, there is enough hydrogen in the wastes that the chloride is emitted as HCl rather than Cl_2. Sources that emit significant amounts of chlorine gas appear to be a special case that is left to other references. Chlorine gas in small amounts can be a factor in dioxin formation.

5.3 PARTICULATE MATTER

Particulate matter emissions are composed of fuel ash, products of incomplete combustion (PIC) and sulfates. PIC are usually a small part of the particulate emissions except for certain sources such as diesel engines. Ash is any inorganic substance in the fuel that is solid at typical stack temperatures and that survives, or is formed, at combustion temperatures. Combustion-generated particulate matter falls into two groups:

- *Large particles* – those larger than 1-2µm that are descended primarily from large fuel particles and,

- *Fine particles* – those smaller than about 1µm that are composed primarily of material that was in vapor form in the combustion zone and condensed as the exhaust gases cooled.

Large particles derive almost entirely from the breakdown of even larger particles of fuel or ash. As a general rule, large particles are responsible for most of the weight of measured particulate emissions (Method 5). Fine particles derive primarily from the agglomeration or condensation of vapors or large molecules – the opposite process from the formation of large particles. Fine particles are frequently responsible for most of the visible emissions (Method 9). This is not to say that there is no relation between opacity and particulate emissions, but the connection between these two measurements can be very inconsistent.

Typically, the primary constituents of combustion particulate from stationary sources are silicon, calcium, metals, a variety of crustal elements, and some sulfate salts. Most particulate matter is composed of inorganic elements, but it can include carbon or small amounts of high molecular weight hydrocarbons. Diesel engines emit very fine particulate composed primarily of organic material. Although the amounts are relatively small, the impact of exhaust outlets near ground level, notably mobile sources, can be very significant.

5.3.1 Particle Formation – Large Particles

There are basically two mechanisms that form large particulate matter relating to the ash and the carbon in the fuel. Fuel ash constituents, such as silicon and most metals, may melt briefly in the combustion zone, but they tend to pass through the combustion zone unaltered chemically. Usually the main physical alteration is the removal of organic (fuel) and volatile species or the change in the crystal form of certain minerals. Simply stated: whatever rocks went into the furnace, will also come out of the furnace. Pulverized coal is a good example. If coal with 10% ash is pulverized to 100µm particles and combustion burns away all the organic material, then the remaining ash particle will be about 50µm diameter if the ash has the same density as the original coal. In reality, however, the resulting particle may be a little smaller if the ash is denser than the original coal particles or may be considerably larger if it is very porous. But in either case, its composition will be very similar to the original coal ash and its size proportional to the size of the original coal particle. Figure 5-4 illustrates the formation of large particles in the combustion zone.

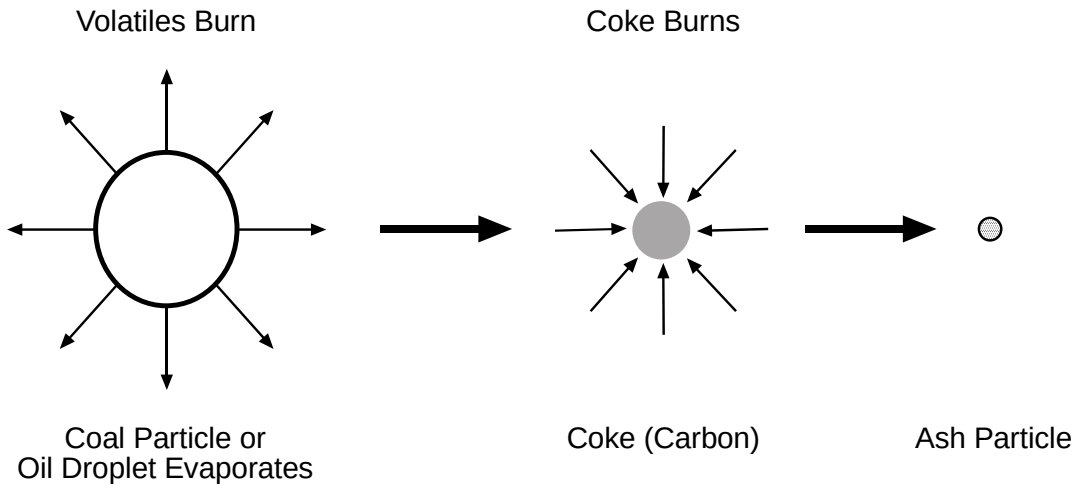


Figure 5-4. Formation of Coke and Ash Particulate

5.3.2 Particle Formation – Fine Particles

Fine particles are formed "from the bottom up"; that is, they start as atoms or molecules that condense or agglomerate into particles. These particles can grow to be large particles, but their growth rate slows by the time they reach about 0.5µm in size. This size is a kind of temporary ceiling in particle growth. The fundamental explanation for this limit is that 0.5µm is about the size where particles become too big to undergo Brownian motion. They stop bouncing around, so they stop running into other particles to combine with; therefore, further growth is much slower. Although some fine particulate can be formed by the breakup of larger particles, for the most part, fine particles are composed of chemicals that are in a gaseous or vapor phase in the combustion zone. Obviously this includes carbon, sulfur oxides, and any heavy hydrocarbons that survive combustion. It also includes any metals and minerals that are heated to liquid or vapor phase during combustion.

As the exhaust gases leave the combustion zone and begin to cool, some vapor species begin to condense on existing particles. These vapors prefer to condense on existing particles (nuclei) rather than to start new particles from scratch (nucleation). When there are no nuclei already present, and the vapors are cooled to a supersaturated condition, nucleation can occur, resulting in new particles. When this happens, a very large number of very small particles are formed. If, for whatever reason, there are already significant numbers of small "seed" particles available, the vapors will not supersaturate and will tend to condense on the seed particles. The result is usually a smaller number of somewhat larger particles. However, the subject of nucleation and particle formation is well beyond the scope of this text.

5.3.3 Pulverized Coal Particulate

Pulverized coal is ground finely enough that most of the particles are smaller than about 150µm diameter. This dust has a large surface area and it burns very rapidly after it is blown into the combustion zone. Once all the fuel is burned away there remains an ash particle – the fly ash that leaves the furnace. The small particles burn up faster than the big particles. If any of the coal particles are too large, they may not be in the combustion zone long enough to burn completely. A large particle of pulverized coal, passing through a typical combustion zone with residence time of one or two seconds will not burn completely leaving the residual particle with carbon as well as ash. The larger the original particle, the more carbon will remain in the particle. As a general rule, any coal particles larger than 150-200µm will not burn completely and the resulting fly ash will contain some carbon.

Example 5-3. Amount of particulate generated by pulverized coal combustion.

What will the particulate emissions be at the exit of a furnace (before the dust collector) fired with pulverized coal? The coal properties are 9% ash and 12,500 BTU/lb higher heating value. Assume that 10% of the ash drops out into furnace hoppers and express the answer in units of lb/mmBTU.

Solution.

Divide the coal ash content by the HHV and multiply by 90% to account for 10% of the ash that stays in the furnace.

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

Note that the potential emissions are much larger than typical regulatory emission limits. If, for example, the regulatory limit was 0.05 lb/mmBTU, the dust collector could only allow 0.05/6.48 = .0077 or less than 0.8% of the total particulate to escape.

5.3.4 Particulate from No. 6 Oil

No. 6 oil contains less than 0.2% ash, so the particulate emissions resulting from fuel ash is small. However, with No. 6 oil there are two other particulate formation mechanisms that are usually more significant than fuel ash. One is sulfate formation, discussed in a subsequent section, and the other is coke. Droplets of No. 6 oil in the combustion zone behave quite similar to particles of coal. As they are heated, volatile material is driven off leaving behind a carbon particle. If the particle is small enough, it burns up in the one-second or so of available combustion time. If it is larger than about 200µm, it takes longer than one second to burn and the residual carbon particle will leave the furnace with the flue gas. Thus the amount of particulate formed in a No. 6 oil flame depends on the amount of coke, which in turn depends on the size distribution of droplets in the fuel spray. If the oil atomizers generate a spray with a

mean droplet diameter less than about 150µm, there should be little or no particulate coke emissions. Coke emissions increase with spray droplet size for mean diameters greater than 150µm and can amount to 0.3 lb/mmBTU or more. These particles are usually large enough to be visible without a magnifying glass – 0.1 mm or more. They are called "cenospheres" and when viewed with a scanning electron microscope they look like sponge balls (see Figure 5-5). They are composed mostly of carbon plus the ash that was present in the original fuel droplet. They usually also contain some sulfate or condensed sulfuric acid.

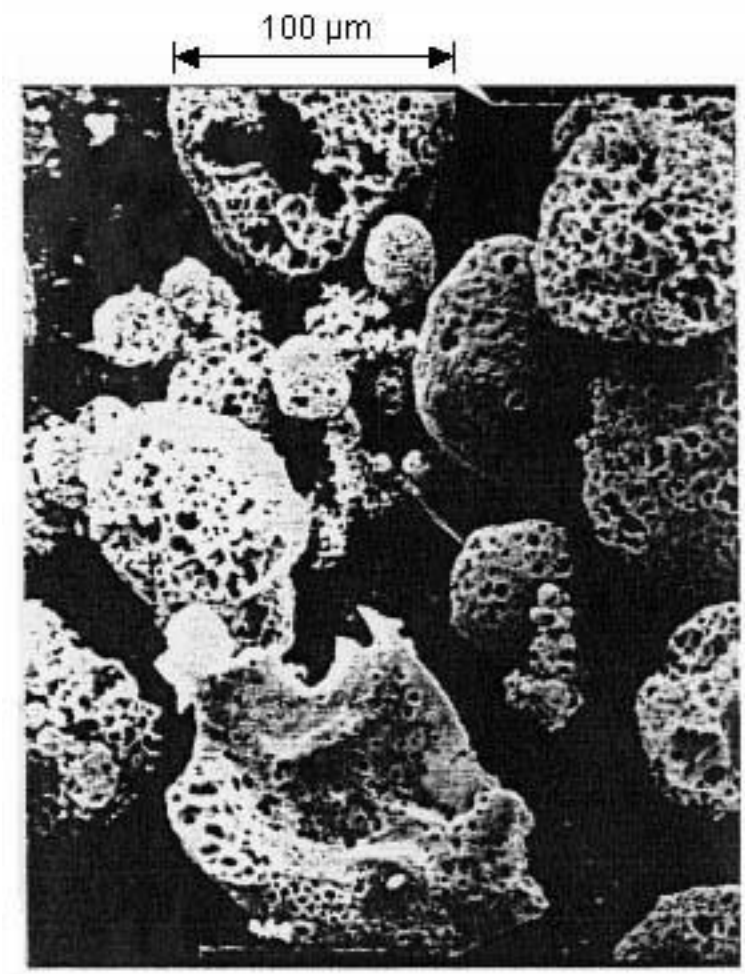


Figure 5-5. Coke Cenospheres from No. 6 Oil Combustion

5.3.5 Black Smoke

Coke carbon is the residue of fuel particles or droplets. Particulate carbon can also be formed from the condensation of carbon atoms or extremely small carbon particles generated during the combustion of vaporized fuel. These particles grow from the vapor phase; whereas, coke particles derive from the break down of larger clumps of

fuel. Fine particulate carbon is the main constituent of soot and of black smoke. This is also the main reason that a flame is white to red in color. Flame visibility is due to incandescent carbon particles, most of which are much less than 0.5µm in diameter. Fine particulate carbon forms in the flame when combustion occurs, and the hydrocarbon fuel molecules break down, but only in regions where there is not enough oxygen available to burn all the fuel. Typically both hydrogen (H^+) and CO are more aggressive in capturing oxygen than is atomic carbon.

Whenever the air-fuel ratio is below about 0.3 times stoichiometric (very fuel rich), the carbon concentration is high enough that carbon atoms agglomerate into very small particles. When liquid fuel mixes with air in the flame there is always a point early on in the process where combustion has started, but the mixture is below the critical air-fuel ratio; therefore, particulate carbon is formed and the flame becomes a bright visible yellow. Once the fine particulate carbon is formed, it does not burn up unless there is oxygen available. If enough air is not mixed in with the flame before it cools below combustion temperatures, some of this carbon (soot) will be emitted as visible black smoke. So if a visible flame is quenched, or the flame goes out before enough air mixes with the fuel, the same carbon that makes the flame visible now makes a visible black plume. This principle can be illustrated by sticking a metal spoon into a candle flame. The cold metal will quench combustion and the unburned carbon will leave a black smudge on the spoon.

Note that natural gas flames are not normally visible, except perhaps for a faint blue glow. The reason is that natural gas has low carbon content and it mixes very rapidly with air. Therefore, the air-fuel equivalence ratio is usually below 0.3 before combustion frees enough carbon atoms to create particles. There is no fine particulate carbon to create either a visible flame or black smoke. If the flame does not get enough air, the result will usually be CO or unburned CH_4, not black smoke. The faint blue glow of a natural gas flame is the radiation from CO_2 and H_2O molecules, the radiation produced from electron transitions in the molecules, not the incandescence of hot solid particles.

5.3.6 Sulfuric Acid and Sulfate Particulate

Most of the fuel sulfur burns to SO_2 and remains in gas phase long after it is emitted from the stack. But some of the fuel sulfur is oxidized to SO_3, most of which shows up as some form of sulfate ($SO_4^=$) in the particulate. On a coal-fired furnace, where the uncontrolled particulate emissions are on the order of 10 lb/mmBTU, the additional sulfate is not significant to the particulate mass emissions. But on a No. 6 oil-fired source where there is almost no ash, sulfate constitutes most of the particulate. If 2% of the sulfur in oil with 1% sulfur content is oxidized to SO_3, then sulfate will contribute about 0.03 lb/mmBTU to the emissions. In practice, on No. 6 oil-fired sources, the amount of sulfate captured in particulate emission tests varies from about 0.015 to more than 0.06 lb/mmBTU. The amount depends on a number of factors including:

- the amount of sulfur in the oil
- the amount of vanadium in the oil
- excess air levels in the combustion zone and in subsequent gas passes, and
- the amount of ash deposits throughout the boiler.

Although these factors are known to influence sulfate formation, there is no consistent quantitative relationship to the amount of sulfate formed. In short, sulfate is usually the primary contributor to particulate emissions from oil-fired sources, but the amount cannot be predicted except through experience with the facility in question.

Example 5-4. Sulfate emissions from a source fired on No. 6 oil.

A source is fired with No. 6 oil containing 1.4% sulfur and a higher heating value of 18,500 BTU/lb. If 2% of this sulfur is oxidized to sulfate, which is normally a solid or condensable liquid, what is the potential contribution of sulfates to the particulate emissions in units of lb/mmBTU?

Solution:

Divide the fuel sulfur content by the HHV to get the sulfur emissions in units of lb/mmBTU. Adjust the sulfur emissions by the ratio of molecular weights of sulfate and sulfur, and then multiply by 2%.

$$0.014\left(\frac{\text{lb S}}{\text{lb oil}}\right) \div 0.0185\left(\frac{\text{mmBTU}}{\text{lb oil}}\right)\times\frac{96}{32}\left(\frac{\text{lb } SO_4}{\text{lb S}}\right)\times 2\% = 0.045\left(\frac{\text{lb particulate}}{\text{mmBTU}}\right)$$

5.3.7 Enrichment of Some Chemicals in Fine Particles

Fine particles are formed primarily from volatile species, which means their chemical composition tends to be quite different from that of large particles. Volatile substances formed during combustion begin to condense as the exhaust gases cool. As they condense, they deposit on any available surface – which includes the surface of fly ash particles. Large ash particles have much less surface area relative to their volume (or mass) than do small particles. Since the amount of a volatile chemical deposited is proportional to the available surface area, the amount deposited per unit volume of particle is inversely proportional to the size of the particle. The layer of deposits on the surface of a large particle is relatively thin compared to the size of the original particle. In other words, small particles gather a disproportionate share of the volatile chemicals regardless of the core composition of the particles. If the large particles in coal fly ash are analyzed, their composition looks like the original coal ash. Analyze the small particles and higher concentrations of volatile chemicals are found as compared to the amounts in the original fuel ash.

Table 5-2 lists some elements that are likely to be enriched in the fine particles of fly ash of a coal-fired boiler. Most of these elements are present in the ash as oxides,

hydroxides or sulfates. The list will vary considerably depending on which elements are present in the fuel and on what compounds they are formed during combustion. The availability of sulfur, chlorine and other reactive elements can result in the formation of volatile compounds from elements that are not normally considered volatile.

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	

5.3.8 Mass Emission Transients from Soot Blowing

Most of the emissions from combustion sources have very short residence times – from the time fuel enters the combustion zone to the time the resulting pollutants are emitted into the atmosphere. In fact the only pollutants that accumulate in almost any combustion source are particulates. Ash, especially from solid fuel fired sources, accumulates on heat transfer surfaces and has to be removed to maintain the heat transfer or load capacity of the system. Boilers are designed with “soot blowers” that remove ash/dust deposits in order to maintain performance. Operators routinely use soot blowers to maintain normal operating temperatures throughout the system. Soot blowing can be continuous based on the discretion of the operator, or it may be performed periodically (once a shift, once a day, etc.). If an operator sequentially activates all the soot blowers on a big utility boiler, the complete cycle can take more than two hours. On a small factory boiler, manual operation of a single soot blower may take only 30 seconds. Whenever the soot blowers are operated, accumulated dust is released into the exhaust gas stream and particulate emissions usually increase. Depending on where the soot blowers are located and on the performance of the dust collector, the resulting emissions may increase several fold or not at all.

5.4 METALS

With the exception of mercury, all metals are in the form of particulates when emitted from combustion sources. Mercury compounds are nearly always in vapor form in combustion exhaust gases. Usually heavy metals or toxic elements are a small fraction of the total particulate. However, their classification as hazardous air pollutants (HAPs) means they are a concern independent of their contribution to total

particulate mass emissions. In addition, many of the heavy metal species are volatile in the combustion zone and they make a disproportionate contribution to fine particulate ($PM_{2.5}$) emissions. Fine particulate matter is more difficult to capture in a dust collector than large particulate matter. In addition, fine particulates are a greater health hazard. Hence heavy metals merit special attention in this course.

5.4.1 Volatility of Metals and Compounds

The fuel fed to waste combustors contains a broad spectrum of chemical compounds and sometimes contain significant amounts of lead and other heavy metals. Although they may be present in trace amounts, other fuels such as coal may contain an equally wide array of metals and trace elements. In a preceding section we showed that volatile compounds are preferentially concentrated in the smallest particles. When the volatile compounds are HAPs, this means the fine particles may be more toxic that the larger particles. Table 5-3 lists some elements, their associated combustion products, and the temperature that indicates their volatility.

Table 5-3. Vaporization of Metal Compounds

Metal	*Melting Temperature (°F)*	*Main Vapor Species*	*Temp. (°F) for one ppm*
Antimony	1166	Sb_2O_3	1220
Arsenic	1135	As_2O_3	90
Barium	1337	$Ba(OH)_2$	1560
Beryllium	2332	$Be(OH)_2$	1930
Cadmium	610	Cd	417
Chromium	3375	CrO_2 or CrO_3	2935
Gallium	86	unknown	unknown
Lead	622	Pb	1160
Molybdenum	4730	unknown	unknown
Mercury	-38	Hg	57
Nickel	2651	$Ni(OH)_2$	2210
Selenium	423	SeO_2	605
Silver	1764	Ag	1660
Thallium	578	Tl_2O_3	1330
Vanadium	3434	unknown	unknown
Zinc	787	unknown	unknown

The last column of Table 5-3 is the approximate temperature at which the compound will evaporate to a concentration of 1 ppm in the exhaust gas. This is also an indication of the combustion zone temperature required to begin to evaporate the species and cause it to concentrate in small particles. Although combustion zone temperatures can momentarily reach temperatures above 3000°F, many of these compounds require a longer time period or higher temperature to evaporate significantly. But clearly some of them are likely to evaporate during combustion and will thus appear as fine particulate at elevated levels.

This table does not list compounds that might be present if there is some form of chlorine in the fuel. Chloride compounds tend to have low melting temperatures, so chloride can cause more species to appear in the fine particulate. Obviously, the array of elements that will predominate in the fine particulate depends on how all the various inorganic species interact in the combustion zone – a subject that goes far beyond the scope of this course.

5.4.2 Mercury

Any mercury entering a combustor is vaporized and leaves in the exhaust gas. The pollutant all goes up the stack unless some of it is captured by carbon in the fly ash. So unless a combustion system includes a mercury control system, we normally assume that 100% of the fuel mercury is emitted into the atmosphere.

Public concern over mercury in the environment has risen steadily since about the time of the 1990 Clean Air Act Amendments. At one time municipal waste combustors were believed to be primary combustion source of mercury emissions. Waste control and recycling combined with air pollution control devices have substantially reduced mercury emissions from waste combustors. Coal-fired boilers were not an immediate focal point, because mercury levels in coal are very low – typically 0.15 ppm by weight. However, considering the amount of coal burned and the fact that nearly all the mercury in the coal is emitted, the air emissions from a typical power plant are on the order of one or two pounds a day. Thus power plants are coming under increased pressure to control mercury emissions.

Mercury emissions can be any or all of several chemical forms that include Hg, HgO and HgCl. The predominant form depends on temperature, excess air and the amount of chlorine in the fuel. In all cases, mercury appears in the vapor phase in typical combustion exhausts; although, it can be adsorbed onto ash particulate, particularly if the ash has a significant amount of carbon. Carbon particulate from any solid fuel fired source will be captured in a dust collector. So if a source generates considerable carbon, normally an undesirable waste of fuel, mercury in the fly ash increases and the air emissions of mercury may be reduced. Control of mercury by this, and other related measures, is discussed in Chapter 6.

Example 5-5. Mercury emissions rate.

Determine the average daily mercury emissions for an 800-megawatt power plant. The plant has a heat rate of 9900 BTU/kw-hr, and a 60% utilization factor. It burns coal with an average mercury content of 0.13 ppm and a higher heating value of 11,900 BTU/lb.

Solution.

Determine the emissions rate by dividing the mercury content by the HHV.

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

Determine the power plant fuel energy use by multiplying the rated load by the heat rate, adjusting for utilization and multiplying by 24 hours.

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

Finally multiply the emissions by the daily energy use to get the emissions.

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

So even though the amount of mercury in the coal is minuscule, the cumulative emissions are significant.

Although the chemical form of mercury emissions does not change the amount emitted, it does affect the method of measurement, which can alter the reported emission rate. Mercury tends to be scrubbed from the atmosphere by precipitation, which then transports it to water bodies where it can move up the food chain. Once in the environment it can be transformed to methyl or dimethyl mercury that is even more toxic than the inorganic forms.

5.5 NITROGEN OXIDES

5.5.1 Overview of NOx

NOx is an acronym for the sum of two compounds: nitric oxide (NO) and nitrogen dioxide (NO_2).

$$NO_x = NO_2 + NO$$

Both compounds are formed in a combustion zone, but NO usually accounts for 95% or more of the total. However, once emitted into the atmosphere, NO promptly

oxidizes to NO_2. Thus from a regulatory perspective it does not matter which compound is emitted because it will all show up as NO_2 in the atmosphere. This has led to the regulation of the sum of the two or NOx. When determining the mass of emissions we need to assign the molecular weight – in this case the number is 46, which is the molecular weight of NO_2.

Although both NO and NO_2 are toxic, atmospheric concentrations threaten air quality standards in only a few locations. Exceedances have been recorded in some heavily polluted urban areas and in the downwash from poorly designed combustion source stacks. The main reason NOx is regulated is that it is a key contributor to the formation of ozone, which is not emitted from combustion sources. Ozone is formed in the atmosphere from reactions between NOx and volatile organic compounds (VOCs) in the presence of sunlight (a so-called "photochemical reaction"). In addition to its role in ozone formation, NO_2 has a red or brown color and is a small contributor to reduced visibility – usually in or around urban areas.

There are other oxides of nitrogen, notably nitrous oxide, N_2O, which does not appear to be involved in ozone formation and is not currently regulated. N_2O is a stable compound that is usually present in small amounts in the atmosphere. But it is a powerful greenhouse gas. Like methane and CO_2, it can be formed in some selected types of combustion systems, usually in small amounts. N_2O has been used as an anesthetic (laughing gas).

NOx is the one pollutant emitted by nearly all combustion sources independent of what is in the fuel or the configuration of the combustor. The reason is that even when there is no nitrogen in the fuel, NOx is created from the breakdown of atmospheric N_2 and O_2 in the combustion zone and the subsequent reaction to form NO.

$$N_2 + O_2 \leftrightarrow 2NO \qquad (5\text{-}3)$$

5.5.1.1 Control Approaches

Control of NOx emissions is discussed in detail in Chapter 6, but it is useful at this point to know that control approaches fall into one of two categories:

- Combustion strategies and/or devices that control NOx formation, and
- "Back end" controls that destroy NOx after it is formed.

As a general rule combustion controls are relatively inexpensive to install and operate, but in most cases they have limited effectiveness. Back end controls are comparatively expensive, but they are applicable to most types of sources and they can achieve high control efficiencies. Most of the control efforts on stationary sources in the U.S. from 1970 to 1990 focused on combustion system modifications. The need for further emissions reduction is resulting in combined back end and combustion controls on both new and existing sources.

5.5.1.2 Formation Mechanisms

In order to understand combustion based NOx control technologies, one needs an appreciation of the basic NOx formation mechanisms and their relationship to different types of fuel and types of combustion systems. NOx is generated in all combustion sources, but the amount depends on:

- temperature and the flame structure including the amount of oxygen available in the peak temperature regions of the combustion zone (see Equation 5-11), and

- the amount of nitrogen in the fuel (see Eqn 5-1) in combination with the flame structure.

These two mechanisms, centered around flame temperature and fuel nitrogen, lead to the terms “thermal NOx“ and “fuel NOx”. This classification is useful in understanding what types of “low NOx “ control methods will be effective on a given combustion source.

There is a third NOx formation mechanism that we will mention; although, it is not significant in most combustion systems. Small amounts of “prompt NOx” can be formed at the flame front. Prompt NOx is formed very fast and generally in small quantities. The fact that prompt NOx formation appears to differ from the models developed by researchers for fuel and thermal NOx, is not enough to justify further exploration in this text.

5.5.1.3 Typical Emission Rates

This section presents a general overview of the primary NOx emission formation mechanisms, which is needed to understand NOx control methods. Actual or typical emission rates are not easy to predict analytically, so one must rely on experience. The EPA Compilation of Emission Factors (AP-42) is the most comprehensive compilation of air emissions experience. Note that these are average emissions for the available data and emissions from any individual source can be very different. Table 5-4 is a very limited set of data from AP-42 for uncontrolled NOx emissions.

Table 5-4. AP-42 data for Uncontrolled NOx Emissions		
Combustion Source	*AP-42 Units*	*Heat Input Units*
Combustion Turbine (gas/diesel)		0.32/0.98 lb/mmBTU
Large Diesel Engine		3.2 lb/mmBTU
Utility Boiler, 6 Oil with. 0.4% N[1]	62 lb/1000 gal. fuel	0.41 lb/mmBTU
Boiler Firing No. 2 Oil	24 lb/1000 gal fuel	0.17 lb/mmBTU
Pulverized Coal Boiler	12 - 31 lb/ton coal	0.46 – 1.10 lb/mmBTU
Wood Fireplace	1.8 lb/ton wood	0.15 lb/mmBTU

(1) Residual oil NOx emissions vary depending on fuel nitrogen content.

Note here the large difference between No. 6 and No. 2 oil, basically because of the nitrogen content of heavy oil. Note also that diesel engines produce far more NOx than any of the other sources. Some of the reasons for these emission rates are discussed in this chapter. Chapter 6 discusses control technologies for these sources.

5.5.2 Thermal NOx Formation

Thermal NOx formation by the "Zeldovich" mechanism (see Equation 5-3) requires very high temperatures. Both N_2 and O_2 are extremely stable molecules. O_2 molecules are broken apart by combustion chemical reactions and high combustion temperatures are required to break apart the nitrogen molecules. Figure 5-6 shows the theoretical equilibrium NO concentration versus temperature. Equilibrium conditions are not usually achieved in typical combustion zones, but this curve shows that temperatures approaching 3000°F are required just to push Equation 5-3 toward NO formation. In practice nearly all the NOx is formed in the hottest regions of the flame. In the hottest regions the high equilibrium level and the fast reaction rate form so much NOx that contributions from cooler regions are relatively insignificant. Figure 5-6 suggests that as the combustion gases cool, NO should decompose. While this may actually happen, the chemical reaction rate also slows as the gases cool, effectively freezing the amount of NO formed at higher temperature. In general, NOx is formed rapidly in the hottest regions of the flame and there is no further creation or destruction as the exhaust gases cool and are emitted to the atmosphere.

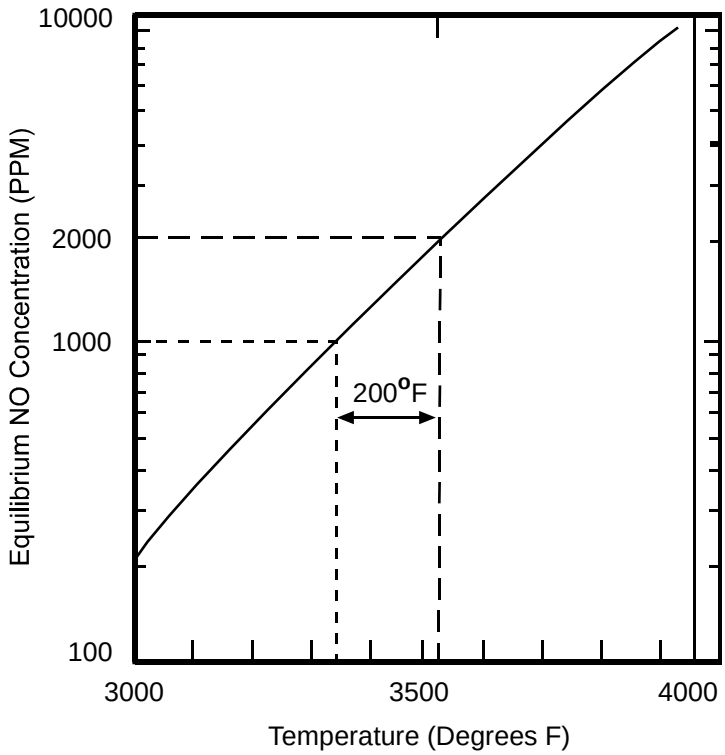


Figure 5-6. Theoretical NO vs. Temperature

Natural gas and distillate (No. 2) oil have very little nitrogen, so NOx emissions from these sources are generated entirely by flame temperature (thermal NOx). This means that NOx control concepts that reduce flame temperature are quite effective. Residual (No. 6) oil and all solid fuels have a significant amount of nitrogen and, as a general rule, more than half of the emissions from these sources originates from fuel nitrogen (fuel NOx). A control concept that reduces flame temperature will be much less effective at reducing NOx on these sources. So the type of fuel used by a source becomes a key factor in selecting the emissions control technology.

There are no simple analytical tools for predicting NOx emission levels. It is not easy to calculate either the peak temperature or the amount of flame that reaches the peak temperature; so analytical prediction of thermal NOx formation requires very sophisticated modeling. Nitrogen in the fuel can be converted either to N_2 or NOx during combustion, but the proportions depend on a number of flame details, so here again the NOx emissions caused by fuel nitrogen cannot be predicted analytically. NOx emission levels must be measured or estimated from past experience.

5.5.3 NOx Formation from Fuel Nitrogen

During combustion every nitrogen atom in the fuel will do one of two things:

- react with oxygen to form NO, or
- react with another N atom to form N_2

Chapter 6 provides a substantial discussion on NOx reduction technologies that attempt to drive nitrogen atoms to form molecular nitrogen during combustion. Fuel nitrogen is not an issue for most engines and combustion turbines because they do not normally use fuel that contains nitrogen, so this discussion is restricted to boilers or furnaces. When no low-NOx technology is applied, typical burners convert about half the fuel nitrogen to NOx. The exact amount depends on combustion zone excess air and burner design. Low NOx burner systems in boilers can reduce fuel nitrogen conversion to the range of 15% to 25%.

Example 5-6. Fuel Nitrogen Conversion to NOx

A power plant fires coal with 1.3% nitrogen and a higher heating value of 13,200 BTU/lb. If all of the fuel nitrogen were converted to NOx, what would the NOx emissions rate be?

Solution:

Use Eqn 5-1 and divide the fuel nitrogen content by the fuel HHV to obtain the fuel nitrogen emissions. Then multiply ratio of molecular weights of NO_2 and N to obtain the NOx emissions.

$$0.013\left(\frac{\text{lb N}}{\text{lb coal}}\right) \div 0.0132\left(\frac{\text{mmBTU}}{\text{lb coal}}\right) \times \frac{46}{14}\left(\frac{NO_2}{N}\right) = 3.2\left(\frac{\text{lb NOx}}{\text{mmBTU}}\right)$$

This is roughly three times the uncontrolled emission level of a typical coal-fired boiler, so we know that less than a third of the fuel nitrogen is normally converted to NOx in these systems.

Figure 5-7 is based on a nitrogen mass balance for residual oil and shows the relationship between fuel nitrogen and fuel NOx emissions. To get total NOx emissions you must add the thermal NOx, roughly 0.15 lb/mmBTU to the data in Figure 5-7. A similar figure could be drawn for bituminous coal and would show emissions about 50% higher because of the lower heating value of coal.

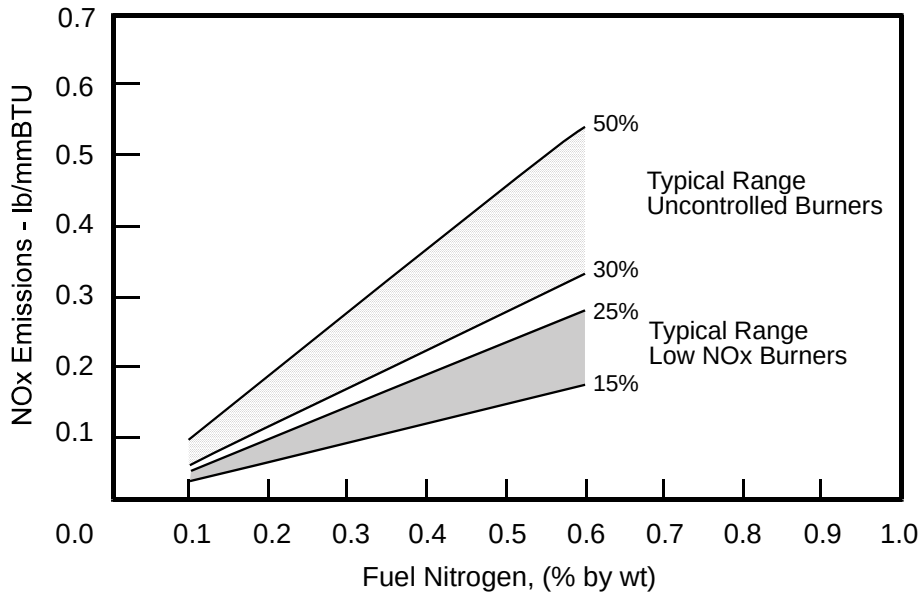


Figure 5-7. Oil Fuel NOx Emissions vs. Fuel Nitrogen Content

Fuel nitrogen content depends on the source of the fuel and it varies considerably. Although fuel with a specific limit on the sulfur content can be purchased, it is not yet practical to purchase fuel with a limit on nitrogen content.

Diluting residual oil with enough No. 2 oil to meet a nitrogen content target can create low nitrogen oil. Table 5-5 shows typical ranges for fossil fuel nitrogen contents. Natural gas may contain nitrogen, but the nitrogen in natural gas is molecular nitrogen, not organic nitrogen that could contribute to NOx formation.

Table 5-5. Typical Fuel Nitrogen Content

Fuel	*Nitrogen (% by wt.)*
Coal	0.5 - 2
Residual Oil	0.3 - 0.6
No. 2 Oil	< 0.1

Nitrogen in residual oil appears to have increased over a period of years as indicated by the data in Figure 5-8. This data is from utility plants in the eastern and northeastern U.S. One possible explanation for the increase is that the recovery methods used to draw oil from diminished reserves are pulling up crude oil that has more nitrogen. This would correlate with anecdotal reports of heavier (higher specific gravity) oil trends during the same time period.

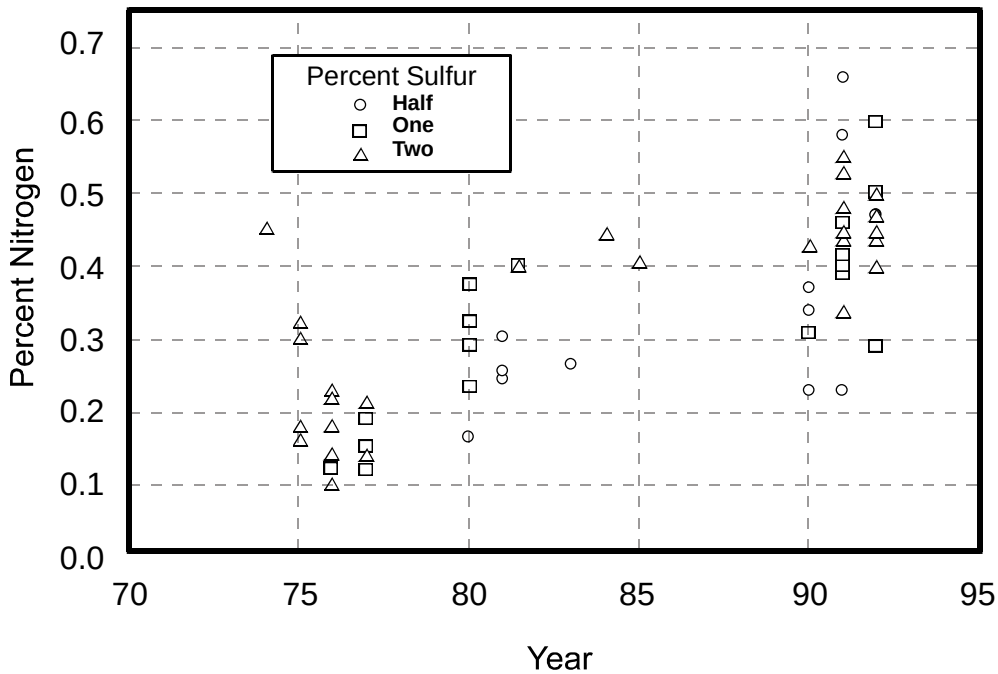


Figure 5-8. Residual Oil Nitrogen Content vs. Time

5.5.4 Premixed and Diffusion Combustion

Most combustors inject the fuel and air separately into the combustion zone where they mix and burn simultaneously; this is a diffusion flame. A few, such as natural gas-fired engines, premix the fuel and air before entering the combustion chamber where the mixture is ignited giving a premixed flame. In most cases, diffusion combustors are easier to design and operate. Only gas fuel or vaporized liquid fuels can be used in real premixed combustors. Burners that premix pulverized coal or atomized No. 6 oil could be conceptually built, but they would not be truly premixed. Only a gas can be fully premixed with air.

The difference between diffusion and premixed combustion was described briefly in association with Figure 4-5 (p. 4-29) and flame temperatures. When fuel and air are premixed, the maximum flame temperature is equal to the average flame temperature because the mixture burns at a uniform temperature. Figure 4-5 and the premixed excess air or stoichiometric ratio can be used to determine the maximum flame temperature. So the more excess air that is present, the lower the temperature will be of a premixed flame. (Refer to the right side of Figure 4-5.) Therefore, lean premixed combustion can dramatically reduce thermal NOx formation.

Now consider the diffusion flame in which fuel (pulverized coal, an oil spray or a jet of gas) is injected into the flame along with air. As each little parcel of fuel mixes with air and burns, its air-fuel ratio goes from zero (pure fuel) to whatever the final air-fuel ratio is at the exit of the combustion zone. Figure 4-5 indicates that as it passes through an equivalence ratio = 1.0, its temperature could reach the adiabatic

maximum. The fuel passes through and creates a hot spot before it mixes with the excess air and cools off to the average combustor exit temperature. So diffusion flames are locally hotter than premixed flame and thus they make more thermal NOx.

There is another factor that plays a role in NOx formation in diffusion flames, and that is the amount of oxygen or excess air that is present in various regions of the flame. NOx is not created when there is little or no oxygen available. When the air-fuel ratio is fuel rich, the left side of Figure 4-5, NOx formation is suppressed because there is not any available oxygen; and, for the same reason, combustion is not completed either. NOx formation only starts after the air-fuel mixture passes the stoichiometric point and oxygen becomes available for NOx formation. Both fuel NOx and thermal NOx formation become active only on the right side of stoichiometric in Figure 4-5. The conceptual basis for most boiler NOx control devices is to accomplish most of the combustion on the rich side of stoichiometric, then add enough excess air to finish combustion without creating a lot of NOx.

At the present time the only combustion devices that premix fuel and air are gas or gasoline-fired reciprocating engines and gas-fired combustion turbines with dry low NOx combustors. Attempts to vaporize No. 2 oil have been demonstrated in combustion turbines, but these systems run into durability problems. They tend to develop coke deposits in the process of continuously vaporizing fuel for long periods of time. Residual oil and all solid fuels can only be fired in diffusion flame combustors.

5.5.5 NOx from Typical Combustion Systems

Most of the NOx control efforts of stationary sources prior to about 1990 involve changes to combustion systems to reduce NOx formation. While back end NOx controls are becoming increasingly important, the design of *low NOx combustion systems* will continue to be an important element in NOx control. There are many types and configurations of combustion systems and low NOx systems are site specific. One aspect of combustion and NOx formation that is common to all systems is the difference between premixed and diffusion flames.

Combustors can be divided into three general categories:

- Furnaces & boilers
- Reciprocating engines
- Combustion turbines

These combustion systems are all very different as are the NOx control strategies. In all cases NOx is formed in the combustion zone, then emitted into the atmosphere through an exhaust pipe.

All large combustion systems operate continuously over some load range and most have continuous operator supervision. They are not “off-on” devices like a residential furnace or water heater. This means that emissions may be an issue not

just at full load, but also over the load range. In fact, emissions during start-up or shut-down, which can be lengthy, may also be an issue.

5.5.5.1 NOx from Boilers and Furnaces

Boilers burn a wide variety of fuels at atmospheric pressure. They range in size from home furnaces to electric utility boilers that stand 200 feet high and burn oil at a rate of 800 gallons/minute. A boiler consists of a firebox where the fuel is burned followed by banks of tubes where heat from the combustion gases is transferred to water or steam. Combustion temperatures are in the range of 3500°F and the flue gases are cooled to about 300°F at the stack.

Boilers have separate systems to supply fuel and air to the combustor and there are automatic controls driving these systems. Fuel is supplied at a sufficient rate to satisfy boiler load demand. Air is supplied at a rate that matches the fuel flow. If the controls supply insufficient air, combustion will be incomplete and the boiler will smoke. So the controls always supply a bit more air than it takes to prevent the boiler from smoking. Air flow to the boiler is generally characterized by the amount of excess air, which is the amount above and beyond that which is theoretically required for complete combustion. It is measured by the amount of O_2 in the flue gas. This O_2 is associated with the air that was not consumed during combustion, so by definition it is "excess". Figure 5-9 shows the general relationship between excess air (or stack O_2) and emissions of NOx and CO. The figure illustrates the general form of the data if one were to systematically vary the excess air while measuring NOx, CO and O_2 in the flue gases. This same type of behavior will be observed on all boilers and furnaces. It would also hold true for combustion turbines and many reciprocating engines, except that it is not practical to systematically vary the excess air levels on those sources.

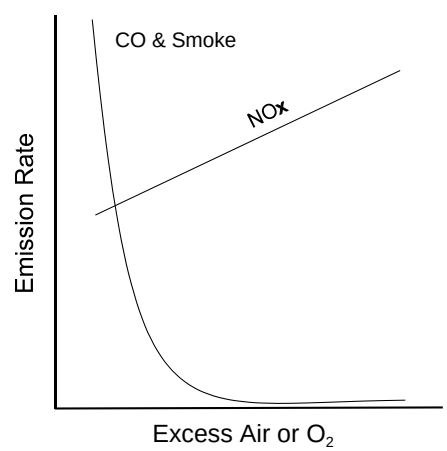


Figure 5-9. Typical NOx and CO vs. Excess Air

Figure 5-9 shows NOx increasing with excess air and this behavior is true on all suspension-fired furnaces and boilers, regardless of fuel type. We know from Figure 4-5 (p. 4-29) that the average combustor temperature decreases with increasing

excess air. That should mean that NOx also decreases, but Figure 5-9 shows the opposite. The reason that NOx increases with excess air is that as we increase excess air, more and more of the combustion is occurring in a region with extra oxygen. An increasing amount of the flame volume is to the right of stoichiometric in Figure 4-5, so more of the flame can generate NOx. Since all boilers operate with diffusion flames, all the fuel has to pass through stoichiometric as it mixes with air. As we increase excess air we simply move more of the flame from fuel rich to air rich and NOx increases proportionately.

Figure 5-9 illustrates several important points. First note that CO emissions (black smoke will behave similarly to CO) are negligible at high excess air levels. As excess air is reduced, CO appears abruptly and increases rapidly; this is commonly referred to as the knee in the curve. NOx, on the other hand, decreases almost linearly as excess air is reduced. There is an optimum excess air operating point near the knee in the curve where NOx is minimized, but where CO (and/or smoke) is not excessive. Any further reduction in excess air would reduce NOx at the expense of significantly increased CO or smoke. Any increase in excess air will increase NOx without reducing CO. In general, on nearly all combustion systems, emissions control will be a compromise between NOx and CO, or smoke. To some degree, one must trade one type of emission for the other.

This highlights the need to control air flow precisely on any combustion system that is attempting to minimize NOx. Air flow needs to be maintained near the minimum practical (not quite smoking) level. The automatic air flow control system needs to do this continuously as the boiler load changes. Precise control of excess air is the first and most important step in controlling emissions from boilers and furnaces. This can only be achieved by using an O_2 monitor tied into an intelligent (microprocessor based) control system.

5.5.5.2 Fuel Effects on Boiler Emissions

It is useful, from a NOx perspective, to divide fuels into three categories:

Category No. 1: Clean fuels (natural gas and distillate oils)
Category No. 2: Residual oil, pulverized (powder) coal, and sander dust, and
Category No. 3: Solid fuels

Clean fuels contain very little nitrogen, which means that NOx from these sources is generated only by the heat of combustion (thermal NOx). Generally, simply lowering the flame temperature can reduce NOx. Note that most engines and all combustion turbines only burn clean fuels. Fuels in categories No. 2 and No. 3 contain enough nitrogen that it accounts for much or most of the NOx emissions. Flame temperature based controls are much less effective with these fuels, so effective NOx reduction requires some form of staged combustion (*low NOx burners*) or back end controls.
We have separated solid fuels (coal, wood, etc) into two categories because there are two very different types of combustors. When fuel is divided into fine particles (a

powder or atomized spray), it burns very rapidly; typical residence times are less than ½ second. However, by contrast, a small lump of coal, a wood chip, or material in solid waste will take a minute or more to burn. Category No.2 fuels are sprayed into the combustion chamber and burn in suspension with no significant settling of particulate matter. Category No. 3 fuels settle to the floor of the furnace where they burn on a grate, similar to the fire in a home fireplace.

From the perspective of NOx control, suspension burning (Category No. 2) offers the opportunity to control the fuel and air mixing in the flame in a way that affects NOx formation. Grate burning (Category No. 3) offers very little ability to control the combustion. Hence stoker furnaces (stoker coal, wood chips, and solid waste) offer a very limited opportunity for combustion-based NOx controls. They are amenable to the relatively new technology of *reburning*, but for the most part NOx reduction from these units is achieved by back end controls.

Although boilers come in all sizes, many of the basic features are common to all of them. Size does have some influence on NOx emissions and NOx controls. First, small boilers usually burn clean fuels, while larger boilers burn the least expensive fuel available, which usually means higher NOx emissions. Second, while industrial boilers generally have only a single burner, large utility boilers have multiple burners, anywhere from 12 to several dozen. This has both advantages and disadvantages when it comes to NOx control. The advantage is that low NOx staged combustion firing can frequently be achieved by taking one or more burners out of service, which typically does not reduce the full load capability. However, the disadvantage is that low NOx operation requires that each burner get the same amount of fuel and air; each one needs to operate at the same air-fuel ratio. While this seems like a straightforward requirement, it can prove very difficult to achieve in practice.

5.5.5.3 NOx from Reciprocating Engines

Reciprocating engines, similar to a car or truck engine, are used for stationary power sources. Land based engines fire either natural gas or No. 2 (or diesel) oil – clean fuels. Combustion occurs at very high pressure (several hundred psi) and at high temperature. Temperatures are particularly high because the compression temperature, before ignition, is on the order of 1000°F. As a consequence of very high temperatures, NOx emissions are high, roughly 10 times the emissions from a boiler burning the same amount of fuel. Note that transportation vehicles generate more NOx in the U.S. than do stationary sources.

Reciprocating engines typically are designed to run on either gas or distillate oil. Although marine diesels commonly use residual oil, this is rare for land based engines. In a diesel engine, the diesel oil is injected into the cylinder where the compression temperature is high enough to ignite the fuel. Injection is normally timed for maximum power, which means just before the piston reaches the top of its stroke. Delaying (retarding) the injection timing reduces both power and NOx emissions. Excess air levels on diesel engines vary from near zero when under heavy load to very high levels when load is reduced. The reason this occurs is that air flow

is determined by engine speed while fuel flow is determined by load. Air and fuel flow are controlled independently, and excess air varies with speed and load.

When operating on gas, the fuel is premixed with the incoming air and is ignited with an electric spark from the spark plug. The mixture has to be fairly close to stoichiometric to be ignitable. If the mixture is too lean, the engine stops running; if it is too rich, it smokes. Engines are characterized as lean burn or rich burn depending on whether they are designed to run with an exhaust O_2 level more or less than 1% O_2, (i.e., about 5% excess air). Figure 5-10 shows the theoretical relationship between air-fuel ratio and emissions. Rich burning invariably generates CO, hydrocarbons and smoke and slightly reduced power. Lean burn engines operate slightly above stoichiometric where NOx emissions are high, but PIC are low Figure 5-10 helps to illustrate why NOx emissions are high from all types of reciprocating engines. Standard engines require an air-fuel ratio near a stoichiometric ratio of one in order to ignite the mixture. So engines won't run in the low emission region on the right side of Figure 5-10. Viable concepts for dramatically reducing emissions from both rich burn and lean burn engines are discussed in Chapter 6. However, the news is much less promising for diesel engines where diffusion flames thwart low NOx concepts.

Reciprocating engines are factory built as opposed to many boilers that are built on site. In contrast to boilers, their combustion systems and operating controls are built-in and not amenable to simple adjustment or alteration. Any changes or alterations to the engine are usually provided by the manufacturer or developed in conjunction with the manufacturer. This is in contrast to boiler burners that are readily adjusted, modified or changed completely. Thus engines generally have much more predictable NOx emissions than boilers.

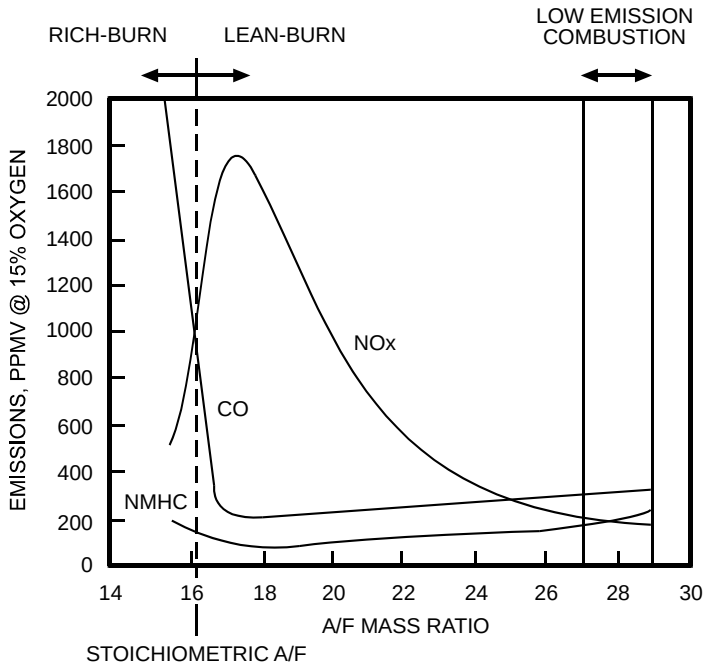


Figure 5-10. Emissions vs. Excess Air for Gas-Fired Engines

Environmental Protection Agency. Alternative Control Techniques Document: NOx Emissions from Stationary Reciprocating Internal Combustion Engines, July 1993, EPA Report 453/R-93-032, NTIS PB94-104494.

5.5.5.4 Combustion Turbines

Combustion turbines are aircraft "jet" engines adapted for stationary power sources. Combustion in turbines is steady state; starting the engine corresponds to establishing a stable fire in the combustor. The new "dry low NOx" turbine combustors premix fuel and air, but all earlier combustors have a hot diffusion flame that generates relatively high NOx emissions.

Combustion turbines can, in concept, burn any liquid or gaseous fuel. But in practice they only burn clean fuels, and the cleaner the better. Any contaminants in the fuel will eventually deposit on the turbine blades leading to frequent and expensive maintenance. So, for the most part, NOx is the only significant emission from gas turbines. Uncontrolled NOx emissions from turbines are higher than from boilers, but water injection has kept NOx emissions from diffusion-flame units relatively low beginning in the mid 1970s.

Like reciprocating engines, the NOx emissions from gas turbines are very predictable because there are no "non-factory" variations from one engine to another. Given the engine load and ambient conditions, NOx emissions can typically be predicted about as accurately as they can be measured by an emissions monitoring system. NOx emissions will vary predictably with ambient conditions unless there is a NOx control device that is programmed to compensate. It is common practice to integrate NOx control with the turbine fuel control. Any increase in ambient absolute (not relative) humidity will reduce NOx emissions. The reason is that water vapor has a very high specific heat, so as high humidity cools the flame, NOx emissions decrease. The effect can be significant in areas with humid summers or if the engine inlet has a fogging system designed to increase engine power on hot days.

5.6 SMOKE, CARBON MONOXIDE AND ORGANIC COMPOUNDS

If combustion is complete there will be no products of incomplete combustion (PIC) and no emission of black smoke, CO or organic compounds. Most stationary sources come close to this ideal most of the time so emission of PIC are not a major concern. For many sources, small or moderate amounts of PIC are emitted during initial start-up and drop to negligible levels as soon as the combustor is warmed up.

As a general rule, black smoke and CO are the primary PIC [normally black smoke is composed of fine particulate carbon]. The amount of organic compounds is nearly always less than the amount of CO – in most boilers organic compounds are at non-detectable levels even when there is significant CO and/or visible smoke. The amount of organic compounds from combustion sources is isn't normally sufficient to create a visible mist or white plume, except during start-up. So a visible white plume usually represents water vapor or inorganic species, not PIC.

5.6.1 Complete Combustion and Fuel-Air Mixing

When fuel is burned there is a complex series of chemical reactions leading to the final products of H_2O and CO_2. The last reaction in the string is normally the oxidation of CO to CO_2. Thus when there is a low level of CO in the exhaust it is a strong indication that all the hydrocarbons have been consumed. Viewed in another way, boiler combustion zone exit temperatures are typically 1800°F or above. Practical experience shows that when there is CO remaining at the furnace exit, it does not burn up and will appear at the stack; in effect it stops burning at about 1800°F. Virtually all hydrocarbons break down at temperatures in the range of 1400°F to 1600°F. So when CO is low, one is virtually assured that combustion is complete and that hydrocarbons are destroyed. In practice, the minimum CO levels from boilers are in the range of 5 to 50 ppm. Hydrocarbons are highly unlikely to be present when CO is less than 200 to 300 ppm and, depending on the source, may not be measurable even at CO levels of 2000 to 3000 ppm.

The key elements of complete combustion are:

- An effective air-fuel mixing pattern. This is mostly a matter of burner geometry to control the injection flow pattern of fuel and air. Pulverized coal must be finely ground and residual oil must be finely atomized. In a stoker, the fuel must be evenly distributed on the grate and the overfired air pattern must provide effective mixing.

- Sufficient O_2, meaning precise operational control of excess air.

- The absence of cool combustion quenching regions in the flame. This is mostly a matter of combustion chamber geometry, but the cold walls of a reciprocating engine combustion chamber are unavoidable. Too much air in the wrong place can also quench the flame.

Some texts offer a rather simple criteria for good combustion, touting the need for adequate *time, temperature and turbulence*. – the "3 T's of combustion" While these are certainly basic combustion parameters, they are seldom helpful in assessing combustor performance or in resolving problems. Given a good flame pattern (e.g. mixing pattern), the trouble with these parameters is:

- Combustion is normally very fast, tenths of a second or less, and simply increasing residence time in a combustion chamber will not solve an underlying problem of ineffective mixing caused by poor combustor design. Residence time is relevant to basic combustion design but is seldom a useful consideration when evaluating an existing combustion system.

- Adequate temperature to drive the combustion chemistry is an automatic result of good combustion in most combustors. Incinerators are the only devices where adequate temperature is an issue. Good thermal oxidizers achieve essentially

100% destruction of organic compounds at about 1400°F. Solid waste incinerators and stoker furnaces require higher average temperatures because of unavoidable temperature stratification and cold spots. In general, raising the temperature on these devices is an expensive way to mask an underlying problem of an ineffective air-fuel mixing pattern.

- High turbulence is generated by high velocity air fed through the burner, which results in a high-pressure drop. Pressure drop does not need to be large in a well-designed burner, as witnessed by most of the burners in existence. Gas turbine combustors, with very high intensity combustion, require a pressure drop of less than 3% of the total pressure. Boiler burners operate well at a 1% pressure drop, about 4 inches w.g. High turbulence, or pressure drop, is not a fundamental requirement for good combustion although it may be required to achieve rapid mixing. Turbulence or pressure drop alone tells little about how well the fuel and air are mixing.

5.6.2 Burner Geometry

Burner geometry, as discussed in Chapter 2, governs air-fuel mixing. The basic objective is to completely mix, at a molecular level, all the fuel with all the air. Mixing has to be substantially completed within the flame zone – meaning that it has to be fast. Outside of the flame zone temperatures drop, chemical reactions slow down, and PIC emissions may result. The flow pattern in the flame is controlled almost entirely by the air flow pattern emerging from the burner (e.g., it is governed by the burner air distributor geometry). Air-fuel mixing is controlled primarily by the fuel injection pattern and the size distribution of fuel particles. A secondary factor is the flow and turbulence pattern established by the air. Thus the various geometric aspects of the burner govern air-fuel mixing. A well-designed and adjusted burner will give complete combustion and negligible PIC emissions, provided the firing rate and the excess air levels are within the normal range of the burner.

Having emphasized rapid mixing, low NOx burners introduce another twist. Low NOx burners are explored in detail in Chapter 6, but a key element is to control the mixing very precisely in a way that seems to contradict traditional good combustion. Combustion is staged and the flame is lengthened. PIC may increase slightly, but NOx is substantially reduced.

5.6.3 Excess Air

Excess air was discussed qualitatively in Chapter 2 and quantitatively in Chapter 4. All combustors need a certain minimum amount of excess air to minimize CO and smoke. A well-designed burner will operate at very low excess air levels without producing PIC. In fact, burner performance is characterized by the amount of excess air required to minimize CO and smoke. The best boiler burners will operate with less than 5% excess air or about 1% O_2. Reciprocating engines fired on gas or gasoline also operate in this excess air range.

In the days when the main objective of combustor operation was to minimize PIC, the only requirement for air flow control was to maintain sufficient excess air to eliminate smoke. With the advent of NOx control requirements, air flow must be controlled much more precisely; it must continuously be just enough to minimize PIC and minimize NOx emissions.

Note that while insufficient excess air is the most common cause of PIC emissions, they can also be generated by very high excess air levels, which can reduce average temperatures to the point of local flame quenching.

5.6.4 Incinerator Temperatures

As noted in Chapter 2, most well designed thermal oxidizers achieve complete hydrocarbon destruction at temperatures of about 1400°F. When incinerators and oxidizers require higher average or exit temperatures to destroy organic species, the reason is usually that the temperature is not uniform and the higher average temperature warms up the cool spots. In a thermal oxidizer, which destroys organic gases, good performance can be obtained by adjusting the combustor geometry to achieve effective mixing and thus uniform temperatures.

Figure 5-11 shows the theoretical destruction efficiency of certain hazardous organic materials as a function of residence time and temperature. The curves were drawn for typical solvent materials. Note that there is a fairly sharp temperature demarcation between little effect and complete destruction. Clearly there is no advantage to operating at temperatures far above the destruction temperature. Note also that there is not much difference between a residence time of about 0.5 and 2.0 seconds – the range of practical interest. Long residence time reduces the required temperature by a very small amount. The curves tend to reinforce the point that a well-designed thermal oxidizer does not need either a very high temperature or a long residence time to work well.

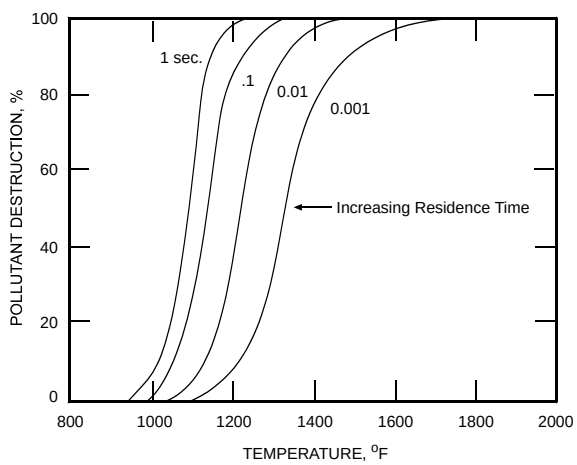


Figure 5-11. Organic Material Destruction vs. Temperature and Time

Solid waste incinerators will inherently have substantial temperature variations in the combustion zone. Good design of the fuel feed and overfired air systems can minimize these variations, but average exit temperatures above 1600°F to 1800°F are typically necessary to achieve complete combustion in the coolest areas. If a solid waste combustor is poorly designed or improperly operated, exit temperatures as high as 2000°F may not be sufficient to achieve complete combustion. Note that when operating a solid waste incinerator, excess air levels of much more than 100% (10.5% O_2) will drop the average exit temperature to the point that some flame quenching and incomplete combustion are likely (see Figure 4-5).

5.6.5 Dioxin-Furan Formation

Polychlorinated-dibenzo-dioxins (PCDD) and polychlorinated-dibenzo-furans (PCDF) are very toxic compounds that are chemically stable and environmentally persistent. Their toxicity combined with their ability to accumulate in the food chain has led to regulation at levels measured in nanograms per cubic meter of exhaust gas. They are produced almost exclusively by combustion systems when the fuel contains chlorine. In addition, there must be some level of incomplete combustion because organic species cannot be created once all the carbon has oxidized to CO or CO_2. Solid waste incinerators are the sources most likely to meet these conditions and, indeed they have been a significant source of PCDD and PCDF. Attempts to reconcile the amount of PCDD in the environment with the amount emitted from various sources have led to conflicting conclusions about which sources are the largest contributors. Other sources include forest fires and automobiles – where the amount of chlorine in the fuel is very small, but the amount of fuel burned is very large. Utility boilers probably emit some PCDD, but the amount of organic material in their exhausts is undetectable by normal test methods and PCDD would have to be generated from carbon.

Dioxin-furan formation can be eliminated by completely burning the fuel. The most efficient method of generating dioxins is to incompletely burn chlorinated aromatic compounds such as chlorinated phenols once used as coolants in electric transformers. Any time there is a fire in an old transformer, downwind or adjacent areas are heavily contaminated with dioxins. Perhaps the next best way to emit dioxins is to incompletely burn any chlorine containing waste – such as PVC plastic. Municipal and hospital waste incinerators built before 1980 frequently fit in this category. Most of these sources generated substantial amounts of dioxins during combustion, although most of them have been regulated out of existence.

Research since about 1990 has shown that dioxins and furans can be created in the exhaust gas after the combustion zone – primarily at temperatures in the range of 250-300°C (480° - 570°F), which can include the normal operating temperature of a dust collector. The mechanism is a chemical reaction between organic PIC and molecular chlorine (Cl_2) in the presence of fly ash that apparently acts as a catalyst. This synthesis apparently requires a time span of several seconds. The way to avoid dioxin formation is (1) to completely burn the fuel, and (2) to cool the gas rapidly

through the critical temperature range of 250°-300°C. This basically means avoiding the installation of a dust collector or a long duct where the exhaust gas is in the critical temperature range. A baghouse operating in the critical temperature range can be particularly troublesome because flue gas passes through the filter cake, which appears to be a catalyst for dioxin formation.

There is some evidence that dioxins might be formed from carbon; although this appears to be much less efficient than forming dioxins from organic material. This possibility reinforces the need for the dust collector to operate well outside of the 250°-300°C temperature range.

5.7 OPACITY

Plume opacity regulations and measurement procedures were first promulgated in the mid 1970s as a surrogate to particulate test methods. Opacity regulations were based in part on the reasoning that the amount of particulate should be related to the relative opacity of the plume. Particulate testing is cumbersome, time consuming and usually gives the source ample opportunity to prepare for the test. The resulting data shows the capabilities of the source, but may have little bearing on its normal performance. Opacity monitoring by Method 9, on the other hand, can be performed at almost any time and at a considerable distance from the source. So opacity monitoring by trained observers was intended to provide an indication of how well a source was complying with a required particulate emission rate. However, since there is not a clear correlation between opacity and particulate emissions, the opacity requirements are enforceable separately from the particulate emission requirements.

With certain sources, such as pulverized coal-fired boilers equipped with electrostatic precipitators, the particulate emissions rate usually correlates fairly well with the relative opacity. On average, these sources have emissions less than about 0.1 lb/mmBTU when the plume opacity is less than about 20%. However, on other sources the quality of the correlation can deteriorate rather badly. The first difficulty with trying to relate opacity to particulate emissions is that opacity depends as much on particle size as it does on mass of emissions. Figure 5-12 is the theoretical relationship between particle size and opacity. The ordinate shows the relative opacity of a fixed amount (mass) of particulate distributed in a fixed volume of air. For particulate matter larger than 1-2µm, the opacity is inversely proportional to particle size. 5µm particles will generate 10 times the opacity of the same amount of material in 50µm particles. As particle size approaches the wavelength of visible light (0.4 - 0.7µm), the relative opacity depends on particle composition as well as particle size.

A coal-fired power plant with an electrostatic precipitator will emit particulate with a fairly constant size distribution. The precipitator controls emissions and the size distribution does not change dramatically as precipitator performance changes. So opacity variations generally reflect changes in particulate mass emissions. If the

source has a baghouse, then this correlation breaks down. When emissions increase because of holes developing in the bags, there is a change in the size distribution of particles being emitted. Particles are no longer the tiny particles that seep through the filter. Particles going through holes in the bags have the same size distribution as the inlet particles. This means the particulate emissions from a baghouse-controlled source can increase substantially with little impact on plume opacity.

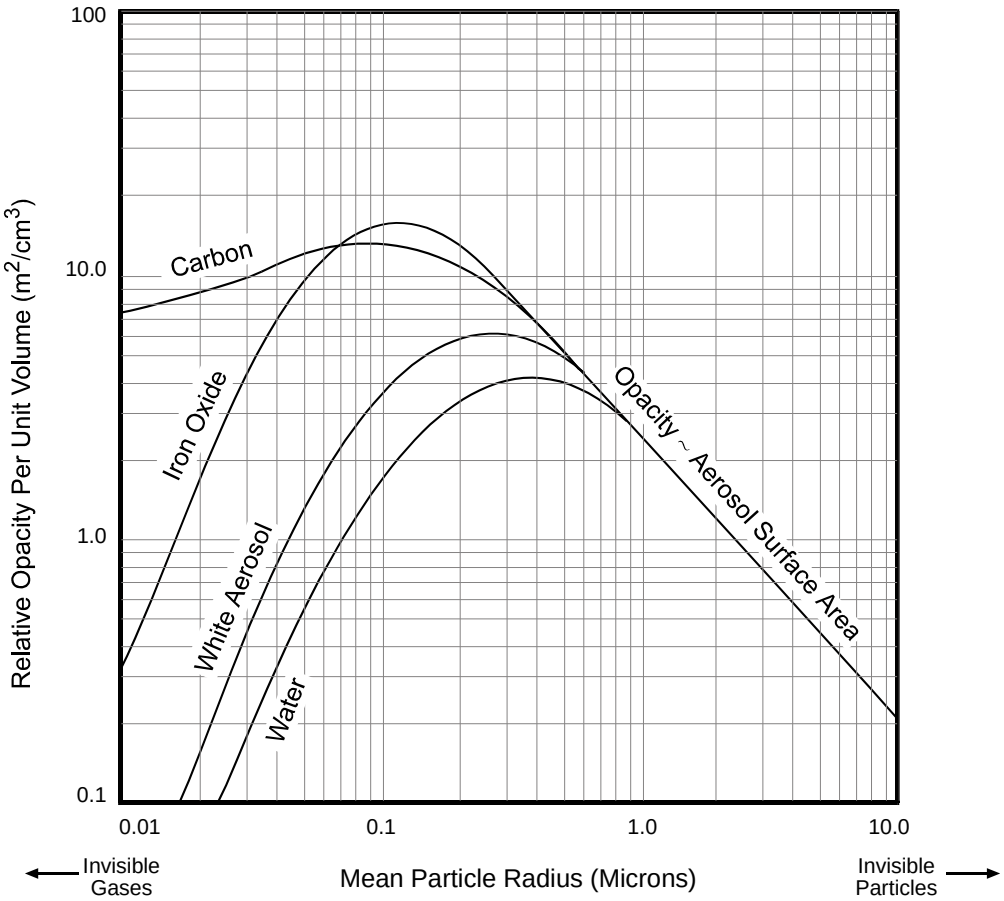


Figure 5-12. Dust Opacity vs. Particle Size
Interpretation of data by Ensor & Pilat, 1975

The correlation between opacity and emissions rate on a residual oil-fired source is capricious. Black or gray visible plumes, associated with low excess air, are caused by submicron soot, which has maximum opacity, but relatively little mass. If the source emits coke from poorly atomized oil, the mass emissions can be large, but these 100+µm particles are essentially invisible in the plume. So this source can have a highly visible plume with low emissions or an invisible plume with high emissions. In short, plume opacity tells almost nothing about the particulate mass emissions from a residual oil-fired source.

Sulfuric acid in the exhaust introduces further complications. The acid will contribute significant mass to a Method 5 (filter) test depending, to some extent, on

the operating temperature of the test equipment. Although it is not normally visible in the stack it may generate a highly visible condensation plume after it leaves the stack. The plume can be clear at the stack exit, but increase steadily in both dimension and opacity as it moves downwind. Both the visibility of the plume and its color depend on the angle of the sun and other atmospheric factors.

Plume opacity observations are an effective way to gauge the visual impact of a source, but they may or may not be related to the particulate mass emissions rate.

5.8 CONCLUSION

This chapter explores air pollutant formation in combustion sources, while the next chapter reviews air emission control. For most pollutants this is a logical separation of topics. However NOx formation and control are closely linked when combustion controls are used. This linkage is addressed in part by providing a modest overlap in these two chapters in the area of NOx emissions.

Air emissions from combustion sources are generated by inorganic elements in the fuel, by incomplete combustion of the fuel, and, in the case of NOx, simply by the heat of combustion. The maximum possible amount of inorganic emissions from a source can be bracketed using a simple conservation of mass calculation. However, this approach does not give a good estimate of actual emissions for most pollutants – sulfur/SO_2 being the main exception. Emission control devices capture several pollutants, particulates being the best example, so that only a small fraction of the original fuel contaminant is actually emitted. In the case of NOx, the amount of fuel nitrogen converted to NOx depends on the design and operation of the combustor. In addition, a portion of the total NOx emissions is thermal NOx, which is independent of fuel nitrogen. Many new sources include back-end NOx control devices, in which case there is little relation between fuel nitrogen content and NOx emissions.

Emissions from incomplete combustion vary from near zero on many sources to potentially significant amounts of CO, smoke, HAPs and particulates. Although there are guidelines, such as AP-42, on what to expect from different types of sources, emissions of various products of incomplete combustion (PIC) are strongly dependent on combustor design and operating conditions. Dioxins and furans are products of incomplete combustion, but some secondary formation can occur in the backend of a boiler – usually involving fly ash in the dust collector as a catalyst.

Particulate emissions can be roughly divided into two groups. Most of the mass (weight) of emissions is in particles larger than about 1 or 2µm (larger than $PM_{2.5}$). Large particles for the most part are direct descendents of fuel particles with essentially the same composition as the original fuel ash. The second group is fine particles that are smaller than about 1µm and are derived from gases in the combustion zone that condense or combine with other species to form solid particles. Fine particles are composed almost entirely of species that were in the vapor phase at

some time during combustion. Hence the fine particle chemistry includes sulfates and various metals like lead, arsenic and beryllium. The fine particles are generally more water soluble and more toxic than the large particles. The relative mass of fine particulate may be small, but this material is frequently responsible for most of the plume opacity from a combustion source. Hence fine particulate emissions are just as environmentally significant as large particle emissions even though they may constitute a small fraction of the actual or potential mass emissions.

Review Exercises

1. For which of the following pollutants can the uncontrolled emission rates **not** be predicted by a fuel analysis?
   a. SO_2
   b. Dioxins and furans
   c. Particulate from pulverized coal firing
   d. HCl

2. Calculate the SO_2 emissions for an uncontrolled source firing 1.0% sulfur oil. Assume the oil higher heating value is 18,500 BTU/lb.
   a. 0.54 lb/mmBTU
   b. 0.93 lb/mmBTU
   c. 1.08 lb/mmBTU
   d. Insufficient data to determine the emission rate.

3. Which of the following fuels cannot generate pollutants other than NOx and CO in significant quantities.
   a. Landfill gas
   b. Distillate oil
   c. No. 6 oil
   d. Natural gas

4. Sulfur oxide emissions exhibit which of the following characteristics?
   a. Nearly all fuel sulfur is converted to SO_2 in the combustion zone.
   b. Any SO_3 formed during combustion will be in the form liquid sulfuric acid when cooled to ambient temperature.
   c. Small amounts of sulfuric acid can form a highly visible plume downwind of a stack.
   d. All of the above

5. Which of the following statements is **not** true?
   a. Any particle larger than 5 μm was probably formed by the breakup of a larger particle.
   b. Any particle smaller than 1μm is composed largely of condensed gas-phase species.
   c. The chemical composition of fine particulate (<1μm) is similar to that of large particles.
   d. Fine particulate is much more visible (higher opacity) than an equal mass of large particulate.

6. What is the maximum possible emission rate for particulate leaving a pulverized coal furnace when the coal ash content is 12.6% and the higher heating value is 10,900 BTU/lb?
   a. 11.6 lb/mmBTU
   b. 5.8 lb/mmBTU
   c. 0.12 lb/mmBTU
   d. 10.4 lb/mmBTU

7. In a typical large boiler, particles of coal or drops of No. 6 oil larger than 200 μm will do which of the following?
   a. Burn completely because of their long residence time in the furnace.
   b. Burn incompletely and created carbon particle emissions.
   c. Fail to ignite
   d. Require a very low excess air level to allow sufficient residence time for combustion

8. Estimate the sulfate contribution to the particulate emissions from a No. 6 oil-fired source if the oil has 0.9% sulfur, a heating value of 18,100 BTU/lb and 2.5% of the sulfur is oxidized to sulfate?
   a. 0.037 lb/mmBTU
   b. 0.0124 lb/mmBTU
   c. 1.49 lb/mmBTU
   d. None of the above

9. Which statement is **not** true of mercury emissions from coal-fired sources?
   a. Most of the mercury in the exhaust is in the vapor phase.
   b. The low concentration of mercury in the typical stack is a result of mercury capture in the dust collector
   c. Although coal contains only ppm levels of mercury, the emissions from an electric utility can amount to several pounds each day.
   d. Air emission of mercury will be reduced if there is a substantial amount of carbon in the fly ash.

10. Which of the following statements is/are true of NOx emissions?
   a. NOx emissions from a furnace will increase as excess air increases.
   b. In a gas-fired reciprocating engine, with the fuel and air premixed before combustion, NOx is always reduced by reducing excess air.
   c. Most combustion modifications that reduce NOx also reduce CO and PIC emissions.
   d. Fuel NOx formation can be reduced by reducing excess air

11. Reciprocating engine NOx emissions are _____.
   a. high because of the amount of nitrogen in the fuel
   b high because of high temperatures during combustion
   c. high because engines operate at high excess air levels
   d. not much higher than other sources fired on similar fuels

12. Complete combustion generally requires which of the following?
    a. Effective air-fuel mixing and adequate excess air.
    b. Adequate amounts of time, temperature and turbulence.
    c. An absence of cold surfaces in the combustion zone.
    d. All of the above.

13. Which statement is **not** true of the destruction of organic gases in a thermal oxidizer _____.
    a. improves dramatically when residence time is increased beyond 0.5 seconds
    b. is relatively independent of residence time in actual (as opposed to theoretical) oxidizers.
    c. is typically near 100%, then drops rapid if temperature drops below a critical levels
    d. the minimum temperature is about the same for destruction most organic gases

14. Dioxins and furans _____.
    a. can be formed by catalytic reactions on fly ash particles in a dust collector at a temperature of 500°F
    b. will not be formed if there is complete combustion of organic species in the combustion zone
    c. cannot be formed if there is no chlorine in the fuel
    d. All of the above

15. Which of the following statements is true regarding opacity?
    a. Sulfuric acid can form a mist of particles too fine to be visible.
    b. Large particles emitted from a coal or residual oil-fired boiler have so much mass that the plume is always clearly visible.
    c. The opacity of a given mass of particles increases linearly as the particle size is decreased down to about the wave length of visible light.
    d. Emissions of black soot emissions are visible primarily because of the large mass emission rate.

Review Answers

1. b. Dioxins and furans

2. c. 1.08 lb/mmBTU.

3. d. Natural gas

4. d. All of the above.

5. c. The chemical composition of small and large particles is similar.

6. a. 11.6 lb/mmBTU

7. b. Burn incompletely and create carbon particle emissions.

8. a. 0.037 lb/mmBTU

9. b. The low concentration of mercury in the typical stack is a result of mercury capture in the dust collector

10. a. NOx emissions from a furnace will increase as excess air increases.
    d. Fuel NOx formation can be reduced by reducing excess air

11. b high because of high temperatures during combustion

12. d. A and C above

13. a. improves dramatically when residence time is increased beyond 0.5 seconds

14. d. All of the above

15. c. The opacity of a given mass of particles increases linearly as the particle size is decreased down to about the wave length of visible light.

References

1. Buonicore, Anthony J. and Davis, Wayne T., (Editors). *Air Pollution Engineering Manual*, (Air & Waste Management Association, Van Nostrand Reinhold, 1992). This book has sections on combustion sources as well as various emission control technologies.

2. California Air Resources Board. *Sources and Control of Oxides of Nitrogen Emissions*, August 1997. This gives a relatively current summary of NOx formation and control technology for all types of sources. Summaries of California rules illustrate NOx levels that can be achieved by state-of-the-art technology.

3. Clement, Raymond and Kagel, Ronald. *Emissions from Combustion Processes: Origin, Measurement, Control*, (Lewis Publishers, 1990). The book is a collection of 31 articles that focus primarily on organic pollutants.

4. Gill, James H. and Quiel, John M. *Incineration of Hazardous, Toxic, and Mixed Wastes*, (North American Mfg. Co., Cleveland, OH, 1993). This book focuses on waste combustion in rotating kilns and covers the formation and control of organic pollutants.

5. U.S. Environmental Protection Agency. *Alternative Control Techniques Document: NOx Emissions from Industrial/Commercial/Institutional (ICI) Boilers*, March 1994, EPA Report 453/R-94-022, NTIS PB94-177177. This weighty document is a fairly a comprehensive description of small to mid size boilers and current NOx technology. It includes waste-fired boilers.

6. U.S. Environmental Protection Agency. *Alternative Control Techniques Document: NOx Emissions from Stationary Gas Turbines*, January 1993, EPA Report 453/R-93-007, NTIS PB93-156586. This weighty document is a fairly a comprehensive, if slightly dated, description of combustion turbine technology with a significant database included.

7. U.S. Environmental Protection Agency. *Alternative Control Techniques Document: NOx Emissions from Stationary Reciprocating Internal Combustion Engines*, July 1993, EPA Report 453/R-93-032, NTIS PB94-104494. This weighty document is a fairly a comprehensive, if slightly dated, description of engine NOx technology with a significant database included.

8. U.S. Environmental Protection Agency. *Alternative Control Techniques Document: NOx Emissions from Utility Boilers*, March 1994, EPA Report 453/R-94-023, NTIS PB94-184165. This weighty document is a fairly a comprehensive description of large boiler types and NOx technology with a significant database included.

9. U.S. Environmental Protection Agency. *Compilation of Air Pollution Emission Factors (AP-42)*, available from NTIS, Federal Book Stores, or you may download the latest version from the EPA TTN BBS. This ever-evolving document is organized by source type and has credible descriptions of each one. It is generally the "bible" for estimating emission rates whenever

actual measurements are not available. There are lengthy background documents for each section of AP-42.

10. U.S. Environmental Protection Agency. *New Source Performance Standards, Subpart Da – Technical Support for Proposed Revisions to NOx Standard*, June 1997, EPA Report 453/R-94-012. This inch thick report is narrowly focused on utility boilers, but covers current NOx technology in great depth.

11. U.S. Environmental Protection Agency. *Phase II NOx Controls for the MARAMA and NESCAUM Regions*, November 1995, EPA Report 453/R-96-002. This report provides an in-depth coverage of NOx technology on utility boilers.

12. U.S. Environmental Protection Agency. *The US EPA-DOE-EPRI Combined Power Plant Air Pollution Control Symposium:* The Mega Symposium and the A&WMA Specialty Conference on Mercury Emissions: Fate, Effects and Control, 2001, proceedings available on CD-ROM from www.awma.org. This and other conference proceedings provide current information on air pollutant formation and control.

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Chapter 6: Air Pollution Control Systems

LESSON GOAL

Demonstrate an understanding of how various devices and methods are used to control air pollution emissions from combustion sources through successful completion of the chapter review exercises.

STUDENT OBJECTIVES

When you have mastered the material in this chapter, you should be able to:

1. Describe the basic particle collection mechanisms of impaction, filtration, and electrostatic attraction.
2. Describe one or more types of inertial particle collectors and the size range of particles applicable to each.
3. List the main advantages of particulate scrubbers and discuss how they work.
4. Identify the advantages and operating limitations of baghouses and discuss their operating principles.
5. List the advantages and limitations of electrostatic precipitators and discuss how they work.
6. Describe the most effective means of monitoring the performance of each major type of particle collector.
7. Identify how SO_2 emissions can be controlled by fuel switching, as well as dry or wet scrubbing.
8. Describe why SO_3 emissions can be difficult to control.
9. List three general methods of reducing NOx formation from boilers or furnaces.
10. List two predominant temperature NOx reduction methods used in boilers and combustion turbines.
11. Define the meaning of FGR and the limitations when using it on boilers that fire a sulfur bearing fuel.

12. Discuss what stratified combustion is and how it is applied in several ways to practical combustion systems.
13. Describe how reburning works to reduce NOx and the types of sources on which it is most effective.
14. Identify what constitutes a low NOx burner.
15. Describe the difference between diffusion and premixed flames and how NOx control works in premixed flames.
16. Discuss the basic concepts behind low NOx burners used in gas turbines and reciprocating engines.
17. Identify the basic elements of SNCR, SCR and NSCR NOx control technologies.

Chapter 6: Air Pollution Control Systems

6.1 INTRODUCTION

Pollutants emitted from combustion sources are formed in the combustion zone and, unless they are captured by a control device, they will be emitted to the atmosphere with the exhaust gases. Small amounts of two pollutants, sulfuric acid and dioxins/furans, can be created in cooler areas downstream of the combustion zone. For all practical purposes all the other pollutants are not significantly created nor destroyed once they pass beyond the flame.

Control of air emissions may be done in the combustion zone, with a control device, or with a combination of the two. In many cases, even if a combination of controls is not used, the performance of the control device can be strongly affected by the operation of the combustion system. Thus, air emissions control should always be viewed as a synergistic process involving both the combustion zone and the control device. This chapter provides a brief description of control technologies for most pollutants with a focus more on the relation to the combustion source than on the details of various controls. A partial exception is NOx control where much of the actual control is the design and operation of the combustion system.

Control devices can be combined, they may act synergistically, or more than one pollutant may be controlled with a single device. For example, if a caustic dust is blown into the exhaust gas upstream of a baghouse, the baghouse will collect acid gases as well as particulate. Carbon dust on the baghouse filters will reduce mercury emissions. If coal fly ash is collected ahead of a lime SO_2 scrubber, then both the fly ash and the scrubber residue may have commercial value/uses. There are numerous ways in which control devices may be integrated or combined, depending on the fuel, the source, the environmental requirements and potential reuse/recycle markets.

Emissions are almost always affected by the choice of fuel and emissions control, in some cases, is achieved entirely by choosing the fuel or specifying fuel properties. The pollutant that is most commonly the driving force for switching fuels is SO_2, where the emissions rate is directly related to fuel sulfur content. But NOx emissions can also be strongly affected by the type of fuel – especially when choosing between gas and residual oil or coal. Fuel properties can directly affect the performance of emission control devices. For example, the performance of an electrostatic precipitator may be

influenced by the amount of alkali in coal ash. And, the durability of a catalyst used to control NOx can be affected by sulfur and trace elements in the fuel.

The choice between different types of fuel, say between oil and gas, or between oil and coal, will obviously involve the capabilities of the hardware, relative fuel costs, emission controls/limits and several other factors. But even a choice between two types of coal can be sharply limited by combustion system hardware capabilities. For example, switching from an eastern bituminous coal to a Powder River Basin low sulfur coal can trigger serious ash/slag problems around the burners or problems with electrostatic precipitator performance. While the general nature of such problems may be anticipated, the magnitude and details are specific to the combustion system and the particular fuel. So a source might potentially achieve its emission reduction objectives with a fuel change, but there are usually significant side effects, which can be critical to the feasibility or viability of the fuel choice.

6.2 PARTICULATE MATTER AND METAL EMISSIONS CONTROL

Particulate matter emissions are typically controlled with some type of dust collector. The type of dust collector depends upon the required collection efficiency, the size of the particulate and to a lesser extent on the particle properties. When high collection efficiency is required, either an electrostatic precipitator (ESP) or a baghouse is usually required. If there is no need for high efficiency collection of fine particulate, then an inertial (cyclone) collector may be adequate. If the particulate tends to be sticky, or if there is a severe threat of a dust collector fire, then a scrubber or a wet ESP may be the best choice.

Particle collectors are based on three basic mechanisms with several variations and combinations.

- *Inertial Collectors.* Inertial collectors work by accelerating or curving the gas flow so that particles cross the streamlines and impact or agglomerate on a surface. A particulate scrubber is a special type of inertial collector.

- *Filters.* Filters create passages that are too small for particles to pass through although ultimately filters also work by impaction.

- *Electrostatic Collectors.* Electrostatic collectors use an electric field to draw charged particles to a collection surface.

The performance of all collectors is governed in large part by the behavior of different size particles. Figure 6-1 illustrates the movement of different size particles relative to streamlines; the illustration is not drawn to scale.

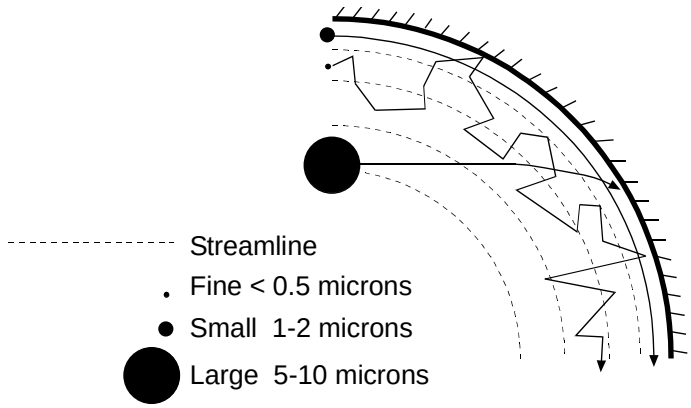

Figure 6-1. Particle Motion vs. Gas Streamlines

The movement of particles larger that about 5µm to 10µm is substantially influenced by inertia. When the flow goes around a bend, these particles tend to go straight; in other words, they cross the streamlines. So when the flow is forced in a circular path, as it is in a cyclone, these particles tend to migrate to the walls where they agglomerate and can be collected.

Mid-size particles from about 0.5µm to 5µm tend to follow the gas streamlines very closely. They are essentially locked or frozen into the flow so that when the flow curves around an obstacle, such as a small drop of water in a scrubber, the particles follow the streamlines and miss the obstacle. In general, the smaller the obstacle, the sharper the flow bend and the smaller the particle that will impact obstacles in the flow. Impactors, used to measure particle size distribution, pass the flow through a series of smaller and smaller orifices to classify the particulate into different sizes. Small cyclone collectors will capture smaller particles better than large cyclone collectors.

Particles smaller than about 0.5µm basically follow the streamlines, but they undergo additional random motion. They are small enough that the gas molecule collisions are strong enough to move them. They undergo Brownian motion, which means they cover more distance and have an increased likelihood of impacting other particles or a solid surface.

6.2.1 Particle Collectors

Particle collectors can be divided into four categories, although some devices are a combination of categories.

- Inertial or mechanical collectors
- Scrubbers (a form of inertial collector
- Filters
- Electrostatic precipitators

The basic operation of each type of collector will be discussed, followed by a brief explanation of some innovative combinations.

6.2.1.1 Inertial Collectors

Inertial or mechanical collectors work by accelerating the flow (a curved flow path accelerates the flow in a radial direction), which causes large particles to migrate across the streamlines to a collecting surface. Cyclones and multiclones are the most common inertial collectors. These mechanical collectors are simple and relatively small. In addition, they require little maintenance or operator attention and have proven to be very reliable. However, for the most part, they do not efficiently collect particles smaller than about 5-10µm. So their use in air pollution applications is limited to cases where most of the particulate is relatively large and where low to moderate collection efficiency is acceptable. Figure 6-2 shows two typical cyclone collectors. The basic concept is to centrifuge the particulate to the chamber wall where it agglomerates into larger particles that drop down into the hopper. They are typically designed for a pressure drop of about 4 in. w.g. Moderate variations in flow or pressure drop usually have little influence on the collection efficiency, but they lose efficiency at high and at low flow rates.

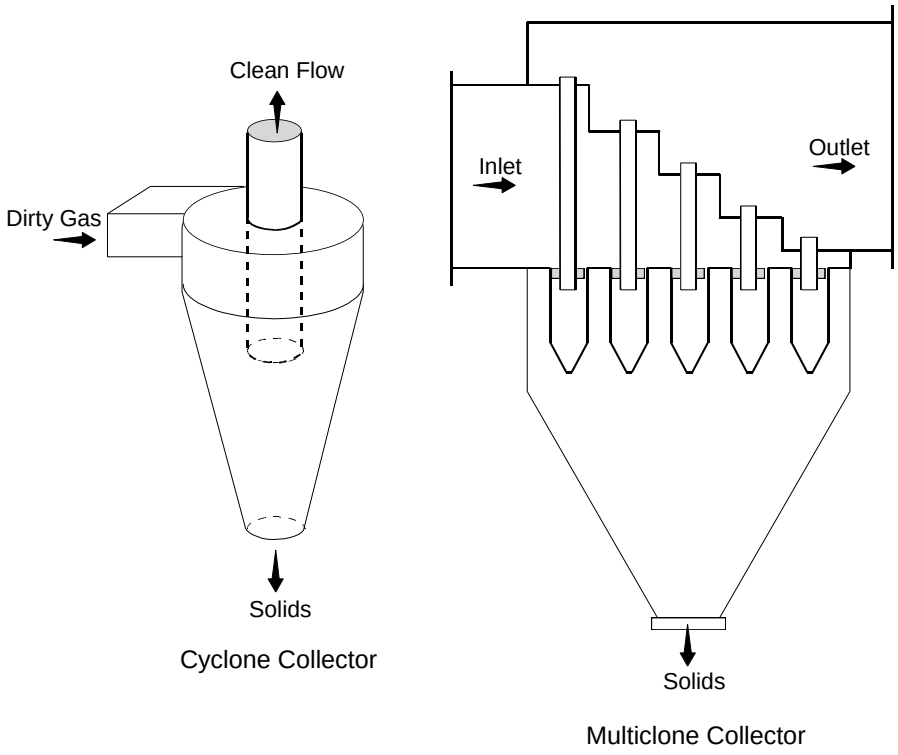

Figure 6-2. Basic Inertial Collector

Cyclone-type collectors are commonly used in industry to separate solid materials like plastic pellets from pneumatic transport systems. In these applications, they may be essentially 100% efficient. Air pollution control collection efficiency for particles

larger than 50µm usually exceeds 90%. Efficiency for smaller particles depends in part on the size of the cyclone – smaller cyclones will collect smaller particles. A sawmill may use a 6-8 foot diameter cyclone to capture chips from a saw, while the wood-fired boiler will use a multiple set of 8" diameter cyclones to capture most of the particulate down to 10µm or somewhat smaller. Overall collection efficiency for a multiclone system on a solid fuel-fired boiler seldom is much above 80%. Most stoker boilers use a multiclone as a primary collector to catch larger particles, some of which may still be burning. Newer units will also have a high efficiency secondary collector to meet air emission requirements.

Because inertial collectors are not efficient when collecting submicron particulate, they cannot be used to control particles formed by condensation such as fume or black smoke. In fact, their ability to control opacity is limited to those sources where the opacity is caused by the emission of relatively large amounts of large particulate matter. When an inertial collector is the only control device on a coal- or wood-fired stoker, the plume is usually visible even when there is no black smoke.

Inertial collectors are small compared to a baghouse or precipitator. A multiclone collector may be integrated with a boiler or it may appear as no more than an enlarged section of the duct with hoppers below. An inertial collector is a simple device with no external adjustments/controls and almost no moving parts. Thus, its performance tends to be very consistent and degraded performance tends to be associated with one of the following:

- *Wear*. Erosion cuts a hole in an internal component, resulting in gas bypassing the collector.

- *Ash Build Up*. Ash builds up in the hopper or flow path to the point that it compromises the operation.

- *Air Leaks*. An air leak in the hopper will blow collected dust into the outlet gas stream.

Although there are some monitoring or diagnostic procedures that may detect these problems, periodic inspections and maintenance are probably the keys to consistent collector performance.

6.2.1.2 Particulate Scrubbers

Scrubbers use water to “wash” the exhaust gas. They are commonly used to control the emission of acid gases and less commonly used for particulate control. Scrubbers have difficulty collecting fine particulate; however, they are more efficient than mechanical collectors. Because of this tendency toward low collection efficiency they are not normally used as the only particulate control device on combustion sources. Some of the features of particulate scrubbers in comparison with other particulate control devices are:

- *Size.* A scrubber is physically smaller than a precipitator or baghouse.

- *Cost.* Gas pressure drop across a particulate scrubber is high, so fan power becomes a significant operating expense. Scrubbers are also considerably cheaper to build than a baghouse.

- *Hazards.* A scrubber may be attractive if the dust is flammable and there is a high probability of a collector fire.

- *Supplemental Equipment.* Some sort of water treatment facility is required before waste water can be discharged.

Thus, scrubbers usually are used in combination with other control devices and/or on unique combustion sources.

The basic concept of a particulate scrubber is to spray water into the flue gas so the particles are captured by water drops, then collect the water. Capture of the particles occurs when they impact water droplets, so collection depends on the velocity difference between the particles and the water drops. Once the particulate and the water drops are combined, the water must be collected and managed for soluble and insoluble particulate matter. While simply spraying enough water into the gas stream will collect much of the particulate, small particle collection requires considerable energy to create movement between the water drops and the gas streamlines. Figure 6-3 shows the basic elements of a particulate scrubber. Accelerating and decelerating the flow using a venturi or restriction in the flow is used to achieve mixing. The higher the venturi velocity (scrubber pressure drop), the smaller the particles will be that are collected. Pressure drops of at least 10" w.g. up to more than 30" w.g. are common. But particles smaller than about 0.5 to 1µm cannot be efficiently collected regardless of pressure drop. The reason is that fine particles follow gas streamlines around the water drops even when the water drops are moving fast.

Once the water has captured the particulate, the water needs to be collected, which means the venturi is followed by one or more mechanical collectors that impact the water drops on a surface that drains to the scrubber sump. The final water collector is called a mist eliminator and usually takes the form of a multi-layer mesh or other tortuous path device.

Exhaust gas can enter a scrubber at any temperature where it is cooled by evaporation and heating of the water. At the scrubber exit, the exhaust will usually be at the saturation temperature, meaning some number below 200°F. Enough water must be supplied to provide evaporative cooling and to scrub out the particulate. The exhaust will be saturated with water and may carry some liquid mist as well, so any downstream control device as well as any exhaust sampling system needs to be designed accordingly.

The collection performance of a particulate scrubber is directly dependent on two parameters: (1) gas pressure drop (delta p) and (2) water flow rate. Any plan to monitor scrubber performance needs to include these as primary parameters.

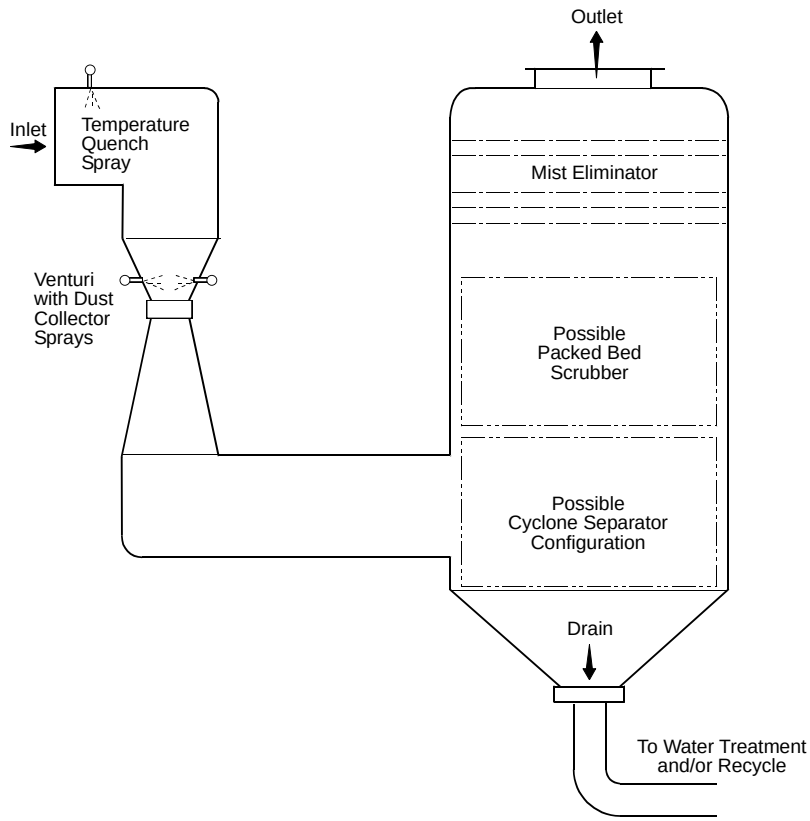

Figure 6-3. Elements of a Scrubber

Example 6-1. Scrubber Water Flow

A scrubber, that is located downstream of an induced drafts fan, is known to require about water at a flow rate of 15 gal/min per 1000 cfm of inlet gas flow rate. Stack measurements at the scrubber outlet show 22,000 acfm @ 155°F. The scrubber inlet conditions are 435°F and +25 inches w.g. How much water is required?

Solution:

Determine the inlet gas flow by correcting the stack flow to inlet conditions using Eqn. 4-14 (p. 4-22).

$$22{,}000 \text{ acfm} \times \frac{435 + 460}{155 + 460} \times \frac{29.92}{29.92 + 25/13.6} = 30{,}163 \text{ acfm inlet}$$

Calculate the water flow rate

$$15\left(\frac{\text{gal}/\text{min}}{1000\ \text{cfm}}\right)\times 30{,}163\ (\text{cfm}) = 452\left(\frac{\text{gal}}{\text{min}}\right)$$

The scrubber will require a water flow of about 452 gpm to operate properly.

6.2.1.3 Fabric Filters

A fabric filter or baghouse is a common, simple and very effective particulate control device. When new, the collection efficiency approaches 100% and the outlet gas will be nearly void of particles. In addition, baghouses can, depending on the chemistry of the dust, remove gases such as SO_2 or HCl, although this efficiency is usually less than 90%-95%.

A baghouse is functionally similar to a vacuum cleaner. Gas is drawn through a filter and the particulate accumulates on the surface. Filter bags are typically 6" to 8" in diameter and can be 30' long. A large baghouse can have hundreds of bags.

Particulate can be collected on either the inside or the outside of the bags, depending on the configuration. Figure 6-4 shows the basic elements of a baghouse. Gas flows into the bag chamber, through the bags and out the top. Periodically the accumulated dust cake is removed from the bags and falls into the hopper below.

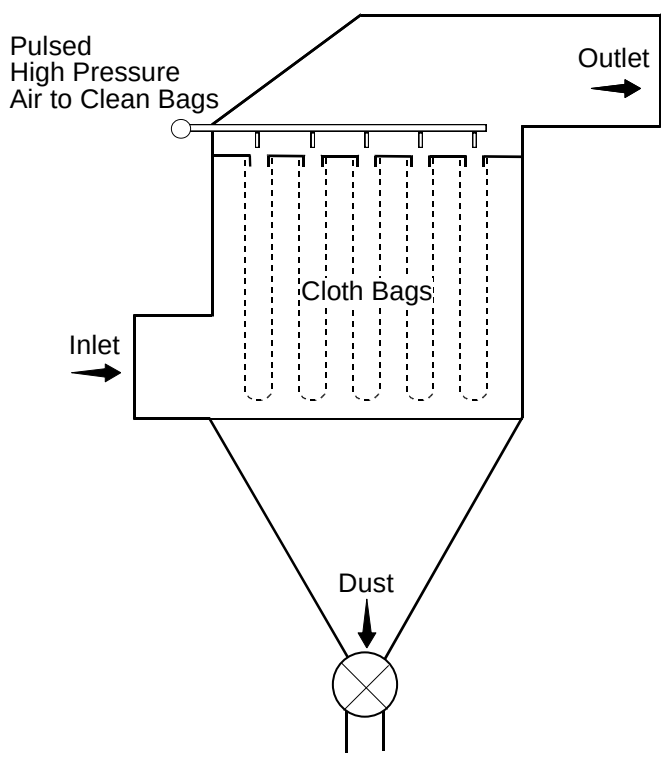

Figure 6-4. Fabric Filter Components

The bags must be cleaned automatically while the baghouse is in service. The two most common methods of cleaning dust from the bags are:

- *Pulse jet.* Dust is collected on the outside of the bags with the open (clean) end upward. A blast of air into the open end momentarily reverses the gas flow through the bag and flexes the bag outward. This dislodges the dust cake, which then drops into the hopper.

- *Reverse flow.* The baghouse is built with a number of compartments, each with isolation dampers. When the bags are to be cleaned in one of compartments, it is isolated and clean air is blown backwards through the bags knocking the dust cake from the bag surface.

As dust builds into a layer on the bag surface, the pressure required to force gas through the bag increases. Cleaning the bag reduces the pressure drop, so over a period of a few hours, the pressure drop across a baghouse has a saw tooth pattern. There may also be a long-term increase in pressure drop, but the average pressure drop should reach a steady value after a period of only a few weeks.

Filters catch particulate more effectively than one would surmise from the size of the openings between the fibers. Some particles are too large to pass through the filter and are captured this way. But as soon as a layer of dust begins to form on the surface, the fine particulate begins to be captured before it reaches the filter. Thus, the filter cake becomes the primary collection media in which very fine particulate is captured. The result is particulate capture efficiency approaching 100% for nearly all particle sizes. The particles near 0.5µm diameter that follow the streamlines, can slip through, but even with these, the collection efficiency tends to be 90% or better. There are a variety of materials used for baghouse filters. The choice depends on factors such as peak operating temperature, characteristics of the dust, and cleaning method. In current practice, the maximum operating temperatures are about 550°F for fiberglass bags. Although higher temperatures are possible, the associated materials tend to be less durable. If the exhaust temperature significantly exceeds the bag's operating limit, damage to the bag causes either holes, or plugging (blinding), or both.

Baghouse Monitoring

A baghouse has two principal failure modes:

- *Bag Wear.* Holes or tears in the bags allow dust to pass through the holes and bypass the fabric filter. Since bags normally last 3 years or more, holes are not something one expects to find on a weekly or even monthly basis until the bags approach the end of their life.

- *Dust Accumulation.* Dust accumulation that plugs up the bags resulting in an increased pressure drop or reduction in flow rate, or both. There are two subcategories: (a) temporary accumulations that can be removed by the normal

cleaning cycle, and (b) permanent "blinding" of the fabric that can only be fixed by washing or replacing the bags.

Excess emissions are usually caused by holes or leaks in the bags; some of the gas passes through the holes carrying its dust burden with it. So a primary objective of monitoring (such as might be required for compliance assurance) should be to detect leaks. The most sensitive monitoring technology in this case is tribo electric sensors. A tribo electric probe generates a current (micro amperes) that is roughly proportional to the mass of particulate striking it. These devices are sensitive enough to give a baseline current reading when the bags are new (no leaks), so any increase in mass loading can be detected as an increase in current. These devices are relatively inexpensive (less than $2000 each) and they give a continuous output.

One might think that an opacity meter would provide an effective indication of bag leaks, but in fact opacity is much less sensitive than a tribo-electric meter. The reason is apparent once you realize that the opacity at the outlet of a leak-free baghouse is probably on the order of 0.1%. Emissions would have to increase by about an order of magnitude before the opacity meter detects an increase; it is simply much less sensitive than the tribo-electric meter at particulate concentrations typical of the baghouse outlet. Of course if the bags have holes and the opacity is already 5% or more, then any further deterioration in the bags will cause a measurable increase in opacity.

Inlet-outlet pressure drop indicates the operational status of a baghouse, but is insensitive to bag leaks, short of sensing a massive failure. For example, if holes cause 1% of the flow to bypass the filter fabric, the emissions will increase by one to two orders of magnitude, corresponding to 1% of the dust leaking through rather than 0.1% or 0.01% with no leaks. The holes reduce flow through the bag fabric by 1%, which will reduce the pressure drop about 2% (Bernoulli's equation for fluid flow). That change in pressure drop is much less than that resulting from bag cleaning and fluctuations in gas flow, so it is not detectable. Emissions can increase by a factor of 10 with no measurable change in pressure drop.

Example 6-2. Effect of Baghouse Leaks

A new baghouse has a measured collection efficiency of 99.95%. Over a period of time the bags develop leaks that allow 0.7% of the gas flow to bypass the fabric. How much will the emissions increase and how much will the Δp decrease as a result of this leakage?

Solution:

Initially 0.05% of the particulate (100% – 99.95%) gets through the fabric filters. The air leakage of 0.7% allows an additional 0.7% of the particulate to get through. Thus the emissions increase from 0.05% to 0.7 + 0.05 = 0.75% of the inlet particulate. The emissions increase by a factor of 0.75/0.05 = 15, or 15 times as much emissions.

The gas flow through the baghouse does not change, but with the leaks only 99.3% of the gas (100% - 0.7%) is passing through the fabric. The pressure drop will decrease in proportion to the square of the flow rate, which has decreased to 99.3% of the original.

$$0.993^2 = 0.986$$

The pressure drops to 0.986 of the original or a 1.4% decrease. Thus leaks would increase emissions by a factor of 15 while only changing the pressure drop by 1.4%.

Although a decrease in pressure drop will not indicate anything less than a major bag failure, a systematic increase in pressure drop can be used to show when the bags are plugging up. As a new baghouse develops a steady dust accumulation, a modest increase in pressure drop is expected. But an increase of more than 30%-50% is cause for concern. Plugged bags will not immediately increase emissions but they are likely to reduce flow rate, and plugging portends accelerated bag failure. When there is a high-pressure drop across the bags, the fabric is eroded rapidly around any pinhole, which then grows larger. So a high-pressure drop is a sign that remedial action is needed to prevent accelerated failure.

Gas temperature has little affect on baghouse performance unless (a) high temperature exceeds the fabric limit, or (b) low temperatures allow water or acid to condense in the fabric. In the second case, the bag can become permanently plugged (blinded) such that it requires bag replacement or washing. Severe temperature excursions signal catastrophe while temperature anywhere in the normal bag operating range has little emissions significance.

6.2.1.4 Electrostatic Precipitators

Precipitators are commonly used on large combustion sources and typically have collection efficiencies nearly as high as a baghouse – well in excess of 99%. They have two advantages over baghouses: (1) the gas pressure drop is negligible, and (2) they are not easily damaged by modest temperature excursions or small dust fires. But there are numerous problems that can degrade performance.

Precipitators work by electrically charging the particles, then drawing them to a collector plate with a high voltage (electrostatic) field. Accumulated dust cake is then removed from the plates by mechanical rappers that periodically bang the plates or by a water wash. The physical hardware consists of parallel plates that form gas passages typically 9" to 18" wide. In the middle of each passage is a set of wires or rods maintained at 40 to 60 kv negative electric charge. A corona of electrons flows from the electrodes to the plates. The electrons hit particles, making them negatively charged. The DC electric field draws charged particles to the collector plates where they accumulate into a dust layer and lose their charge to the plate. Because particles get charged regardless of size, precipitators, like baghouses, can collect very fine particles.

All the internal components are steel or ceramic, so they normally last many years before major components need to be replaced. Operating limitations can be generated either during the charging process or in the discharge/dust removal process. Most of the charging problems result from reduced corona current that results when arcing forces the power supply to reduce the operating voltage. Once on the plates, the particles must discharge before the dust cake will release from the plate. Thus, high resistivity dust is hard to collect. The chemistry of the dust, the temperature of the flue gas, the moisture content of the flue gas, and the flue gas SO_3 content all affect resistivity. The preceding discussion merely introduces a subject so complex that it could fill several volumes of books.

There are two basic types of precipitators, wet and dry. In a wet precipitator, the collection surface is cleaned by a steady or intermittent flow of water. Currently, wet precipitators have been used in special applications where the dust is sticky or flammable; however, they have not seen common use on combustion sources. Nonetheless, they are purported to be better than dry precipitators at catching extremely fine particulate. Tests and initial trials are being conducted to use them for final flue gas clean up on utility boilers. Based on the early success of these tests, these devices may see increased use in the future to control opacity and fine particle emissions from conventional large sources.

Dry precipitators are by far the most common type. Depending on their location in the gas path they are classified as “hot side” or “cold side” precipitators. Hot side precipitators are installed upstream of the air heater in utility boilers and operate at temperatures in the range of 600° to 700°F. Cold side precipitators operate in the range of 300° to 400°F. The advantage of hot side collection lies in the properties of the dust, which can be much easier to collect than when it is cooled to 300°F. Hot side precipitators must be much larger than cold side precipitators in order to handle the larger volume of flue gas. They also operate at lower collection voltage because hot gas is more easily ionized. These disadvantages tend to out weigh the advantages and few, if any, hot side precipitators have been built in recent years.

Precipitators are built with a number of electrical sections in the direction of flow and there is a separate power control cabinet for each section. The controls continuously seek the highest practical operating voltage and they interrupt power momentarily to suppress large sparks or arcs. Most precipitators have sufficient operating margin that they can meet performance requirements with one or more sections out of service and/or with reduced power levels. This has lead to debate in a few cases about whether a large precipitator should be operated at its maximum collection efficiency, or simply operated well enough to keep emissions in compliance. Figure 6-5 shows the basic elements of an electrostatic precipitator with four collection fields in the direction of flow.

Many precipitators are built as two units, side by side, each one taking half the flow. High voltage transformer-rectifier sets are located on top of the box and the electrical cabinets that control them are normally at ground level. Rappers for cleaning the

plates are not shown in Figure 6-5. Precipitator collector plates in a large unit are typically about 35 feet high. The high-tension electrode grids built prior to about 1980 were made of wires with weights at the bottom. A rigid frame in most current designs has replaced this design.

In order for a precipitator to work well, the gas must move slowly enough to give sufficient residence time for dust collection. Local (or general) high velocities will sweep gas out before it is fully treated; there is a critical gas velocity, above which performance degrades rapidly. So precipitator performance is very sensitive to distortions in gas distribution and to excessive gas flow rate.

Precipitator Monitoring

Perhaps the first thing to note about precipitator monitoring is that opacity is a more effective tool on a precipitator than it is on a baghouse. The reason is that a precipitator preferentially captures the largest particles first. Small particles penetrate further and when performance deteriorates the finest particles are the first to slip

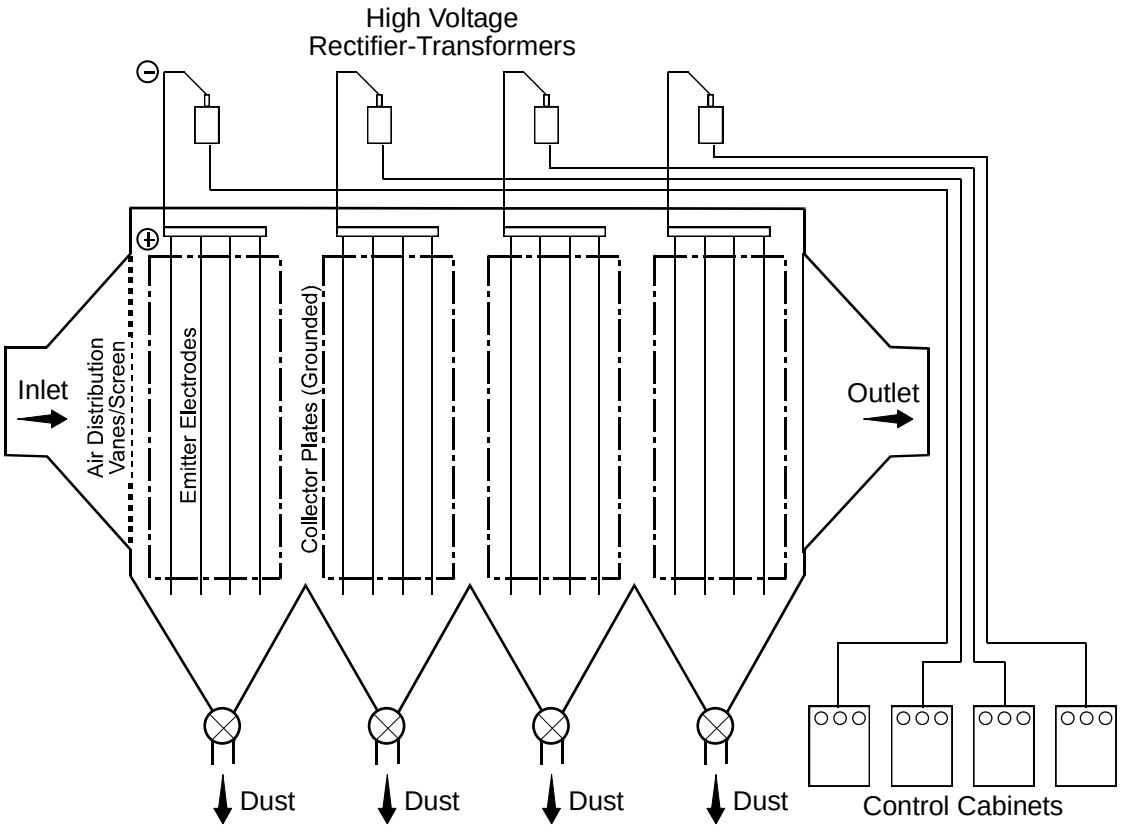

Figure 6-5. Elements of an Electrostatic Precipitator

through. Opacity is inversely proportional to particle size, so the fine particles generate significant opacity while contributing very little to mass loading. When dust begins to penetrate the precipitator, it is the fine particles with the highest opacity and least mass that appear first. So an opacity increase is an early indicator that mass emissions are starting to increase.

Although there are a number of potential causes for reduced collection performance, nearly all of them can be divided into two categories:

- problems with the flow geometry, and
- problems reflected in reduced power levels.

Flow geometry problems are a consequence of the internal configuration. They cannot be diagnosed by external measurements or tests and they cannot be corrected by any operational control. When the configuration of the precipitator inlet duct generates an uneven flow distribution, the precipitator can achieve its design efficiency only when the highest flow area is at or below the design velocity. So the total flow has to be reduced to accommodate the worst section. Most collectors are built with some excess capacity or operating margin. A poor flow distribution consumes this margin leaving the unit vulnerable to emissions excursions as it approaches full load.

Most operating problems are reflected in reduced voltage or current to the affected section. Problems that interfere with precipitator collection performance include: thick dust accumulations due to a change in dust characteristics or inadequate rapping, hopper overflows resulting from failed fly ash transport, and short circuits or electrical control failure. Note that dust collection performance can be significantly affected by variations in gas temperature, gas moisture content, chemical composition of the dust, particle size and other source controlled parameters. To the extent that they affect emissions, most of the variables that affect the ongoing performance of a precipitator can be tracked by monitoring the (DC or secondary) current and voltage levels at the control cabinets that power each of the sections. Current is the more useful of the two readings, because it drops when there are dust layer buildups that interfere with the electric field (which is responsible for particle collection). The collection performance of any section in the precipitator is almost directly reflected in the current and voltage readings. By tracking these readings over time, one can immediately see the effects of dust accumulations or changes in the dust characteristics. These readings tend to be fairly constant because changes, when they occur, take place over days or weeks. Abrupt changes are usually a result of process changes or mechanical malfunctions.

6.2.1.5 Collector Combinations

There are numerous ways to combine the basic collection concept, but this section will touch on only a few of them. First, it is possible to combine electrostatic precipitation with other collector types, such as a baghouse. The advantage is that charged particles tend to stick to the collecting surface. This can boost the performance of an inertial

collector or a scrubber, which normally cannot collect fine particulate. Used in combination with a baghouse it changes the character of the filter cake making it more porous. This allows the design to use higher gas velocities resulting in a smaller, less expensive, baghouse.

Combining control systems for particulate and gaseous emissions is not a new concept, but it has seen increased use as more and more large boilers are required to control SO_2 emissions as well as particulate. Either a precipitator or a baghouse can be placed downstream of certain types of scrubbers to catch either fine particulate that passes through a particle scrubber or the dust that results from a dry scrubbing process (see Section 6.3.1.2) controls. Although dry chemistry is generally less effective than wet chemistry, acid gases will tend to react with basic dust. So SO_2 will react with dry $Ca(OH)_2$ to form calcium sulfate; although the reaction is much slower than when the two compounds are in liquid solution. Thus both SO_2 and HCl will, to some extent, react with available compounds in the fly ash to remove the gases from the exhaust and create particulate matter. This mechanism is much more effective in a bag house than in an electrostatic precipitator.

6.2.2 Dust Collector Fires

Dust collector fires are an unusual but significant concern because the damage can take weeks to repair. When there is a fire in a baghouse the bags in the affected area will almost certainly have to be replaced. A substantial fire in a precipitator will warp the plates, which reduces the electrical spacing and hence the operating voltage. In most cases, operators are not aware of fires until the damage is discovered at a later date. Fires, for the most part, are preventable because it is always possible to eliminate one of the three essential fire elements: (1) fuel, (2) oxygen, and (3) ignition.

Unfortunately, there are two possible fire scenarios that are not altogether avoidable:

- A rare, but possible, occurrence is an explosion from the ignition of combustible gases mixed with air in the dust collector.

- The most common scenario occurs when combustible dust accumulates in the hoppers or on the plates and ignites when air is introduced through leaks, or a process upset.

Combustible gas fires are rare because it is very unusual to have sufficient combustible gas and air present simultaneously. Under normal operating conditions, a combustion device only generates combustible gas when there is no excess air, so gas explosions in the dust collector cannot occur. Almost the only way to get a gas explosion is for the fire to go out and fuel flow continue – as can happen during startup if there is a failure in the flame safety system. During startup, it is normal practice to have a precipitator shut off so there is no ignition source to trigger an explosion.

Dust collector fires can be ignited either by the sparks in an electrostatic precipitator or by burning embers generated in a biofuel-fired stoker. Most dust collector fires occur in the hoppers where they are sustained by an air leak. However, maintaining the mechanical integrity of the hopper and the dust evacuation system can usually prevent air leaks. Fires are also possible in a precipitator if there are significant layers of combustible dust on the plates and the excess air level is allowed to rise above 12–15% O_2 – which happens during a combustion upset or when the combustor is shut down. Dust collector fires are most common on wood-fired stoker boilers because of the amount of carbon typically in the fly ash. However, most solid and liquid fuel combustors are, under certain operating conditions, capable of generating combustible ash.

As a general rule, dust collector fires occur during or immediately following a combustion process upset or shut down. Eliminating one or more of the three critical elements – fuel, air and ignition – can prevent fire. Contingency planning to establish operator response or control system actions during an upset is an effective way to prevent fires.

6.2.3 Oil Fired Particulate

Particulate emissions from oil-fired sources are relatively low because there is very little ash, even in the heaviest residual oil. Most of these sources do not have dust collectors and stack emissions consist of all the particulate formed in the combustion process, as discussed in the preceding chapter, not the emissions remaining after a dust collector. Emissions are controlled by maintaining good fuel atomizer performance to limit carbon emissions and, in some cases, by using low excess air levels to limit sulfate formation. Using low excess air levels generally results in emission rates below 0.1 lb/mmBTU and in most cases below 0.05 lb/mmBTU.

Operation of dust collectors on oil-fired sources is challenging because most of the ash is submicron size particulate and a substantial fraction of it may be sulfuric acid. This makes the ash difficult to collect, corrosive and, unless it is kept warmer than the sulfuric acid dew point, there is enough liquid to turn the ash into a sticky paste. The only way to deal with this troublesome ash is to keep the dust collector, the hoppers and the ash handling system hot enough to limit acid condensation – typically above 280°F. This translates into a lot of hardware to maintain and service, so an electrostatic precipitator on a large utility boiler can require one full time operator just to monitor and maintain the system and all its heaters. A baghouse is probably not a feasible particulate control device for an oil-fired source because under some operating conditions the ash will tend to permanently plug the bags.

6.3 SULFUR OXIDES AND HYDROGEN CHLORIDE CONTROLS

Limiting the amount of sulfur or chlorine in the fuel can effectively control the emissions of both SO_2 and HCl. However, fuel limitations are not always feasible or economical, in which case some sort of back-end control is required.

6.3.1 Approaches to SOx Control

The CAAA of 1990 imposed SO_2 emission caps on most utility boilers that required a large reduction in emissions. Economic analysis performed prior to enactment of the new legislation indicated that compliance would be achieved by the extensive use of scrubbers to capture SO_2 emissions. However, the forecasts were inaccurate and most utilities complied by changing to lower sulfur fuel (which was coal in most cases). There were also cases in which the cost and availability of natural gas allowed some utilities to replace some high sulfur coal or oil with gas. These choices reflected market conditions more than they reflected uncertainty about the cost and practical implications of scrubbers. However, at the present time, much or most of the possible fuel switches already have taken place, so that future SO_2 emission reductions will have to be met primarily by installing scrubbers.

We noted earlier that virtually all fuel sulfur burns to SO_2 and will be emitted from the stack unless it is captured by a control device. A few percent of the fuel sulfur will be oxidized to SO_3 (a gas) or a solid sulfate salt. Since SO_2 constitutes 95% or more of the total sulfur emissions, control devices focus on this gas. However SO_3, although small in quantity, can be noxious in several ways, so most SO_2 control devices must deal with SO_3 in some manner.

6.3.1.1 Fuel Switching

SOx emissions can be reduced by reducing the fuel sulfur content, as with low sulfur coal, or by reducing the amount of sulfur-bearing fuel used, as by firing gas in place of coal. If fuel sulfur is reduced as a result of a continuous emission limit, this establishes a limit on the fuel sulfur content, as a restriction to firing oil with less than 1.0% sulfur. If, however, the restriction is an emissions cap – such as a limit of 100 tons of SO_2 per year – then the source can fire any fuel it chooses, so long as the emissions do not exceed the cap. In this case, the source could fire sulfur-bearing fuel part of the year and use natural gas during a season when natural gas is less expensive. Furthermore, if there is a market for emission allowances, a source can buy or sell allowances in the course of meeting its requirement to keep total emissions within the capped amount. Overall, emission caps provide a source with considerable flexibility in their approach to emissions control.

Fuels can be changed only within the limits and capabilities of the combustion hardware. These restrictions go beyond the simple requirements for appropriate burners and fuel handling systems. For example, natural gas (with virtually no sulfur)

can be fired in boilers designed for coal, wood or oil. However, gas flames are much less radiant than the flames from pulverized coal or oil, so less heat is transferred by radiation. This means that in a boiler designed for oil or coal, natural gas fires carry more heat out of the fire box and into the convective sections of the boiler. For power boilers this means more energy flows into the superheat and reheat sections, which translates into higher steam temperatures when fired on natural gas. In some units excessive temperatures can mean the maximum boiler load is reduced.

Changing to a coal with lower sulfur content usually means that the coal comes from a different mine and that it has different characteristics than the original coal. There are a number of important coal properties, but some of the most significant relate to the behavior of the coal ash in a pulverized coal boiler. To some extent, laboratory tests can be used to determine whether a proposed coal will work in a given boiler. However, test firing is normally used to determine how well a proposed coal will work. An inappropriate coal can generate molten slag on the boiler walls, or massive slag build-ups on the walls or in the convective passes. This defeats heat transfer and can force reduced capacity and/or availability

6.3.1.2 Flue Gas Desulfurization

Sulfur oxide gases can be converted to solid oxides such as sodium sulfate or calcium sulfate during the combustion process, or they can be removed from the exhaust gas with a scrubber. Most of the control methods use an alkali, such as calcium, to convert the sulfur to a solid salt. The amount of alkali and the efficiency of sulfur capture depend on the process and operating variables. Scrubbers, as the word implies, use water, but sulfur oxide scrubbers can be either wet or dry. APTI Course 415, *Control of Gaseous Emissions*, discusses control technologies in some detail, so the following discussion only reviews the highlights.

As with most systems, the resulting solids are a waste material, but a few systems generate commercial gypsum or other sulfur products. Calcium is the most common cation, but sodium, magnesium and combinations are also used. The choice of cation, and associated system, is based in part on availability and cost.

Wet Scrubbers

SO_2 is a water-soluble gas that dissolves into the drops of water in a scrubber as long as the water does not become acidic. So a wet scrubber sprays water with a high pH into the flue gas, cations in the water react with the acid gases, and the liquid effluent carries the sulfate salt either in suspension or in solution. Hence, a wet scrubber has two systems: (1) the spray system, or contactor, to mix the exhaust gas with the scrubber liquid and then collect the water, and (2) a water management system to maintain sufficient pH, remove the solids from the water and manage the solids. The contactor usually includes some kind of packed bed as shown in Figure 6-3 with a large wetted surface area. Sometimes waste water can be evaporated into the exhaust stream in the scrubber, so there is no water discharged from the plant.

Wet scrubbers are conceptually similar to particulate scrubbers in that they spray a large amount of water through the exhaust gas to achieve complete contact between the liquid and the gas. However, they do not require a high gas pressure drop (unless they are also intended to collect particulate) and they may use an even larger water flow rate. Water circulates in a loop from the spray to the scrubber sump to a recirculation tank and back to the spray. The exhaust gas leaving the scrubber is saturated and it will carry any fine particulate or mist that is not captured in the mist eliminator. Mist escaping from a wet scrubber will include most of the SO_3 (sulfuric acid), which, though highly soluble, condenses into submicron particles that seldom impact the scrubber water drops. So wet scrubbers do a poor job of controlling the emissions of sulfuric acid, mercury or any submicron particulate.

Semi-Dry Scrubbers

Semi-dry or spray drying scrubbers begin the scrubbing process similarly to wet scrubbers, but they spray much less water into the exhaust gas. The amount of water is controlled so that it evaporates completely, leaving behind dry salt particles that can be captured in a dust collector. The exhaust temperature is typically 15° to 30°F above saturation temperature. The semi-dry scrubber must be followed by either a baghouse or an electrostatic precipitator to collect the sulfate dust created in the scrubber. In some systems, this is the only dust collector. When a baghouse is used, there is some secondary scrubbing of the gases as they pass through the filter cake on the surface of the bags. This can be a key factor when very high collection efficiency is required, or if the system is also required to remove mercury from the exhaust gas. A baghouse also assures high collection efficiency for fine particles and mists, such as sulfuric acid. Semi-dry scrubbers can remove SO_2 with 90%-95% efficiency. Semi-dry scrubbers with baghouses have seen wide application on municipal waste combustors.

Dry Scrubbers

Dry scrubbing is less efficient at removing SO_2 than either wet or semi-dry scrubbers. However, it can significantly reduce SO_2 emissions when high efficiency is not required. This method blows powdered reagent directly into the exhaust gas or the combustion zone where some of it reacts with the acid gases. In most cases, the amount of reagent must be much larger than the amount calculated from a chemical balance – sometimes 5 to 10 times as much reagent. A fluid bed combustor can work as a dry scrubber if limestone is added to the bed.

Several factors affect the performance of a dry scrubber. First, the reagent must be highly reactive with SO_2 in order to be effective. Dry scrubbing is typically more efficient in capturing SO_3 (sulfuric acid) than in capturing SO_2. Second, the reagent needs to have a large surface area – meaning it must be in very small particles (5-10µm), which must be fairly porous. Third, it needs to be injected beyond any temperature zone that could fuse the particles or destroy their chemical reactivity.

Finally, dry scrubbing benefits greatly from reactions between the exhaust gas and the filter cake in a baghouse. An electrostatic precipitator is usually much less effective in a dry scrubbing application than a baghouse.

6.3.2 SO_3 Control

SO_3 emissions are problematic for several reasons:

- SO_3 emissions are not significantly controlled by scrubbers or electrostatic precipitators. In fact wet scrubbers simply condense the SO_3 acid, exacerbating downstream problems. Control with a baghouse requires an alkali dust in the filter cake.

- Relatively small amounts (10 ppm or less from a large utility boiler) can condense downstream of the stack to create a highly visible plume that is difficult to control.

- SO_3, if allowed to condense as sulfuric acid, seriously damages ductwork and any unprotected pollution control devices.

- If an SO_3 bearing plume touches down near the source, it is a highly toxic gas with ambient impacts that include a pungent odor and corrosion.

Sulfuric acid exists in different forms, depending on the temperature. Above 500°–600°F, SO_3 is a gas. As it cools, it combines with increasing amounts of water and below about 250°F it condenses to liquid sulfuric acid. Condensation can occur on cool surfaces or it can form a mist or cloud of submicron size drops. When combustion exhaust gases with SO_3 are vented to the atmosphere, the condensed acid can form a visible cloud. Either a wet or semi-dry scrubber will drop the temperature below 250°F and cause any acid present to condense into submicron drops. As described in the discussion of particulate scrubbers, the acid drops are so small that they do not impact the scrubber drops. So the scrubber causes the acid to condense, and that makes it impossible for the scrubber to capture most of the acid mist. However, if the scrubber is followed by a good dust collector, it will capture most of the acid mist. In fact, a baghouse will capture nearly all the acid mist.

If the SO_3 is not condensed, it can be captured by a dry scrubber in which an alkaline powder is mixed with the flue gas. SO_3 in the gas phase will react with dry alkaline materials, which then can be captured by a dust collector. However, this method of SO_3 capture tends to be relatively inefficient – requiring several times as much alkali reagent as is theoretically necessary. However, since the amount of SO_3 is typically in the range of 10 ppm, supplying excess reagent may not be a problem. If the system is an oil-fired boiler, with no dust collector, adding alkali dust to the flue gas can easily increase the particulate emissions to unacceptable levels.

6.3.3 HCL Control

Hydrochloric acid can be collected in the same way as SO_2. However, the biggest difference is that HCl is more water soluble than SO_2, so it is easier to collect and, in the same scrubber, HCl collection efficiency will generally be much higher than SO_2 collection efficiency.

6.4 NITROGEN OXIDES CONTROL

6.4.1 Approaches to NOx Control

NOx control is driven by the need to control ambient ozone levels. Although NO_2 is yellow or brown gas, it is rarely present in sufficient concentrations to be visible in the plume from combustion sources (most of the NOx emissions are NO). On a regional scale, NO_2 may be a small contributor to haze and visibility impairment.

NOx control follows a two-tiered approach. The first level is to minimize the amount of NOx formed by adjusting the combustor design and operation. When further reduction is required, a system is installed to remove NOx from the flue gas – similar in function to a dust collector or a scrubber. Combustion controls are generally inexpensive to build and operate although many of them provide only modest NOx reductions. Back-end controls incur significant expenses, but they typically remove 90% or more of the NOx remaining after implementation of low NOx combustion. As the science of NOx controls evolves, we are seeing continued advances in both combustion and back-end control technologies. These advances are closely coupled to ever lower expectations for NOx emission levels on new sources. One should remember that the very low NOx emissions from many new major sources are only possible when firing natural gas. When these sources fire distillate oil emissions are usually much higher than when firing gas.

6.4.2 Combustion Modifications

In general, there are three levels of combustion modifications that are used to reduce NOx formation.

- *Excess air control.* Any effort to reduce NOx emissions begins with precise air flow control. It is the first step taken to reduce NOx and it is an integral part of any subsequent combustion based control effort.

- *Reduce peak flame temperature.* Modest reductions in peak flame temperatures will dramatically reduce the formation of thermal NOx with little or no effect on fuel NOx.

- *Staged combustion.* Staging the combustion will control the formation of both thermal NOx and fuel NOx, but it requires considerable sophistication to achieve

significant NOx reductions without incurring unacceptable emissions of black smoke or CO.

The order here reflects both the difficulty of implementation and the potential effectiveness of NOx reduction from most sources.

6.4.2.1 Excess Air Control

Figures 5-9 and 5-10 show that the amount of excess air in the combustion zone affects NOx emissions. Reducing excess air reduces NOx emissions on most types of sources, including virtually all boilers and furnaces. Thus, the first step toward NOx reduction on boilers and furnaces is to reduce the excess air as far as possible. All sources require some excess air because, as you can see from Figure 5-9 and 5-10, when the excess air is too low, there is a sharp increase in emissions of CO, smoke and other products of incomplete combustion (PIC). Thus, there is an optimum excess air level where NO_x is minimized and PIC are not excessive. This means that the air flow must be precisely controlled in order to continuously minimize NOx. On newer boilers good air flow control is a matter of operating practice and does not require additional hardware. On older systems the controls may need to be upgraded with the installation of an O_2 meter linked to the automatic controls.

There is one NOx control method that combines precise excess air control with a catalytic reaction. It is called non-selective catalytic reduction (NSCR) and is used on reciprocating engines. The concept is presented here and outlined again in Section 6.4.4 on back end control methods. NSCR uses a catalyst to make NOx react with PIC to destroy both species. The general chemical reaction is:

$$NO_x + CO \rightarrow N_2 + CO_2$$

or

$$NO_x + HC \rightarrow N_2 + H_2O + CO_2$$

As written here, these reactions have not been balanced, but it should be obvious that the amount of unburned fuel needs to be closely matched to the amount of NOx in order to destroy all of both types of pollutant. If there is any oxygen present, it burns the VOC and CO, leaving the NOx untouched. This balance is achieved by precisely controlling the excess air level. As illustrated in Figure 5-9 and 5-10, at very low excess air levels any change in the amount of excess air will change PIC and NOx in opposite directions. So the NSCR reactions can be balanced by operating at exactly the right excess air level.

Although this is a simple concept, its implementation is daunting because of the precision required. In practice, NSCR is accomplished with a sensitive O_2 or CO meter linked to the air-fuel control device of the engine. We will not get into the details of this control technology here; however, it is worth noting that this technology requires not only the right catalyst, but also a very good gas concentration instrument linked to very good controls. The fact that gasoline powered automobiles operate very well for many years without major repair or adjustment is testament to

the successful development of this technology. This technology has been used primarily on gas fired reciprocating engines, but it is potentially applicable on boilers and furnaces.

6.4.2.2 Temperature Reduction

NOx is formed during combustion because the high temperatures break apart a few N_2 molecules making N atoms available to react with oxygen. N_2 is very stable and only decomposes at very high temperatures, so NOx is formed primarily in the hottest regions of the flame – typically at temperatures above 3000°F. Any change in combustion that reduces peak flame temperature will reduce the formation of thermal NOx. Temperature reduction approaches can be very effective in reducing NOx when there is no nitrogen in the fuel, in some cases reducing emissions by 90% or more. Even when there is nitrogen in the fuel, flame temperature reduction is normally part of a NOx reduction effort.

The theoretical equilibrium curve in Figure 5-6 suggests that a 200°F temperature reduction will reduce NOx by 50%. Although equilibrium is not achieved in most combustion systems, the effect of peak temperature on NOx levels in a real system is probably similar to equilibrium theory. It should be noted that NO is quite stable and once formed in the combustion zone, it does not decompose as the flue gas cools off. If NOx formation can be suppressed in the flame zone, it will not be formed by secondary reactions downstream.

There are a number of methods of cooling the flame including:

- Spraying water or steam into the flame.
- Cooling the combustion air supply.
- Recirculating cool exhaust gas into the flame.
- Retarding the ignition of an internal combustion engine.
- Raising the excess air level of a premixed flame.

None of these methods are particularly advantageous to combustion, aside from reducing NOx, but some incur less efficiency penalty or fewer operating problems than others. The methods that have become common practice for different types of sources are discussed in the following sections.

Water Injection

Water injection has been the accepted method to reduce emissions from combustion turbines for about 25 years. The flame cooling effect of spraying water in with the fuel is obvious. Figure 6-6 is an example of the effect of water or steam injection on emissions. The process requires very clean water, but the penalty to engine efficiency is quite small for two reasons. First, water provides cooling that would otherwise have to be provided with air because the maximum allowable turbine inlet temperature is far below the peak flame temperature in the primary zone. Second, injected water turns to steam, which provides added mass flow through the turbine,

thus adding power to compensate for the energy lost to evaporating water. The water mass flow rate into a turbine combustor can be as high as the fuel flow rate. The resulting NOx emissions can be reduced by more than 70% without dramatically increasing the emissions of CO and hydrocarbons. Water injection is not commonly used on boilers because there are other less expensive alternatives for reducing NOx. Water injection has been tried on reciprocating engines, but it significantly reduces engine efficiency and tends to cause operating problems.

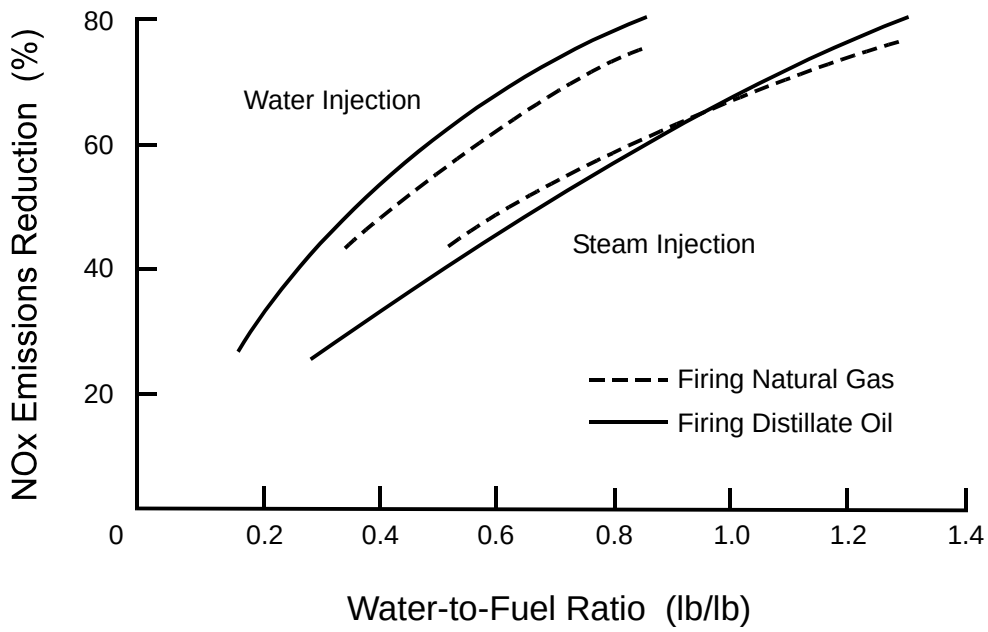

Figure 6-6. Effect of Water Injection on Combustion Turbine Emissions.
Source: Schreiber, 1991

Flue Gas Recirculation

Flue gas recirculation (FGR) or exhaust gas recirculation (EGR) works by mixing some flue gas with the incoming combustion air. This increases the mass flow through the combustion zone and decreases the concentration of O_2 available for combustion. Increasing the gas flow in the combustion zone decreases the temperature because the same amount of energy is distributed to a larger thermal mass. Figure 6-7 shows the basic elements of a FGR system. Note that FGR operates without changing the inlet air flow, the stack exhaust flow or the fuel flow. The only flow that increases is the flow through the combustor and through most of the heat transfer elements.

Flue gas recirculation has been used both on boilers and on reciprocating engines. The penalty on boiler efficiency and performance is almost negligible with recirculation rates up to 20%-25%. When there is no fuel nitrogen present, NOx can be reduced by 75% or more as indicated in Figure 6-8. FGR is typically a part of any effort to substantially reduce NOx emissions from a boiler.

Exhaust gas recirculation can reduce NOx emissions on reciprocating engines, but it requires considerable development and tuning to avoid significant degradation of performance and efficiency.

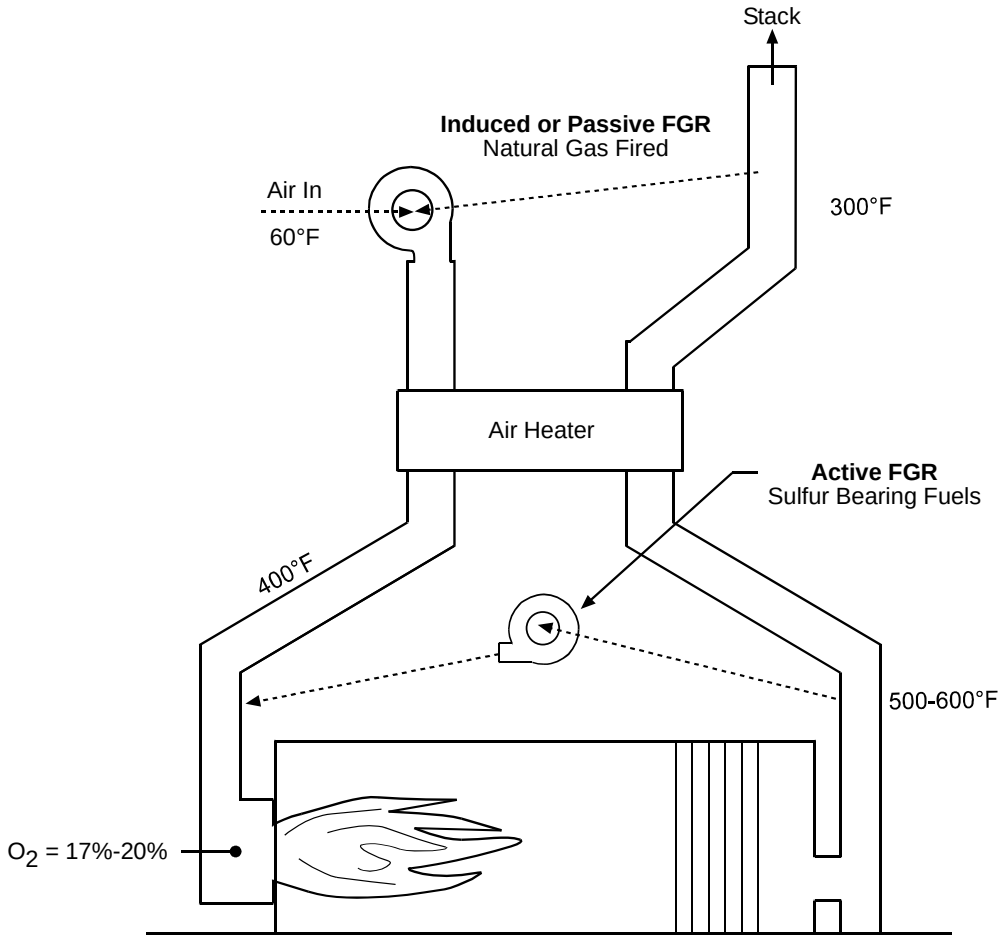

Figure 6-7. Flue Gas Recirculation

Two possible FGR systems are shown in Figure 6-7. In most boiler FGR systems a fan is required to mix hot gas from the exhaust side, at low pressure, with hot combustion air at higher pressure. Electric power to operate the gas recirculation fan is a significant operating cost because the fan moves a substantial volume of hot gas across a significant pressure differential. It is also possible to recirculate gas from the stack to the inlet of the FD fan, which does not require a separate fan (called passive or induced FGR). However, this is only practical if the fuel is free of sulfur. Whenever there is sulfur in the fuel, there will be a significant amount of sulfuric acid in the exhaust gas. If acid vapor is introduced into the combustion air supply, it will condense and corrode in the inlet air duct and the burner. Passive or induced FGR is suitable only on combustors where natural gas or sulfur free petroleum is the only fuel. In other cases, the FGR system must be entirely on the hot side of an air heater

in order to prevent acid corrosion problems. This limits its application on industrial boilers, many of which do not have air heaters.

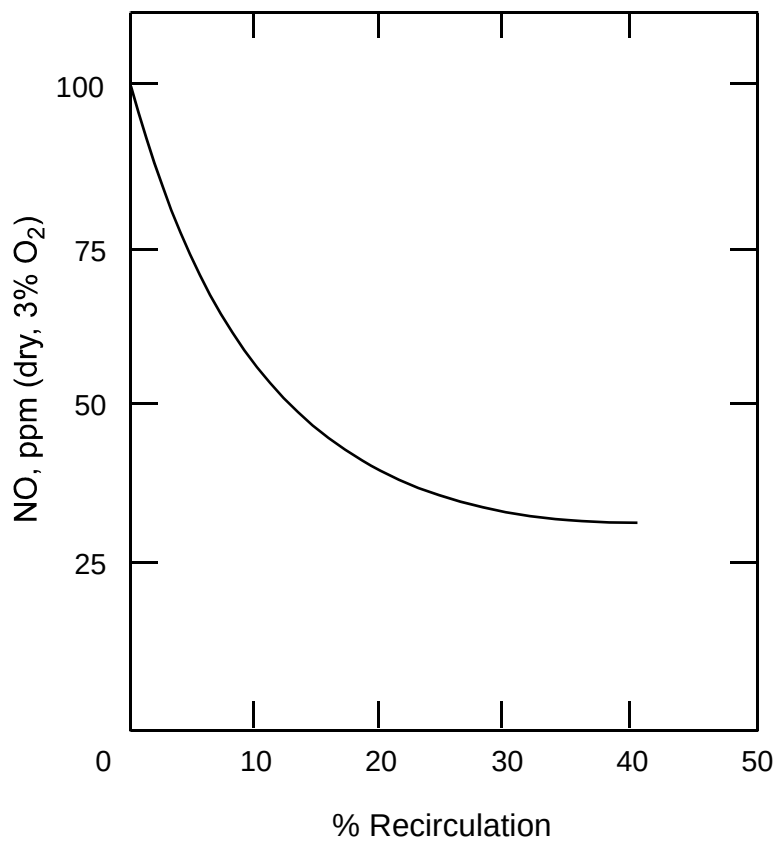

Figure 6-8. Effect of Flue Gas Recirculation on Emissions

The FGR systems illustrated in Figure 6-7 imply that the recirculated exhaust gas is uniformly mixed with the combustion air, and many systems do exactly that. However, the FGR system can be built to deliver the gas to a specific region of the burner so that one part of the flame is affected more than another. This approach can amplify the NOx reducing effect of FGR, but if it is not carefully developed, it can also decrease flame stability or increase CO emissions. In summary, FGR is an effective method of reducing NOx emissions especially on natural gas-fired sources, but its effectiveness depends in part on design details.

Ignition Retard

The combustion process in reciprocating engines is linked to crankshaft rotation and is normally timed to generate maximum pressure in the cylinder, which corresponds with maximum temperature and, hence, maximum NOx. If the ignition is delayed by a few degrees of crankshaft rotation, then pressure, temperature and NOx are all reduced as is engine power and efficiency. On most engines, ignition – or fuel injection – timing is a relatively simple adjustment so it can be used to reduce NOx

emissions on existing engines. The resulting NOx reduction is considerably more than the resulting loss in engine efficiency, so there is a net decrease in NOx emissions. NOx reductions of 20-25% can be achieved

6.4.2.3 Staged Furnace Combustion

When boilers fire coal or No. 6 oil, more than half of the total NOx comes from fuel nitrogen, so thermal approaches like flue gas recirculation are much less effective than when firing clean fuels. When firing nitrogen-bearing fuels, combustion based approaches to NOx reduction use some form of staged combustion. Staged combustion is capable of controlling both thermal and fuel NOx. There are several fuel staging concepts, but two are noteworthy:

- *Stratified combustion*. Fuel and an insufficient amount of air mix and burn in a primary combustion zone. With insufficient oxygen available for complete combustion, all the O_2 is consumed by carbon and hydrogen, leaving none available to form NOx. The fuel nitrogen combines to form N_2. During the few hundredths of a second it takes for combustion to occur, the flame cools slightly. Once this cooling has occurred, the rest of the air is added to complete combustion. Since the fuel nitrogen radicals have disappeared, and the flame is too cool to generate a lot of thermal NOx, relatively little NOx will be formed in this secondary combustion zone. This is the conceptual basis for low NOx burners and for burners-out-of-service or over-fired air applied to a large furnace. The trick has been to get this concept to actually work consistently in real furnaces. To be successful it requires precise control of fuel-air mixing throughout the combustion zone. Stratified combustion is being used with considerable success on suspension-fired boilers; it is not applicable to stokers. An inevitable side effect of staged combustion is longer, less brilliant fires.

- *Reburning*. A normal boiler combustion zone is operated with minimum practical NOx emissions. Then a second combustion zone is added downstream after the flue gases have cooled significantly. This second zone is staged by injecting fuel – usually natural gas – with no additional air. With insufficient oxygen, this fuel creates a reducing zone, which actually consumes NOx formed in the initial combustion zone. Then further downstream additional air is injected to complete combustion. No additional NOx is formed because the temperatures are too low. While this approach works (conceptually) on any furnace with sufficient space, it is particularly attractive on systems like stoker boilers where no other combustion NOx control can be implemented.

With this introduction, each of the staged combustion concepts can be discussed in greater detail.

Stratified Combustion in Large Furnaces

Early efforts to reduce NOx from utility boilers in Southern California paved the way for technologies still used today. Utility boilers have many burners on multiple levels

and the fuel can be shut off from a few of the burners without affecting the boiler load. The remaining burners pick up the slack. If fuel is shut off to a few of the top-level burners without shutting the burner air dampers, the bottom of the furnace will be fuel rich. Air flow through the *burners out of service* (BOOS) will make up the air deficit without generating much additional NOx. Figure 6-9 illustrates this concept. Typically, this approach can achieve a 15% to 30% NOx reduction without seriously affecting boiler performance or generating excessive smoke. This is not always as simple as it sounds and there will be one or more particular combinations of burners-out-of-service which are more effective than others. However, the BOOS approach is still used on some boilers.

Removing burners from service frequently incurs some sort of operating restriction on a large boiler. To get around this, utilities began installing overfired air (OFA) ports above the top row of burners as shown in Figure 6-9. OFA ports have become a fairly standard component of a low NOx system on large utility boilers.

One consequence of staged combustion in any form is that flames are longer and generally less brilliant. In fact, some low NOx fires have an alarmingly dark and dirty appearance, which is counter to the traditional operating philosophy of optimizing performance with short bright flames.

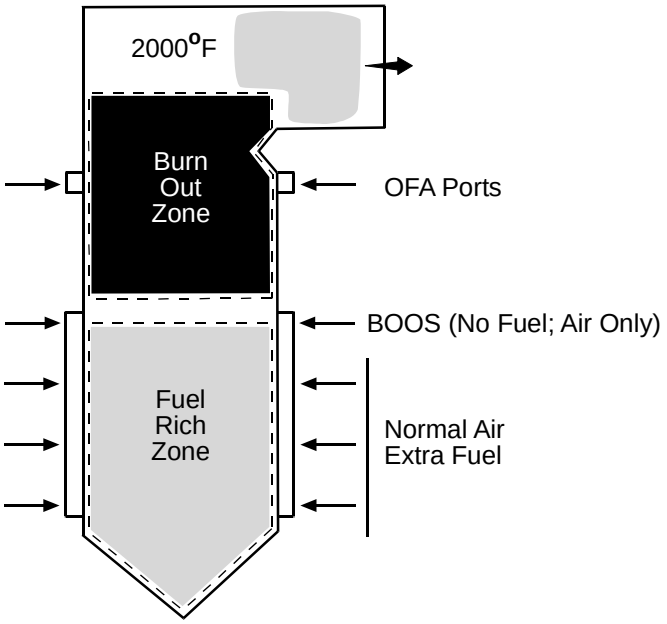

Figure 6-9. Burners-Out-of Service (BOOS) and OFA Ports

U.S. Environmental Protection Agency. Alternative Control Techniques Document: NOx Emissions from Utility Boilers, March 1994, EPA Report 453/R-94-023, NTIS PB94-184165.

Reburning is a relatively recent NOx reduction technique that is particularly attractive for existing boilers when traditional combustion control technologies are not applicable. Reburning is not restricted to large utility boilers, but there are geometric limitations. Figure 6-10 is a general schematic of reburning in a large utility boiler.

The reburning section is installed just downstream of the main combustion zone where the amount of NOx present will be typical of uncontrolled emission levels. Therefore, it can be used on stoker furnaces and cyclone-fired boilers.

Reburning seeks to reduce (literally and chemically) the NOx by injecting more fuel with no accompanying air. This creates a fuel rich zone where no additional NOx will be formed because of (1) the lack of oxygen and (2) temperatures are below that required for NOx formation, but are still hot enough to ignite the supplemental fuel. In this fuel-rich zone, hungry fuel species take oxygen away from the NOx, reducing it to N_2. Of course the gases leaving this reducing zone are full of PIC, so additional air is now required to complete combustion. Overfired air can be added without creating much NOx because the gases beyond the primary flame zone have lost heat to the furnace walls and temperatures are too low to generate thermal NOx.

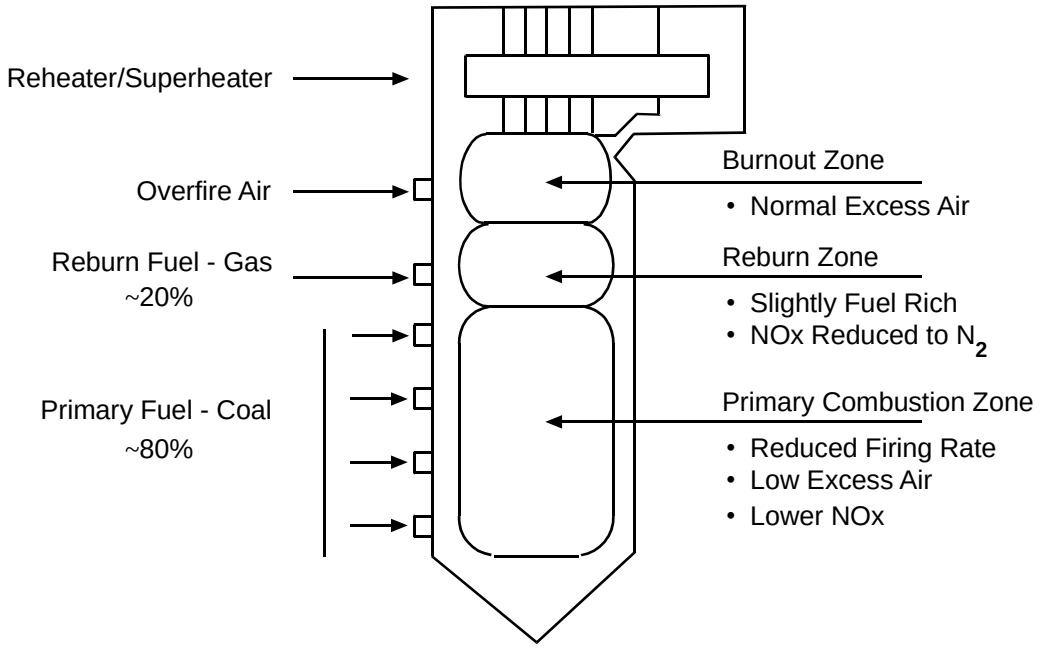

Figure 6-10. Reburning on a Utility Boiler

U.S. Environmental Protection Agency. Control of NOx Emissions by Reburning, February 1996. EPA Report 625/R-96/001.

NOx reduction levels using reburning depend on how much fuel is burned in the reburn zone. Full-scale demonstration projects firing up to 25% of the total heat input has reduced NOx by about 50%. Since this scheme works by creating a fuel rich zone, the amount of reburn fuel must, in theory, be more than enough to consume all the excess air present in the original combustion zone. In practice, nonuniform excess air distribution and nonuniform mixing mean that any amount of reburn fuel will have some effect, but no amount will destroy all the NOx.

Typically, the injected fuel is natural gas because it is relatively easy to inject and mix. At least one demonstration project has shown than “micronized” (very finely

pulverized) coal will also work. Although any fuel that can be thoroughly mixed with the flue gases should work, reburning fuel will probably be limited to natural gas for practical reasons.

6.4.2.4 Low NOx Burners

Once the success of BOOS and OFA ports in large furnaces was demonstrated, it was natural to try to extend the concept to individual burners. The BOOS concept cannot be used on smaller boilers with only one or two burners because there are insufficient burners to remove from service and still maintain load. In addition, these boilers frequently lack any location for installation of OFA ports. And if low NOx burners can be combined with OFA ports in large boilers, there should be additional NOx reduction. All the companies that manufacture boiler burners have developed low NOx burners with varying degrees of success.

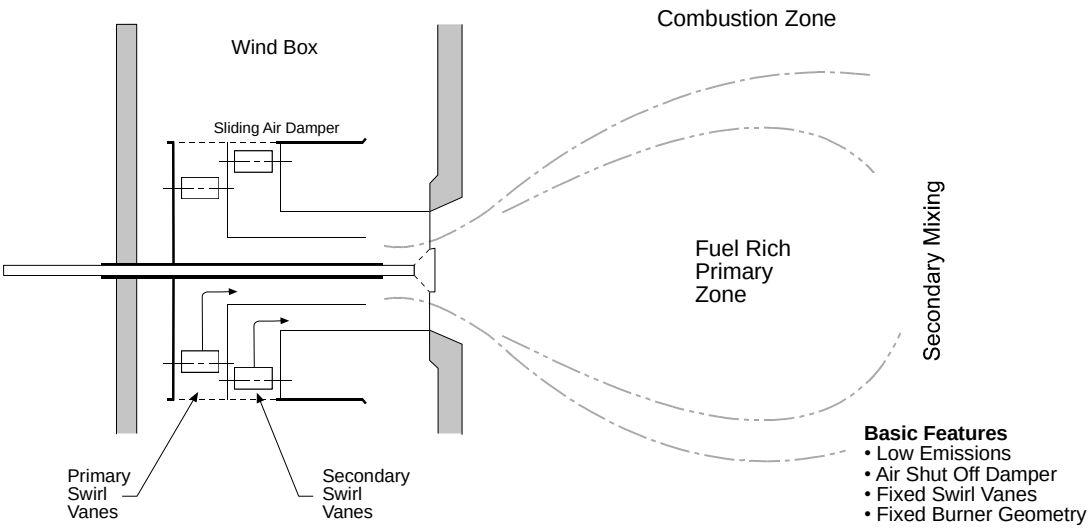

Figure 6-11. Low NOx Burner Concept

Figure 6-11 illustrates the low NOx burner concept. The burner creates a primary zone in which all the fuel burns without quite enough air. Then, a few feet further into the furnace, additional air is mixed into complete combustion. However, the concept is much easier to illustrate than it is to execute in practice.

The first challenge is to design a burner that will actually create two mixing zones – one following the other. A number of vendors with combustion laboratories have been able to develop and demonstrate full-scale burners, but a major challenge has been to get these burners to perform as well in the field as they do in the laboratory. Several problems arise in practice, particularly on multiple burner boilers. First, air flow and fuel flow may not be identical to all burners. If one burner operates with lower excess air than the rest, then the whole furnace has to be fired with enough air to keep that rich burner from smoking. Air velocity in the wind box upstream of the burner may cause more air to enter one side of a burner than the other. A similar

problem can appear in the fuel distribution of a pulverized coal burner. The powdered coal is transported pneumatically and may not enter the combustion zone in a circumferentially uniform pattern. A critical element of combustion NOx control on large boilers is to get all the burners to behave in exactly the same manner. This has frequently taken a great deal of tuning and troubleshooting.

A question that is frequently asked is, "What is a low NOx burner?" The best answer appears to be: "A burner with low NOx emissions". There is no hardware specification that assures low emissions. Most low NOx burners have a couple of features worth noting:

- *Manufacturer Presets.* All adjustable features are configured so the boiler operators will not routinely alter them. Adjustments should be made when the system is initially tuned, and then left alone. Boiler operators are accustomed to adjusting burners to get a nice looking fire, and this kind of tinkering will defeat low NOx performance.

- *Separate Air Flow and Direction Dampers.* Air registers that control swirl must be separate from those than control flow. Burners used to have dampers that combined swirl and air flow control. With a low NOx burner you need to be able to shut off the burner and its air flow without adjusting the swirl (flow pattern).

- *Precise Air Flow Control.* The system will have air flow controls that can maintain the air flow at the minimum level practical without generating excess CO or smoke.

Note that low NOx burners will only give low NOx performance if the whole furnace installation works as intended. Low NOx burners alone will not necessarily give low NOx performance.

6.4.3 Premixed vs. Diffusion Flames

With the exception of reciprocating engines that burn gasoline or natural gas, most combustion sources use diffusion flames so the fuel and air mix as they burn. These burners are generally easier to build and operate than burners based on premixed fuel and air. Premixed combustion is impossible with solid fuel (e.g., coal, etc.) or residual oil and has yet to be achieved commercially with No. 2 oil. So premixed combustion is limited to natural gas and very volatile liquids such as gasoline. Premixed burner designs offer a unique opportunity to reduce NOx emissions because (1) there is no fuel nitrogen to make fuel NOx, and (2) ultra lean combustion, where it can be achieved, is cool combustion that makes very little thermal NOx.

6.4.3.1 Theoretical Differences

The difference between premixed and diffusion combustion in real systems becomes apparent in NOx emission levels and in the choice of NOx control strategies. As

previously noted, the peak flame temperature in premixed flames is equal to the adiabatic flame temperature; in other words, it decreases as excess air increases. Figure 6-12 is similar to Figure 4-5 and it shows NOx emissions versus excess air for both premixed and diffusion flames. The NOx curves are drawn to illustrate a concept and are not the result

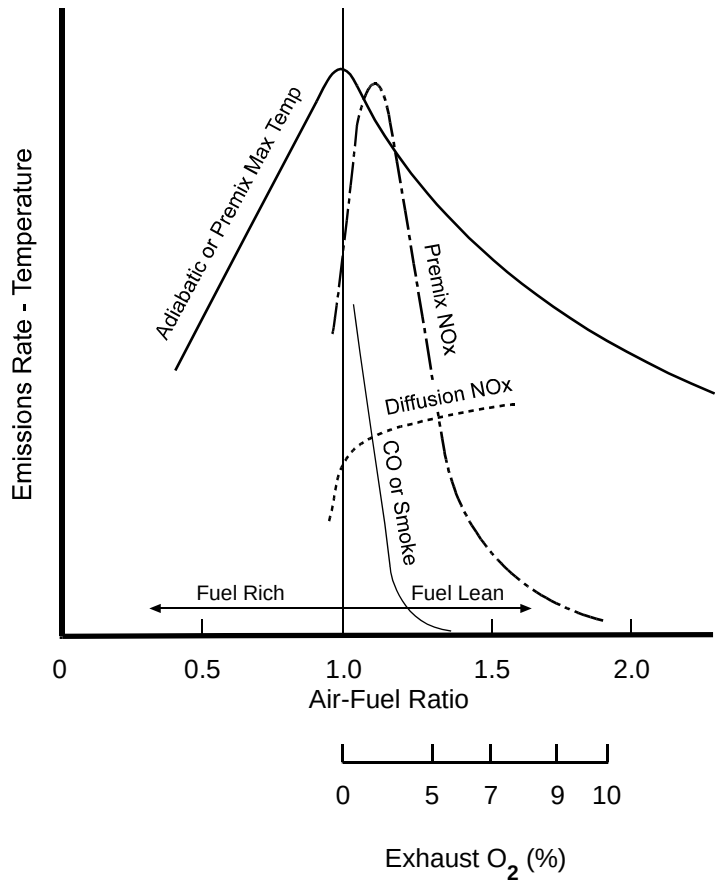

Figure 6-12. Flame Temperature and Emissions versus Air-fuel Ratio

of any specific analytical model. Note that the premixed flame NOx emission rate peaks at a point slightly to the right of the line of equivalence ratio equals one, and then falls rapidly as excess air increases. By contrast, diffusion flame NOx emissions steadily increase as excess air increases.

In a premixed flame all the combustion occurs at a fixed air-fuel ratio – the same excess air level as measured at the combustor exit. Thus, nowhere in the flame can the temperature exceed the adiabatic temperature for that air-fuel ratio. The higher the excess air level, the lower the flame temperature and the lower the NOx, except at very low excess air levels where the lack of oxygen inhibits NOx formation. A diffusion flame is different because all of the fuel passes through the mixture point where the air-fuel ratio = 1.0 at some point in the flame. So diffusion flame temperatures can locally approach the peak adiabatic temperature regardless of the exhaust excess air level (assuming the excess air level is greater than zero). Diffusion flame NOx levels depend on how much of the combustion occurs in regions of the flame where there is a

finite amount of oxygen available (e.g., where not all the oxygen has been consumed by fuel combustion). The higher the overall excess air level, the more of the flame that has excess oxygen available for NOx formation and the higher the NOx. So diffusion flame NOx levels increase with increased excess air.

If one can operate a premixed burner at a fairly high air-fuel ratio (on the right side of Figure 6-12) both the NOx and CO emissions will be low. The challenge has been to get these burners to operate reliably. Very lean flames are hard to light and they blow out easily. Flames that blow out and engines that quit are unacceptable regardless of their exceptional emission characteristics.

6.4.3.2 Combustion Turbine Burner

Emissions from combustion turbines have been controlled to relatively low levels for many years by the use of water injected into the combustion chamber with the fuel. Water injection incurs a relatively small engine performance penalty because the steam helps to drive the turbine and offsets most of the losses associated with evaporating the water. The main drawback is the need for substantial amounts of ultra pure water. Any contamination in the water gradually builds up on the turbine blades and degrades engine performance. Combustion turbine (CT) power plants have had to operate large water treatment facilities to supply water for the turbines. This is a significant burden in remote facilities, especially where water is scarce.

It has taken many years to develop, but the major CT vendors are now offering “dry low NOx” or “lean-premix” combustors for their gas-fired turbines. The basic concept is to premix the fuel and air, then operate the combustor very lean – on the far right side of the curves in Figures 4-5 and 6-12.

The challenge is to get the engine started. Figure 6-13 shows the sequence involved in starting the engine and bringing it up into its operating range. The emissions associated with this operation are shown in Figure 6-14.

Normal operation is shown in the last illustration. The first three figures show how the engine is started and reaches its normal operating mode. Initial light off and low load operation is in a conventional combustion mode with characteristic high NOx emissions. Then the engine fuel controls take the combustion process through a transition (lower two figures) in which fuel is shut off to the primary zone to extinguish the flame followed by reintroducing most of the fuel into the primary zone. Here the fuel is premixed with air before being ignited in the secondary zone. The result is lean, cool combustion that generates very low NOx emissions. There is no engine efficiency penalty and the hardware is only moderately more expensive than a traditional combustor. The biggest cost is the years of engineering work required to develop this type of combustor. These costs must be amortized in the price of the new hardware.

“Dry” low NOx turbine engines have very low emissions when operated above the critical transition point – 40% to 50% load in the example shown here. However, the emissions are high at low load, so extensive operation at low load must be avoided.

Fortunately, these engines by themselves can start and come up to load quite rapidly; typically less than 30 minutes from a cold start. However, if the engine is feeding a waste heat boiler, a load ramp limit may be imposed by the boiler. Boilers generally take many hours to heat up.

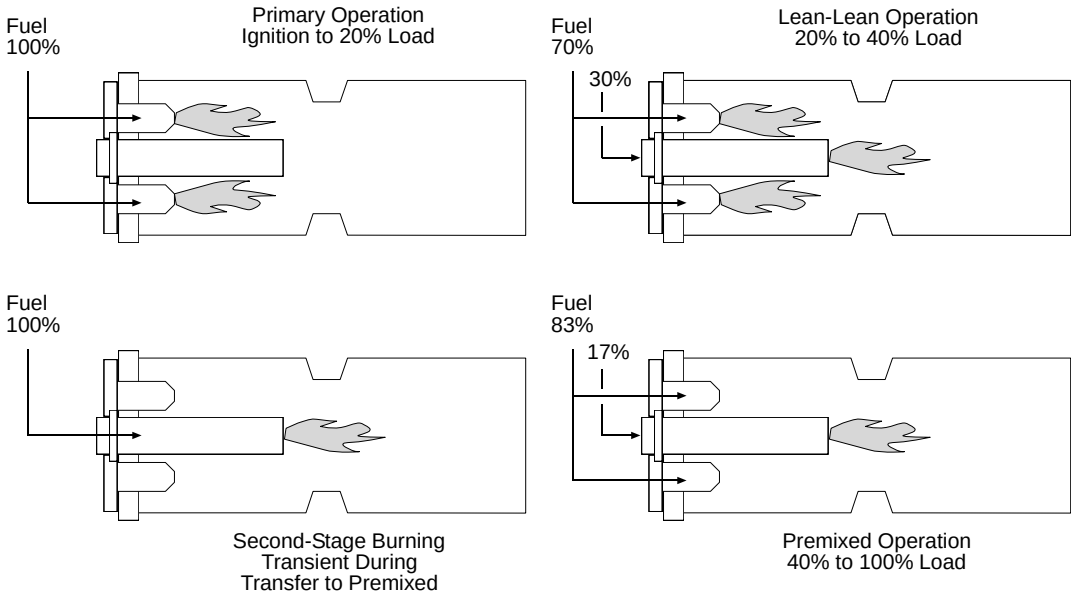

Figure 6-13. Dry Low NOx Combustion Concept – Gas Firing
Marvin Schorr, GE Industrial & Power Systems, 1993

Although gas turbines are conceptually simple, the systems can get complex and they are still evolving. Here are several issues to consider when evaluating emissions from a CT system.

Maximum power from a combustion turbine is controlled by the amount of air that is pumped through the engine. This means that on a hot day or at altitude – when the air is thin (less dense) – engine power diminishes. In many cases, there can be a 20% power difference between summer and winter. NOx emissions are also sensitive to the amount of moisture in the air. Emissions are higher on a dry day than on a warm, moist day. The effect of ambient conditions on power and on engine emissions is highly predictable for each engine design. The dependence of emissions on ambient conditions is engine specific and each manufacturer has developed a correlation for each engine model. There is a default correlation listed in Subpart GG of 40CFR63 to correct NOx emissions to standard conditions, but the manufacturer's correlation should always be used when it is available.

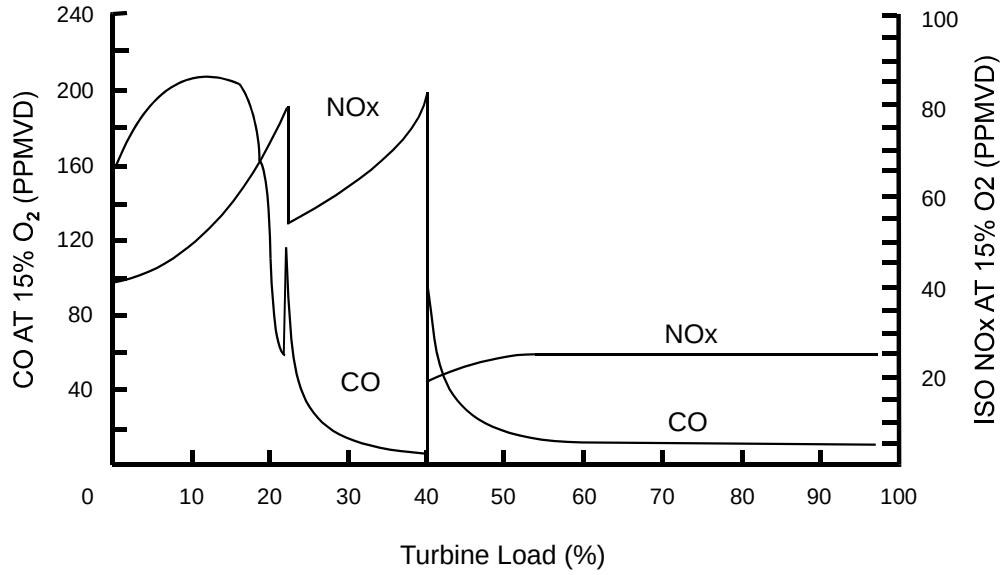

Figure 6-14. Dry Low NOx CT Emissions – Gas Fired
Marvin Schorr, GE Industrial & Power Systems, 1993

One way to compensate for warm ambient conditions and to get more power from the engine is to cool the inlet air. Spraying a fine mist of water into the air at the engine inlet cools the air by evaporation and adding water lowers NOx emissions. Thus, the maximum engine power and emissions are both significantly influenced by inlet evaporative coolers – also called inlet fogging.

A gas turbine has a device called a fuel control that correlates fuel flow with air flow, engine speed and load demand. Originally, the fuel control was a complex mechanical device, but the advent of microcomputers allows software to absorb the complexity. Computers also allow the fuel control to serve an emissions control role. Emissions from a gas turbine are highly predictable, so the amount of water injection required either in the combustor or in the form of inlet fogging can be programmed into the engine's control system. So, to a substantial degree, a turbine engine can be programmed to meet an emission limit over its load range and over a range of ambient conditions without relying on any actual emission measurement.

6.4.3.3 Catalytic Turbine Combustion

A recent development in gas-fired combustion turbine operation is the advent of the catalytic combustor. In place of a combustor with a hot flame followed by dilution air, most of the air and the fuel is premixed, and then passed through a catalyst where combustion occurs at essentially the same temperature as the turbine inlet – much lower than typical flame temperatures. This virtually eliminates NOx formation and typical emission levels are in the range of one to two ppm. The technology is patented and is marketed under the name XONON (no NOx spelled backwards) by Catalytica Systems, Inc. of Mountain View, CA. Figure 6-15 is shows the concepts.

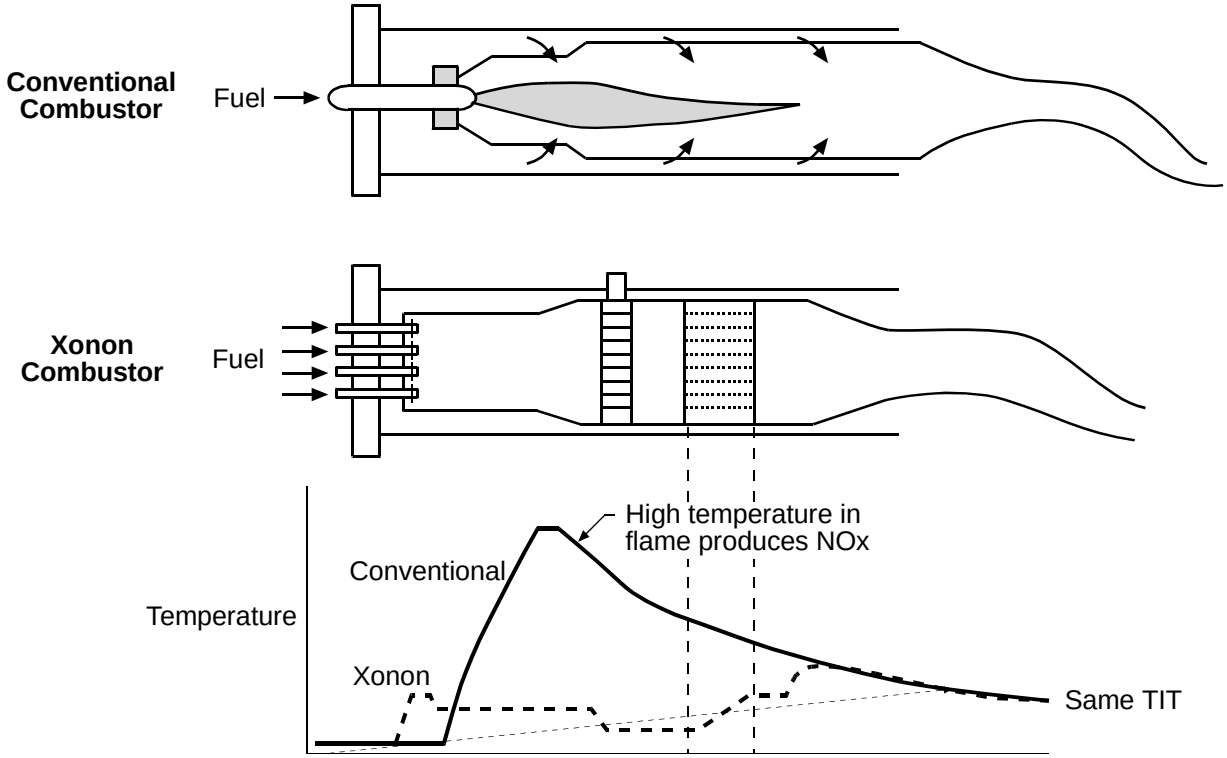

Figure 6-15. Xonon Catalvtic Turbine Combustor
Courtesy of Chuck Solt of Catalytica Inc

In place of a normal primary zone there is an air fuel mixing zone. This includes an ignition or warm up burner that consumes a small fraction of the fuel to maintain adequate inlet temperature to the catalyst. Most of the fuel burns in or downstream of the catalyst where the high excess air level reduces flame temperature and little or no NOx is formed.

The technology appears to be broadly applicable to gas turbines, but is new enough that the durability of the catalyst is not currently known, although it is guaranteed for one year. One drawback is that an engine fitted with a XONON combustor cannot use liquid fuel as a backup. Like all other turbine combustors, the XONON combustor must be specifically developed for each type of engine; there is no such thing as a generic, one type fits all, catalytic combustor. And, like most combustors, one of the biggest challenges has been the development of the start-up procedure to get the engine running. A normal (non-catalytic) flame is necessary for ignition and to warm the catalyst to operating temperature before converting to catalytic operation.

6.4.3.4 Reciprocating Engines

NOx emissions from reciprocating engines have been reduced by several methods that include: ignition retard, modifying the air-fuel ratio, exhaust gas recirculation, and combustion chamber modifications. Exhaust gas recirculation has not been widely used on stationary engines. Ignition retard amounts to detuning the engine because it reduces power and/or fuel efficiency. By delaying ignition, combustion occurs at lower pressure and lower temperature, which reduces NOx formation and may increase PIC emissions. This approach is available on nearly all reciprocating engines, but the effectiveness in reducing NOx and the effect on engine performance varies from one engine model to another. On gas fired and dual fuel engines, ignition retard has largely been superceded by combustion chamber modification. On diesel engines ignition retard continues to be the primary tool available for NOx reduction. While the effectiveness varies, reductions of 40% have been observed (see AP-42).

Air-fuel ratio adjustments, as indicated in Figure 6-12 clearly affects NOx and PIC emissions. This approach to emissions control is viable on gas fired and dual-fuel engines, but not on diesel engines. On gas and dual-fuel fired engines the viable range of air-fuel ratios depends on the engine design. Lean mixtures are more difficult to ignite and richer mixtures generate PIC. These issues are discussed in the following paragraphs

There is a fundamental difference in the combustion process between diesel fuel and natural gas or gasoline, which evaporates before ignition occurs. Natural gas or gasoline is premixed with the air before combustion starts. Diesel fuel is a liquid that mixes with the air and evaporates as it is burning. The result is that diesel combustion occurs at near stoichiometric conditions even though the final exhaust mixture may have a lot of excess air. The difference between premixed and diffusion combustion is a key factor in the ability to control NOx emissions because premixed combustion allows engine designs with low peak flame temperatures. As a result, NOx control efforts have been much more successful on gas-fired engines than on diesel-fueled engines.

Figures 5-10 and 6-12 illustrate the effect of the air-fuel ratio on emissions. Reciprocating engines without emission controls are usually lean burn engines; in other words, they operate with sufficient air to minimize smoke and CO emissions. Diesel engines, on the other hand, approach rich burn conditions at full throttle. Rich burn engines operate with low enough air that there are some PIC. In general, rich-burning is associated with more power and increased emissions while lean-burning implies less power and lower emissions. Extremely lean burning appears, in Figure 6-12, to be the desired operating range for low emissions, but conventional gas or gasoline engines will not operate in this range because electric spark plugs will not ignite a very lean fuel mixture.

NOx reduction efforts on gas-fired engines have made impressive progress since about 1990. By fitting the combustion chamber with a “pre-chamber”, NOx

emissions can be reduced by 90% or more. Figure 6-16 shows this concept. The pre-chamber is a small combustion chamber off the main chamber that operates at an ignitable air-fuel ratio. When it is ignited it shoots a flame into the main chamber that is strong enough to ignite a very lean air-fuel mixture – it acts like a very powerful spark plug. This allows the fuel mixture in the main chamber to be very lean – on the far right side of Figure 6-16 where both NOx and CO emissions are low. In this case there is no significant degradation in engine performance, nor any increase in CO emissions, which is in stark contrast to other NOx control technologies. In some cases, prechamber-equipped engines actually run better than their predecessors. The major engine manufacturers have made retrofit hardware available for some of the existing population of engines.

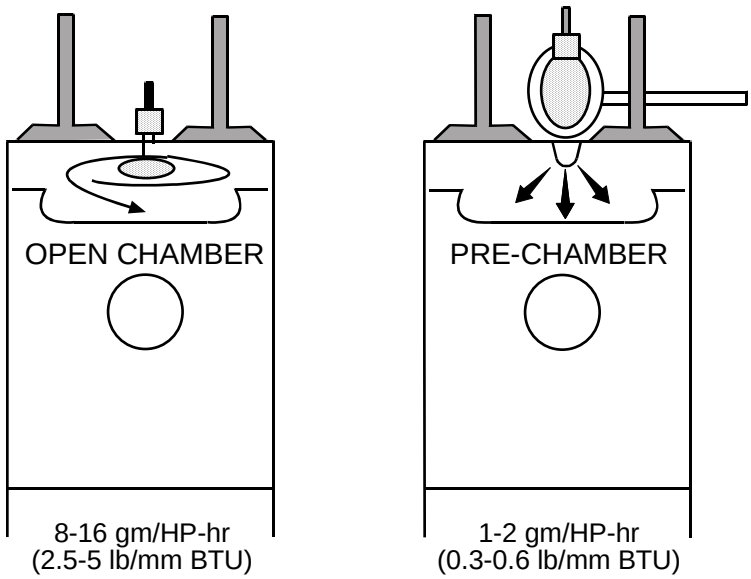

Figure 6-16. Low Emission Combustion Chamber Concept

U.S. Environmental Protection Agency. Alternative Control Techniques Document: NOx Emissions from Stationary Reciprocating Internal Combustion Engines, July 1993, EPA Report 453/R-93-032, NTIS PB94-104494.

Diesel engines have always been high NOx emitters and this continues to be the case. Modest reductions can be achieved by retarding the timing, but this reduces engine efficiency and peak power level. The exhaust temperature from diesel engines is in the right range for use of selective catalytic reduction (SCR), so this may be the appropriate control technology when substantial NOx reductions are necessary.

Table 6-1 shows some typical NOx emissions levels for the different types of engines with uncontrolled and low emission combustion technology. In this table, adjustments refer primarily to the effect of retarding the timing of ignition or fuel injection.

Table 6-1. Reciprocating Engine NOx Emissions - lb/mmBTU			
Concept	*Uncontrolled*	*Adjustments*	*Low Emission*
Rich Burn, Spark Ignition	4.64	3.5±	0.6
Lean Burn, Spark Ignition	5.13	No Change	0.6
Diesel	3.95	2.7	NA
Dual Fuel	2.72	1.9	0.6

Source: U.S. Environmental Protection Agency. Alternative Control Techniques Document: NOx Emissions from Stationary Reciprocating Internal Combustion Engines, July 1993, EPA Report 453/R-93-032, NTIS PB94-104494.

6.4.4 Add-On or Back End NOx Control Systems

The combustion-based NOx controls discussed so far use techniques specific to each type of combustor. By contrast, back end controls work (with some limitations) on any type of NOx source. In general, they are more expensive to install and operate, but can be highly effective. Thus, their predominant use to date has been in those areas where large NOx reductions were required.

Most of the NOx emitted from combustion sources is NO, which is not particularly soluble in water, so water-based scrubbers have little effect on NOx emissions. Most back end controls use a chemical to react with and destroy the NOx. The most common chemical used to destroy NOx is ammonia. Simply stated, the desired reaction is:

$$NOx + NH_3 \rightarrow N_2 + H_2O$$

Although it is not written as a balanced equation, it is clear that the amount of ammonia must be matched to the amount of NOx. One drawback to this approach is that ammonia is highly toxic and a large tank of ammonia raises safety issues. Systems that use urea (NH_2-CO-NH_2) are also in use – the general form of the chemical reaction is similar. Urea is a solid that can be dissolved in water, but it does not pose the same health hazard as ammonia. However, it is considerably more expensive.

Before delving into this in further detail, note that the amount of ammonia or urea must be controlled to match the amount of NOx. Too little reagent and some NOx will be left over, and too much reagent means ammonia emissions (ammonia slip). So nearly all of the back-end approaches need a system that measures NOx levels and controls the reagent injection rate – a cost and maintenance concern.

While increased PIC emissions are normally undesirable, these emissions are a necessary element for one type of catalytic air pollution control – non-selective catalytic reduction system (NSCR). Modern automobile engines operate in a rich burn mode in order for this air pollution control catalyst to work (see Sections 6.4.2.1 and 6.4.4.3).

6.4.4.1 Selective Non-Catalytic Reduction – SNCR

NOx reduction with either ammonia or urea will occur naturally, but only within a fairly narrow temperature window. For ammonia, that window is roughly 1650°-1800°F; the urea window is only slightly wider. If the temperature is too low, the reaction is too slow to be useful. If the temperature is too high, the reagent breaks down and forms additional NOx. This temperature window is inaccessible on engines and combustion turbines, but it does exist on most boilers. As the combustion gases pass from a boiler fire box through the convective heating section, the gases pass through the critical temperature range at some point in the boiler. However, on most existing boilers, the window is located in the middle of a bank of tubes and there is not enough space to insert an ammonia distribution grid.

Only a small amount of reagent is required, but it must be distributed evenly across a large duct. The resulting need for a distribution grid and a few feet of duct length for mixing/reaction means the system needs an empty area several feet long in the direction of flow. This space can be designed into a new system, but is unlikely to be present on an existing system, so retrofit may be impossible. There are several boilers that were built originally with ammonia based SNCR systems. Exxon held the original patents for this system under the name *Thermal Denox*.

One of the challenges in using SNCR, either with ammonia or urea, is that the appropriate temperature location in the boiler moves around depending on the boiler load. The lower the load, the lower the furnace temperatures and the closer the SNCR window is to the fire box. As a result, SNCR systems usually need two or three injection grids. The injection point is moved from one grid to another, depending on the load. Figure 6-17 shows the general configuration of an SNCR system.

Using urea dissolved in water gets around some of the problems with ammonia based SNCR. The urea solution can be sprayed into the right place in the upper furnace and by the time the water evaporates, the reagent has mixed with the flue gas and arrived at the appropriate temperature regime. This requires careful planning and placement of water sprays, which can be done using a fluid mechanic model of the boiler supported by actual temperature measurements. SNCR has been implemented on a number of existing furnaces, but is not possible on all furnaces. The disadvantage of urea compared to ammonia is that urea is considerably more expensive. Nalco held the original patents for urea-based SNCR and has licensed several companies to implement the technology.

SNCR application is limited to boilers and specifically to those with appropriate geometry and temperature windows

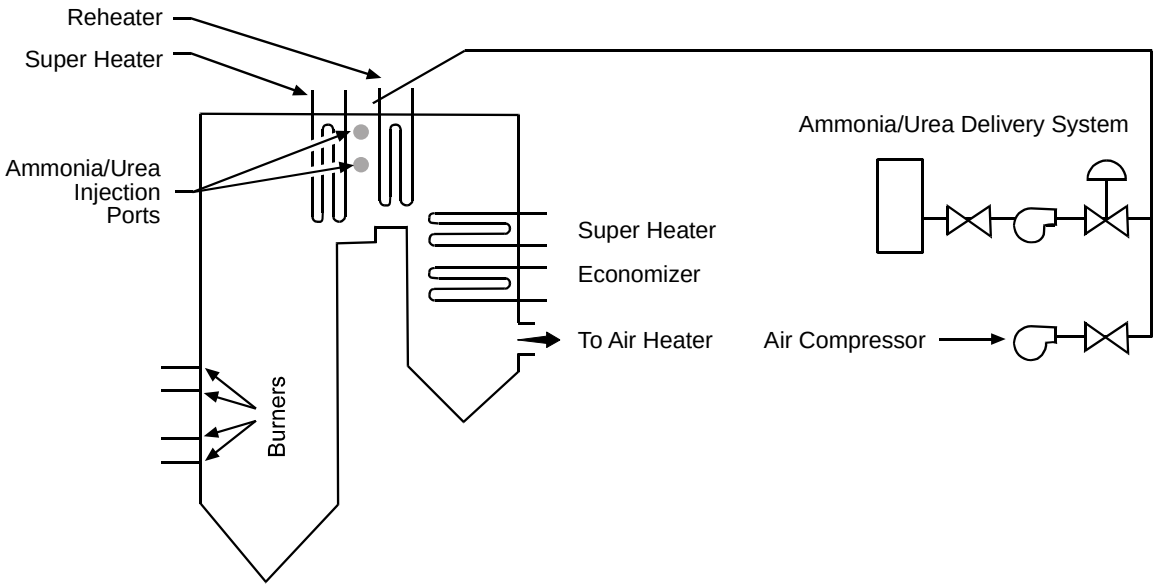

Figure 6-17. SNCR General Configuration

Source: Johnson & Overduin, 1991

6.4.4.2 Selective Catalytic Reduction – SCR

Selective catalytic reduction (SCR) systems are routinely used to reduce NOx emissions from combustion turbines and reciprocating engines. Systems have been demonstrated on coal-fired boilers, but there are very few in operation in the U.S. The main reason there are so few boiler SCR systems is that no new large steam electric plants have been built in this country in the past 15 years and, until quite recently, the rules have not required existing plants to achieve large NOx reductions. However, it appears that the "NOx SIP call" will require existing utility plants to begin implementing major NOx reductions. Since most of the combustion based NOx reductions have been implemented, large additional reductions are likely to mean the installation of SCR systems on many utility boilers.

SCR uses the same reagents as SNCR, but by flowing the flue gas and reagent through an appropriate catalyst; the reaction occurs at a much lower temperature. SCR systems can operate at temperatures ranging from about 600° to 1100°F, depending on the catalyst. Many combustion sources have exhausts in this temperature range, including engines and combustion turbines. The temperature window is wide enough that most systems do not require any temperature controls, so SCR has been successfully applied to many sources of various types. NOx reduction efficiencies are typically in the range of about 90%. Systems are now being built with outlet emissions guaranteed at 3 ppm. The primary disadvantage of an SCR system, is the cost of installing and operating a system that includes the catalyst, injection controls and reagent. Figure 6-18 shows the general configuration of an SCR system.

Many factors go into the design and operation of an SCR system – this text briefly explores some of the major elements. There are three primary types of catalyst and each manufacturer has its own proprietary variations for each.

- Precious metal (platinum) 450° – 550°F
- Vanadium/titanium catalysts 550° – 800°F
- Iron-Zeolite catalysts 800° – 1000°F

Outside of these temperature windows, the catalysts are less effective and less durable. Large boilers typically have temperatures at the exit of the economizer in the range of 600°–800°F where vanadium/titanium catalysts are appropriate. Combustion turbine exhausts are typically above 1000°F where zeolite catalysts have marginal durability. However, most new power plants are combined cycle units so space can be designed in the middle of the boiler where temperatures are appropriate for one of the currently available catalysts.

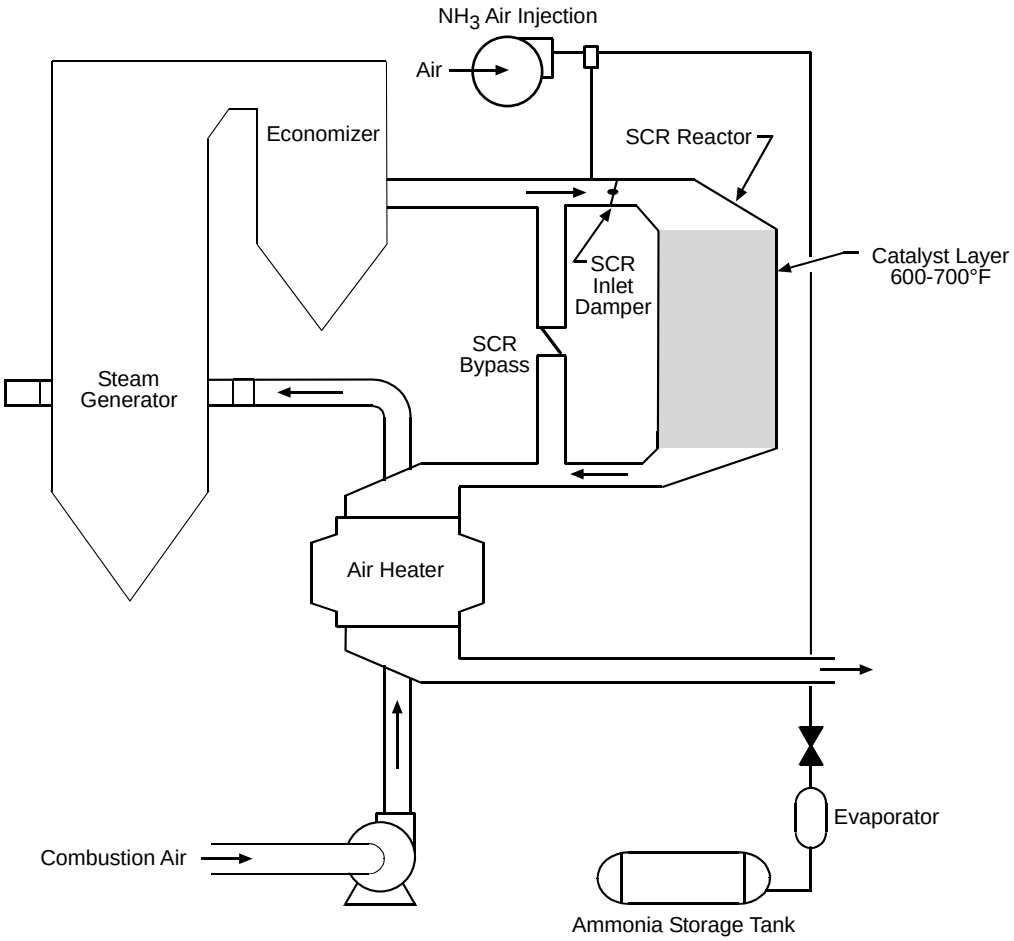

Figure 6-18. SCR General Configuration
Cochran, Gregory & Rummenhohl, presented at Power-Gen in Dallas, TX 1993

A catalyst typically lasts several years before degrading to the point that it needs to be replaced. When the exhaust gas is nearly free of contaminants, as is the case with natural gas, a catalyst may last for many years. Vendors have developed catalysts with considerable tolerance for the primary exhaust contaminants, but eventually performance deteriorates and the catalyst must be replaced. Catalysts on coal-fired boilers are expected to last about three years, but there is wide variation in the contaminants in different coals, so actual catalyst lifetimes should be based on experience. The reference by Ron Heck provides extensive information on air pollution catalysts.

Catalysts take the form of a material coated on a support structure, with the gas flowing through. The support is typically a honeycomb grid or a stack of waffle plates. The amount of catalytic surface area is proportional to the gas flow rate. When the exhaust is clean, as with an engine, the openings in the honeycomb or grid can be small and a fairly large surface area can be achieved in a relatively small volume. However, a dirty exhaust, as from a coal-fired boiler, requires large holes in the support structure that will not clog with ash. This means the size of the catalyst must be much larger in order to keep the same total surface area. Thus, catalysts on a coal-fired boiler are nearly the size of a dust collector, while a combined cycle catalyst can be neatly packaged within the boiler, similar to the heat exchange sections.

6.4.4.3 NSCR with Rich Burning

Non-selective catalytic reduction (NSCR is introduced in Section 6.4.2.1) is a way to destroy NOx using chemicals naturally present in the combustion exhaust – namely CO and hydrocarbons (PIC). The catalysts developed to date are reliable and active over a fairly wide temperature range. The hard part is to get just the right amount of PIC to match the amount of NOx. As discussed in Section 6.4.2.1, PIC can be generated by reducing the excess air, but very precise air control is required to keep the amount of PIC within an acceptable range. Reciprocating engines are the only sources where NSCR is currently being applied; boiler applications may be possible. NSCR is not applicable to combustion turbines because of their inherently high exhaust oxygen content. In order to apply it to a diesel engine, an air flow control would be required, which would be a significant alteration of existing engine technology. However, when NSCR is properly implemented on reciprocating engines, NOx can be reduced by more than 90% while PIC are held to acceptable levels.

6.4.5 Combined NOx Controls

A variety of combustion sources and NOx control methods have been discussed with a focus on the prevailing practice and the most effective technologies. In the following table, the applicability of different technologies to the various types of sources is summarized. In the instances listed as “maybe” the applicability of a technology depends on site-specific conditions, or this technology normally would

not be used in favor of a more effective technology. The use of "??" indicates the application is conceivable, but unlikely, or the technology may not yet exist.

Table 6-2. Combinations of NOx Control Technologies

	Utility Boiler	*Package Boiler*	*Stoker Boiler*	*Combust. Turbine*	*Gas-fired Engine*	*Diesel Engine*
Excess Air Control	yes	yes	??	na	no	no
Low NOx Burner	yes	yes	na	yes	yes	??
Overfire Air	yes	maybe	??	na	na	na
Flue Gas Recirc	yes	maybe	??	na	maybe	yes
Reburning	yes	??	yes	na	na	na
Water Injection	??	??	no	yes	maybe	maybe
Ignition Retard	na	na	na	na	yes	yes
NSCR	maybe	maybe	no	no	yes	no
SNCR	maybe	maybe	maybe	na	na	na
SCR	yes	yes	yes	yes	yes	yes

Most NOx reduction technologies can be combined and the resulting reduction will be approximately the sum of the reductions due to each technology. As an example, a low NOx emissions system installed on a utility boiler will probably include all of the following:

- very good excess air controls
- low NOx burners
- flue gas recirculation
- over-fired air ports

The first two items can be installed on almost any size and boiler configuration. The last two can usually be installed on large utility boilers, but may not be applicable to industrial boilers.

When back end controls – SCR or SNCR – are used, it is customary to apply as many combustion controls as practical in combination with the back end control. Thus, a combustion turbine that requires maximum NOx reduction will use water injection or a dry low NOx combustor in combination with SCR on the back end.

Controls that are not combined include:
- SNCR and SCR
- Water injection and dry low NOx combustor on a turbine
- Detuning and a low NOx combustor on a gas-fired engine

6.5 CARBON MONOXIDE AND ORGANIC EMISSIONS

The emissions of PIC divide naturally into two groups of sources:

- Sources where combustion is the vehicle for generating heat or power, and where PIC might be created.

- Sources where combustion is used to control PIC or organic emissions from other processes.

In regard to the second group, we have discussed incinerators and related pollution control devices in previous chapters. However, with regard to the first group we discussed the formation of PIC in Chapter 5 and provided an understanding of how controlling PIC formation is the basis for prevention. Most stationary sources do not generate significant amounts of CO or hydrocarbons. Boiler CO levels are normally less than 100 or 200 ppm and hydrocarbons are rarely detectable. Engine PIC levels are generally higher than boiler PIC emissions. Diesel emissions tend to include hazardous or toxic organic compounds and organic particulate matter emissions that are rare from boilers.

6.5.1 Trade-Offs with NOx

With few exceptions, combustion-based NOx reduction technologies tend to increase PIC. Most low NOx flames are cooler and have slower fuel-air mixing than conventional flames, which are the opposite of approaches used to minimize PIC. Figure 5-9 illustrates these opposite trends for excess air – the most important combustion control parameter.

With a few notable exceptions, PIC are typically not a serious concern from stationary combustion sources. However, PIC will usually increase when NOx controls are implemented. Thus, it is prudent for regulatory agencies to place a limit on PIC emissions in any permit where NOx is a significant issue. This is particularly relevant on gas-fired boilers where NOx compliance might be achieved simply by reducing the excess air without regard for CO emissions. Natural gas boilers do not normally smoke and CO emissions will not be detected unless they are measured. This does not necessarily mean that CO needs to be continuously monitored, but rather that there should be reasonable assurance that NOx compliance will be achieved without excessive CO emissions.

6.5.2 Catalytic Control Systems

PIC emissions can commonly be controlled using an oxidation catalyst in the exhaust. These catalysts are frequently used on engine and turbine exhausts – either alone or directly downstream of an SCR catalyst. These catalysts operate well over a wide

range of temperatures; beginning at a few hundred degrees Fahrenheit they oxidize CO and most hydrocarbons. Destruction efficiency is generally very high although refractory hydrocarbons like methane require somewhat higher temperatures than other compounds. In order to work, there must be some oxygen in the exhaust – a requirement that will be met in nearly all cases with the possible exception of an exhaust where an NSCR system is in operation.

6.5.3 Hydrocarbon Capture

Control of hydrocarbons in combustion exhausts is normally achieved by adjusting the combustion system to prevent hydrocarbon formation, which is sufficient to reduce organic emissions to less than 1 ppm. No further reduction is required for most pollutants. However, certain highly toxic compounds such as dioxins and furans need to be reduced to much lower levels. Even at very low levels dioxins can usually be controlled by good combustion practices, but passing flue gas through activated carbon will capture essentially all of the residual hydrocarbon species as well as mercury vapor and some other compounds. The temperature of the carbon has to be reasonably low, usually less than about 200°F. The cooler the carbon, the greater is its capacity to absorb various pollutants.

Carbon capture can be achieved in one of several ways. Fixed carbon beds or canisters are common on small sources. When the carbon approaches saturation it can be replaced or regenerated in place. Regeneration means heating the carbon to drive off the collected contaminants (and presumably capturing them for disposal or destroying them). Doing it in place requires a double system with valving to switch from one carbon bed to the other when one is being regenerated. A common approach to carbon adsorption on larger sources is to inject powdered carbon into the exhaust gas, then collect it in a baghouse. The coating of carbon on the bags ensures that high contact will occur between the gas and the carbon so that high capture rates can be achieved. If the same approach is used with an electrostatic precipitator, capture rates typically drop to 50% or less. The contaminated carbon is discarded with the collected dust.

6.6 CONCLUSION

Control of pollutant emissions usually starts in the combustion zone. The first step in SO_2 control is to use fuel with lower sulfur content. All NOx controls depend at least partially on combustion modifications or precise combustion control. On boilers and furnaces CO and hydrocarbon control is totally dependent on the design and operation of the combustion system. Reciprocating engines and turbines frequently rely on catalyst systems for CO and PIC control.

Post combustion or "back end" controls usually come into play when major emission reductions are required and frequently emissions control is the sum of combustion and back end controls. Most NOx controls are in this category, while many back end control technologies are coupled to the combustion system. NSCR is an extreme example in that it relies on exact control of the combustion air-fuel ratio. In all cases, the design of a back end control device must be matched to the combustion source both in terms of the amount of gas to be treated and the character of the pollutants. For example, most dust collectors have very specific maximum gas flow rates and their collection efficiency and durability depend on the physical/chemical/electrical characteristics of the particles. The contaminated carbon is discarded.

Air pollution control from combustion sources involves synergy between the combustor and control devices as well as between the controls for different types of pollutants.

Review Exercises

1. Which of the following statements is true?
   a. The choice of fuel has little effect on most of the emissions from a typical source.
   b. Combustion system design and adjustment can substantially influence the performance of a pollution control device.
   c. NO_x emissions are only marginally influenced by the choice of fuel.
   d. All air pollutants are created entirely in the combustion zone.

2. Which of the following statements is false?
   a. Particles that follow stream lines exactly are the most difficult to collect
   b. The performance of all particle collectors is affected by particle size.
   c. Particles much smaller than 0.5μm are the most difficult to collect because they follow streamlines exactly.
   d. Particles larger than 50μm can be collected by any type of collector.

3. A particulate scrubber _____.
   a. is quite effective at collecting submicron size fume particulate.
   b. will capture nearly all the sulfuric acid mist in the gas because it is water soluble.
   c. will not efficiently catch particulate smaller than about 1μm unless the gas pressure drop is very high.
   d. is not commonly used to collect flammable dust.

4. Which of the following statements is true?
   a. Fabric filters can capture particles of any size with high efficiency.
   b. Fabric filters can be permanently plugged if the dust is sticky or wet when collected.
   c. Baghouse pressure drop is a very insensitive indicator of changes in emissions.
   d. All of the above

5. If the collection efficiency of a new dust collector is 99.6% and leaks subsequently develop that allow 1.3% of the exhaust to bypass the collector, the emissions will increase by a factor of _____.
   a. 4.25
   b. 3.25
   c. 2
   d. Cannot determine from the information given.

6. Which of the following statements is **not** true about electrostatic precipitators?
   a. Dust collection efficiency of an electrostatic precipitator is sensitive to the amount of gas flowing through the unit.
   b. Electrostatic precipitators can be designed to collect more than 99% of the particulate.
   c. Precipitator collection performance can be monitored by tracking the secondary amperage to each field.
   d. All of the above are true.

7. Fires can be a problem in dust collectors on some types of sources. The best approach to dealing with this problem is to _____.
   a. install a wet scrubber even if the emissions may frequently exceed the standard
   b. do whatever is necessary to assure an incombustible dust, including switching to a more expensive fuel
   c. operate the source in such a way that there will never be a simultaneous occurrence of combustible dust, high O_2 level, and an ignition source in the collector
   d. never operate the source with an O_2 level above about 12%

8. Switching fuel is a practical method of reducing SO_2 emissions provided _____.
   a. the sulfur content and heating value of the new fuel are lower than the existing fuel.
   b. the increased cost of lower sulfur fuel is attractive compared with the cost of installing and operating a scrubber for a comparable SO_2 reduction.
   c. the cost of changes to the facility required to burn the new fuel are reasonable.
   d. B and C

9. If a baghouse is installed downstream of a dry or semi-dry SO_2 scrubber one would expect that _____.
   a. all of the SO_2 leaving the scrubber will go up the stack
   b. if there is particulate carbon present at the scrubber exit, a significant amount of any mercury in the gas will be captured in the baghouse
   c. the baghouse will require special bag fabrics because moisture in the exhaust will tend to plug up the bags
   d. no sulfate particulate will reach the baghouse because all the sulfur is removed in the scrubber

10. SO_3 emissions are hard to control because _____.
   a. at temperatures above 270°F they are a vapor that usually is not effectively captured in a dust collector
   b. a scrubber condenses the acid to submicron size particles that are not collected by a scrubber
   c. it is difficult to prevent SO_3 formation in most combustion systems
   d. All of the above

11. When trying to progressively reduce NOx from an existing boiler, one would implement control strategies in which of the following sequences?
   a. SCR, OFA, Low NOx burners.
   b. Excess air control, OFA , low NOx burners, SCR
   c. FGR, SCR, excess air control, low NOx burners
   d. Burners out of service, SNCR, reburning, OFA

12. Flame temperature reduction will _____.
    a. reduce the amount of NOx formed from fuel nitrogen
    b. never increase the amount of CO or VOC emissions
    c. be implemented most frequently with either water sprays or flue gas recirculation
    d. always incur a major penalty in fuel efficiency

13. As a general rule, combustion modifications to reduce NOx will _____.
    a. tend to increase emissions of CO, carbon and VOC
    b. probably lengthen the flame so it fills more of the furnace
    c. require good air flow control regardless of what techniques are utilized
    d. All of the above

14. Which of the following is **not** an element of a low NOx burner?
    a. Features that encourage the operators to tune the burner for best flame appearance.
    b. Separate controls for air flow rate and air direction or distribution.
    c. Low NOx emissions.
    d. Factory tuning of the whole system after the burners are installed.

15. NOx emission control for combustion turbines _____.
    a. never used combustion water spray because it would put out the flame
    b. are using premixed burners in the latest technology
    c. are able to use No. 2 oil in the new dry low NOx burners operating in the low NOx mode
    d. allows the turbines to achieve very low emissions during start up

16. Which statement is **not** true of low NOx combustion chambers for reciprocating engines?
    a. Low NOx combustion chambers can reduce NOx emissions by about 90% from uncontrolled levels.
    b. The new low NOx chambers allow diesel-fueled engines to achieve very low NOx emissions.
    c. Low NOx combustion chambers only work when firing gas fuel.
    d. In some cases, the low NOx chambers exhibit lower CO emissions and better engine performance than the original chambers.

17. In regard to back end controls, which statement is incorrect?
    a. Most systems rely on ammonia or urea to react with NOx and destroy it.
    b. Both SCR and SNCR systems require accurately controlled amounts of reagent well mixed with the exhaust gas.
    c. SNCR systems can be retrofitted to a wide range of existing sources.
    d. The reaction of ammonia with SOx will produce sticky compounds that can plug up heat transfer equipment.

Review Answers

1. b. Combustion system design and adjustment can substantially influence the performance of a pollution control device

2. c. Particles much smaller than 0.5μm are the most difficult to collect because the follow streamlines exactly.

3. c. will not efficiently catch particulate smaller than about 1μm unless the gas pressure drop is very high

4. d. All of the above

5. a. 4.25

6. d. All of the above are true.

7. c. operate the source in such a way that there will never be a simultaneous occurrence of combustible dust, high O_2 level, and an ignition source in the collector

8. d. B and C

9. b. if there is particulate carbon present at the scrubber exit, a significant amount of any mercury in the gas will be captured in the baghouse

10. d. All of the above

11. b. Excess air control, OFA , low NOx burners, SCR

12. c. is most frequently implemented either with water sprays or flue gas recirculation

13. d. All of the above

14. a. Features that encourage the operators to tune the burner for best flame appearance.

15. b. are using premixed burners in the latest technology

16. b. The new low NOx chambers allow diesel-fueled engines to achieve very low NOx emissions

17. c. SNCR systems can be retrofitted to a wide range or existing sources

References

1. Buonicore, Anthony J. and Davis, Wayne T. (Editors). *Air Pollution Engineering Manual*, (Air & Waste Management Association, Van Nostrand Reinhold, 1992). This book has sections on combustion sources as well as various emission control technologies.

2. California Air Resources Board. *Sources and Control of Oxides of Nitrogen Emissions*, August 1997. This gives a relatively current summary of NOx formation and control technology for all types of sources. Summaries of California rules illustrate NOx levels that can be achieved by state-of-the-art technology.

3. Clement, Raymond and Kagel, Ronald, (Editors). *Emissions from Combustion Processes: Origin, Measurement, Control*, (Lewis Publishers, 1990). The book is a collection of 31 articles that focus primarily on organic pollutants.

4. Gill, James H. and Quiel, John M. *Incineration of Hazardous, Toxic, and Mixed Wastes*, (North American Mfg. Co., Cleveland, OH, 1993). This book focuses on waste combustion in rotating kilns and covers the formation and control of organic pollutants.

5. Heck, Ronald M. and Farrauto, Robert J. *Catalytic Air Pollution Control* (Commercial Technology, John Wiley & Sons, Inc., 1995). A 200-page book that is probably the best available reference on this subject.

6. Institute of Clean Air Companies. *Selective Catalytic Reduction (SCR) Control of NOx Emissions*, November 1997. A 'white paper' by the Institute of Clean Air Companies.

7. U.S. Environmental Protection Agency. *Alternative Control Techniques Document: NOx Emissions from Industrial/Commercial/Institutional (ICI) Boilers*, March 1994, EPA Report 453/R-94-022, NTIS PB94-177177. This weighty document is a fairly a comprehensive description of small to mid size boilers and current NOx technology. It includes waste fired boilers.

8. U.S. Environmental Protection Agency. *Alternative Control Techniques Document: NOx Emissions from Stationary Gas Turbines*, January 1993, EPA Report 453/R-93-007, NTIS PB93-156586. This weighty document is a fairly a comprehensive, if slightly dated, description of combustion turbine technology with a significant database included.

9. U.S. Environmental Protection Agency. *Alternative Control Techniques Document: NOx Emissions from Stationary Reciprocating Internal Combustion Engines*, July 1993, EPA Report 453/R-93-032, NTIS PB94-104494. This weighty document is a fairly a comprehensive, if slightly dated, description of engine NOx technology with a significant database included.

10. U.S. Environmental Protection Agency. *Alternative Control Techniques Document: NOx Emissions from Utility Boilers*, March 1994, EPA Report 453/R-94-023, NTIS PB94-184165.

This weighty document is a fairly a comprehensive description of large boiler types and NOx technology with a significant database included.

11. U.S. Environmental Protection Agency. *Compilation of Air Pollution Emission Factors (AP-42)*, available from NTIS, Federal Book Stores, or available online from the EPA TTN BBS. This ever-evolving document is organized by source type and has credible descriptions of each one. Generally considered the "bible" for estimating emission rates whenever actual measurements are not available.

12. U.S. Environmental Protection Agency. John Richards. *Control of Gaseous Emissions*, APTI Course 415, Student Manual, NC State University, 1995. This book has credible sections on incineration and NOx control as well as covering areas not related to combustion sources.

13. U.S. Environmental Protection Agency. *Control of NOx Emissions by Reburning*, February 1996, EPA Report 625/R-96/001. This appears to be a definitive document on reburning, which, in practice, is only applicable to large boilers.

14. U.S. Environmental Protection Agency. *New Source Performance Standards, Subpart Da – Technical Support for Proposed Revisions to NOx Standard*, June 1997, EPA Report 453/R-94-012. This inch thick report is narrowly focused on utility boilers, but covers current NOx technology in great depth.

15. U.S. Environmental Protection Agency. *Phase II NOx Controls for the MARAMA and NESCAUM Regions*, November 1995, EPA Report 453/R-96-002. This report is an in depth coverage of NOx technology on utility boilers.

16. U.S. Environmental Protection Agency. Campbell, Lisa M., Stone, Diana K., and Shareef, Gunseli S. *Sourcebook: NOx Control Technology Data*, (Radian Corporation, 1991), EPA Report 600/2-91-029, NTIS PB91-217364. A report for the Air and Energy Engineering Research Laboratory of EPA. A broad, but very shallow update and overview of NOx technology. The appendix contains a considerable amount of data from existing sources on control technologies in use and permit limits.

17. U.S. Environmental Protection Agency. *Summary of NOx Control Technologies and Their Availability and Extent of Application*, Midwest Research Institute, 1992, EPA Report 450/3-92-004, NTIS PB92-158260. This appears to be a readable and fairly comprehensive review of NOx emissions and combustion control technology for boilers. There is minimal data for SCR and SNCR.

18. U.S. Environmental Protection Agency. The U.S. EPA-DOE-EPRI Combined Power Plant Air Pollution Control Symposium: The Mega Symposium and the A&WMA Specialty Conference on Mercury Emissions: Fate, Effects and Control, 2001, proceedings available on CD-ROM from www.awma.org. This and other conference proceedings provide current information on air pollutant formation and control.

19. Vatavuk, William M. *Estimating Costs of Air Pollution Control*, (Lewis Publishers, 1990). In addition to costs this book provides a lot of information about control systems, because costs cannot be estimated until the system is defined.

Chapter 7: Combustion Source Emissions

LESSON GOAL

Demonstrate an understanding of the relationship between energy efficiency and CO_2 emissions. Understand the units used in emissions measurement through successful completion of the chapter review exercises.

STUDENT OBJECTIVES

When you have mastered the material in this chapter, you should be able to:

1. Describe the difference between combustion efficiency and thermal efficiency.
2. Describe the general levels of thermal efficiency expected from typical combustion sources.
3. Calculate the heat loss from incomplete combustion by using measured CO emissions data or fly ash carbon content.
4. Compute stack thermal heat losses from stack exhaust measurements.
5. Compute the CO_2 emissions from sources fired on commercial fuels.
6. List the causes of variations in emission rates.
7. Describe the common types of continuous emission monitors, Reference Test Methods, and indirect or parametric emission monitoring.
8. Correct an exhaust gas volume or a sample concentration to a standard level of air dilution.
9. Convert between emission units of lb/mmBTU and ppm, corrected.
10. List two methods of determining an emission rate in units of lb/hr.

Chapter 7: Combustion Source Emissions

7.1 INTRODUCTION

This chapter presents several subject areas that do not fit neatly into any one of the preceding chapters. The discussion will also address several topics that combine elements from more than one of the preceding chapters. While this chapter is not intended to serve as a conclusion for Combustion Source Evaluation, it does address much of the material that is not sufficiently discussed in the preceding chapters.

7.2 ENERGY USE AND CO_2 EMISSIONS

7.2.1 Efficiency of Various Systems

Table 7-1. Typical Efficiency Levels

System	*Combustion Efficiency*	*Thermal Efficiency*
Boiler, gas-fired	100%	82%
Steam-Elect. Coal Power Plant	99%	34%
Simple Cycle Gas Turbine	100%	38%
Combined Cycle Gas Turbine	100%	55%
Cogeneration System	100%	50%-80%

Efficiency is defined as the ratio of useful energy to total available energy, where the total energy is that available from complete combustion of the fuel. Table 7-1 lists two efficiencies for several typical combustion sources.

Combustion efficiency shows how much of the fuel was completely burned and converted to thermal energy. For most combustion sources, combustion efficiency is essentially 100%. None of the fuel remains unburned, so there is little air pollution in

the form of CO, black smoke or organic material (PIC). However, one exception is coal-fired boilers that may lose up to one percent of the fuel in the form of carbon or coke collected with the fly ash in the dust collector.

Thermal efficiency is entirely different. There is no way, even theoretically, to capture and use all the heat that is released by combustion and carried away by the flue gas. Boilers are fairly efficient because the only heat loss is the warm flue gas going up the stack; nearly all the remaining energy is present in the steam. However, devices that generate mechanical or electric power are much less efficient overall than boilers and furnaces. For example, note that about 40% of the energy going into a steam electric power plant is dumped from the steam condenser, either into an adjacent body of water or into the atmosphere via a cooling tower.

Most of the electric power plants being built in this country have a combustion turbine at their core. These plants provide an interesting example of thermal efficiency. A combustion turbine (CT) – although it does not generate any steam that must be condensed with the associated energy loss – does have a very large and hot exhaust flow. Most of the input fuel energy to a CT is lost when hot gases escape up the stack. A combined cycle power plant (see Figure 2-4, p. 2-9) captures most of the turbine exhaust energy and uses it to heat a boiler that powers a steam turbine. The net heat loss is diminished, but is still a major part of the input fuel energy. Another alternative is to take the waste heat either from an engine or from a steam turbine condenser and use it to heat a building or an industrial process – a procedure called cogeneration. Cogeneration systems can potentially utilize 80% to 90% of the fuel energy and still generate mechanical or electric power. However, in order to minimize heat loss, there must be a good match between power demand and heat demand – an objective that is often hard to achieve. Peak electric demand usually occurs at a different time of the day or year than peak heat demand. So if the cogeneration system is run to satisfy the electric demand, the heat output will not be coordinated with the heat demand, or visa versa. Overall efficiency depends on how well the two energy demands can be matched.

7.2.2 Combustion Efficiency

The simplest way to measure combustion efficiency is to measure the inefficiency, or measure the amount of unburned fuel and then relate that to the total amount of fuel. While there are many possible pollutant species, in regard to efficiency there are only two of practical interest: carbon monoxide and particulate carbon. CO can be emitted from any combustion source, but among stationary sources only gas-fired sources can emit large amounts of CO without smoking. Carbon can also be emitted from any source, but only sources that generate fly ash, such as coal or wood fired boilers, can create significant amounts of carbon.

CO is a combustible gas with a heating value of 315 BTU/std ft^3, so its presence in the exhaust signals lost energy. The CO concentration is directly related to the fractional heat loss.

$$\%\ \text{Energy Loss} = \left(\frac{\text{ppm CO}}{10^6}\right)\left[\frac{\text{scf CO}}{\text{scf E.G.}}\right] * \left(\frac{315\ \text{mmBtu}}{10^6\ \text{scf CO}}\right) * \left(\frac{8{,}710\ \text{scf E.G}}{\text{mmBtu}}\right) * 100 * \left(\frac{20.9}{20.9 - \%O_2}\right)$$

$$\%\ \text{Energy Loss} = 0.00027 * \text{ppm CO} * \left(\frac{20.9}{20.9 - \%O_2}\right) \qquad (7\text{-}1)$$

Where: ppm CO = CO concentration in E.G., dry basis
% O_2 = Oxygen concentration in E.G., % by volume, dry basis
8,710 = dry F-factor (F_d) of natural gas – see Table 4-5,

Example 7-1. Fractional Heat Loss

How much heat is being lost out the stack of a natural gas-fired source, due to CO, where measured CO = 800 ppm and O_2 = 4.2% by volume, dry basis?

Solution:

Insert the values for CO and O_2 into Equation 7-1.

0.00027 * 800 * 20.9/(20.9-4.2) = 0.27%

So 800 ppm of CO emissions represents slightly more than one quarter of one percent (of total heat input) energy loss.

Coal or any solid fueled furnace can leave carbon in the ash. When the ash is divided between several streams, as between bottom ash and dust collector ash, calculating losses starts to become complicated. Take, for example, the simple case of a pulverized coal boiler, where the dust collector captures nearly all the fuel ash. If the fly ash is analyzed using a test called *Loss on Ignition* or LOI, it gives us the percent carbon in the ash. Analysis of the coal gives us the heating value and the amount of ash in the coal. This is enough information to determine how much carbon is being emitted relative to the amount of coal being fired. The equation for the heat loss associated with unburned carbon in the fly ash is:

% Energy Loss = %A * %C/100 * 14100/HHV (7-2)

Where: %A = coal ash content, % by wt.
%C = fly ash carbon content (LOI), % by wt.
14,100 = heating value of pure carbon, BTU/lb
HHV = heating value of the coal, BTU/lb

This gives an energy loss estimate that can be determined from readily available data.

Example 7-2.

Determine the approximate energy loss from a pulverized coal source where the fly ash has 4% combustibles and the coal properties are 11% ash and 12,700 BTU/lb.

Solution:

Insert the data in Equation 7-2.

$$11\% * 4\% /100 * 14100/12,700 = 0.49\%$$

So 4% combustibles in the fly ash translate to about one half of one percent energy loss.

This calculation of energy loss works well for pulverized coal where the ash content is well known and most of it comes out of the dust collector. However, this method could give misleading results on a wood-fired stoker where the ash content fluctuates between 1% and 3%, and where the ash emerges from several points in the boiler system. The method also will not work well on a No. 6 oil-fired boiler where most of the particulate is sulfates, not fuel ash.

Combustion losses are generally small and usually can be ignored when system thermal efficiencies are calculated. Air emissions of CO or ash carbon content are usually much more important issues than combustion efficiency losses. The bottom line is that large PIC emission rates only represent small combustion efficiency losses.

7.2.3 Thermal Efficiency

Thermal efficiency for a combustion source starts with the energy supplied by the fuel and ends where we choose. For example, on a steam-electric power plant, we can look at the efficiency of the boiler producing hot steam, or we can look at the efficiency at the turbine shaft, or at the generator electrical output, or even the total system efficiency where the end point is the electric power delivered to the user. This course will only deal with the initial combustion source and not get into the details of various thermodynamic cycles. This discussion will look at boilers but not the associated steam turbines, nor the electric generator. The following discussion also applies to combustion turbines. Reciprocating engines are more complicated simply because of heat lost through cylinder cooling water. A schematic illustration of the principal energy flows of a combustion source is shown in Figure 7-1.

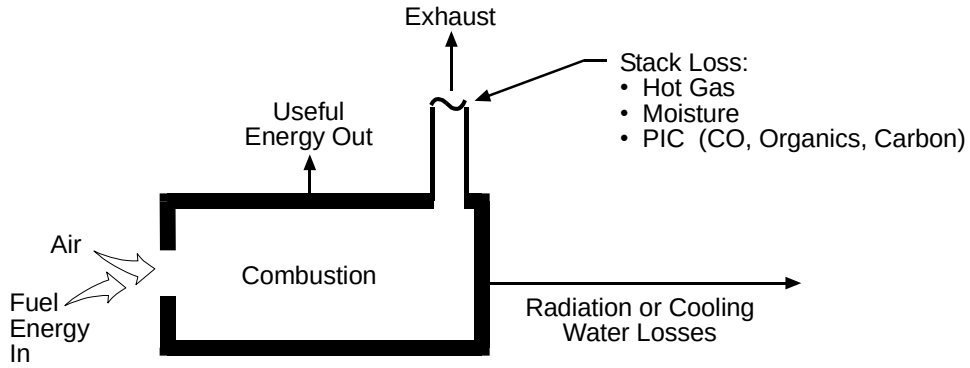

Figure 7-1. Combustion Energy Flows

Thermal efficiency can be expressed either as the ratio of useful energy output divided by the total energy input, or as 100% minus the energy losses (expressed as percent)

$$\% \text{ Thermal Efficiency} = \text{Useful Output Energy} / \text{Energy Input} \qquad (7\text{-}3a)$$

$$\% \text{ Thermal Efficiency} = 100\% - \% \text{ Energy Losses} \qquad (7\text{-}3b)$$

The first equation can be problematic to use in practice because either or both of the energy terms can be difficult to measure. For many combustion sources, the second equation can be disarmingly simple to use. Frequently equation (7-3b) allows a very good approximate efficiency to be determined from measurements of stack temperature, O_2 and some knowledge of the fuel. Small changes in combustion efficiency can usually be determined from simple stack data very accurately with this equation.

Losses from combustion sources fall into one of the following categories:

- *Category 1.* Sensible losses of hot exhaust gases venting to atmosphere.
- *Category 2.* Heat of vaporization losses from venting uncondensed water to atmosphere.
- *Category 3.* Unburned fuel in either the exhaust gases or discarded ashes.
- *Category 4.* Radiation/convection losses from the outside walls of the furnace and cooling water losses (reciprocating engines).
- *Category 5.* Miscellaneous small losses such as the energy in hot ashes that are discarded.

If reciprocating engines are excluded for the moment, then in most cases the first two are significant and the remaining three are each on the order of 1% or less. We have already shown ways to determine the most common losses in Category 3. Category 4

can be determined by standard methods, such as those provided by the ASME Test Codes – assuming there are no cooling water losses.

Category 2, water vapor losses, requires knowledge of the amount of water vapor in the exhaust gases. Table 4-6 provides approximate values for uncondensed water vapor losses for three common fuels. The associated discussion shows how to calculate water vapor losses when exhaust water vapor content is measured.

Category 1, sensible heat losses, were discussed in Section 4.3.3 and quantified in Equation 4-24. This loss can be determined fairly accurately from just two measurements: stack temperature and stack O_2 concentration.

Thus, for boilers, furnaces, and combustion turbines, the thermal efficiency is approximately:

$$\text{Efficiency} = 100\% - \text{sensible loss } (\%\ Q_S) - \text{water vapor loss } (\%\ Q_{LH})$$
$$= 100\% - \%\ Q_S - \%\ Q_{LH}$$

Inserting Equations 4-21 and 4-24 for the two loss terms on a coal, oil or gas-fired system gives:

$$\text{Thermal Efficiency}$$
$$= 100\left\{1 - \left(\frac{\Delta T}{4{,}200}\right)\left(\frac{20.9}{20.9 - \%O_2}\right) - \left(\frac{0.49 \cdot \%H_2O}{100}\right)\left(\frac{20.9}{20.9 - \%O_2}\right)\right\}$$
$$= 100\left\{1 - \left(\frac{20.9}{20.9 - \%O_2}\right)\left(\frac{\Delta T}{4{,}200} + \frac{0.49 \cdot \%H_2O}{100}\right)\right\} \qquad (7\text{-}4)$$

Where: ΔT = Exhaust temperature minus ambient temperature, and $\%H_2O$ and $\%O_2$ are measured exhaust concentrations after the last heat exchanger.

In this equation, the water vapor term, which includes the H_2O and O_2 variables, is actually a constant for any given fuel. So when $\%H_2O$ data is not available, one can estimate the latent loss using values listed in the last column of Table 4-6 (p. 4-34). Typical water vapor energy losses are between 4% and 10%.

Using Equation 7-4 with measured stack data gives an efficiency that is slightly high because it ignored radiation losses, but it will give values that are generally within 2% of the values that could be achieved by a more thorough analysis. Equation 7-4 is a simplified version of an *ASME Performance Test Code* and is a powerful engineering tool. This equation is particularly valuable to air emission professionals because of the ability to determine thermal efficiency fairly accurately without the need for any data on fuel flow or the useful energy output.

Example 7-3.

Determine the approximate efficiency of an oil-fired boiler where the stack temperature is 350°F, ambient temperature is 50°F, stack O_2 is 5% and stack water vapor content is estimated at 11% by volume.

Solution:

Entering these values in Equation 7-4 gives:

$$100 \times \left(1 - \frac{350-50}{4200} \times \frac{20.9}{20.9-5} - 0.49 \times \frac{11}{100} \times \frac{20.9}{20.9-5}\right) =$$

$$100 - 9.39 - 7.08 = 83.5\%$$

So about 7% of the fuel energy is carried in uncondensed water vapor and 9.4% is in the form of hot gas. This leaves 83.5% that is used to produce steam.

It was demonstrated in Chapter 4 that the firing rate of a source could be determined from measured stack flow and O_2 data. Here it has been shown that stack temperature and O_2 are the main measurements needed to determine the thermal efficiency of most sources. This gives air emissions analysts the ability to quantitatively characterize a source using stack data alone.

Equation 7-4 is particularly useful in determining how much the source efficiency changes as a result of changes to the hardware or to the operation. If, through cleaning or other improvements, the exhaust temperature is decreased to 300°F in the previous example, the thermal loss term drops to 7.82% and efficiency rises to 85.1%. If, through some combustion tuning, the exhaust O_2 is decreased to 4% (with the stack at 350°F), the thermal losses decrease to 8.83% from 9.39% and the efficiency rises to 84.1%. So measuring exhaust temperature and O_2 in conjunction with Equation 7-4 provides a very sensitive way to track thermal efficiency changes.

One must remember that combustion efficiency is inherently high in nearly all systems and that only a tiny fraction of the fuel is left unburned, creating emissions. However, the thermal efficiency of combustion devices varies widely, depending on the thermodynamic cycle. The common misuse of the term "combustion efficiency," to characterize overall thermal efficiency, should not be interpreted to mean that unburned fuel is going up the stack. Standard stack emission measurements can be used to determine emissions, thermal losses, and the source firing rate.

7.2.4 Power Plant Efficiency

The traditional steam-electric power plant provides an illustration of how efficiency relates to fuel consumption. The generating units in these plants consist of a very big high-pressure boiler connected to a steam turbine that is coupled to an electric generator. Typical stack parameters on these boilers are 300° to 350°F and 5% O_2, similar to the last example. So, based on the discussion in the preceding Section, we know that the efficiency of the boiler in converting fuel energy to steam energy is in the range of 80-85%. [Boiler efficiency varies with fuel type – coal is more efficient and natural gas less efficient because of the amount of water generated during combustion.] So if the boiler is 84% efficient, then 100 mmBTU of input energy will produce 84 mmBTU of steam energy. Energy loss at this stage of the process is only 16%, which is relatively small.

The overall efficiency of electric power plants is characterized by the *heat rate*, which is the number of BTU required to produce a kilowatt-hour of electric power. In typical steam-electric power plants, this number is around 10,000 BTU/kw-hr; the most efficient plants reach about 9,000 BTU/kw-hr.

Note that if the power generating process were 100% efficient, then heat rate would be 3410 BTU/kw-hr. So the typical power plant efficiency is

$$3410/10{,}000 = 0.341$$

or 34.1% efficient. If the overall generating system is about 34% efficient and the boiler is over 80% efficient, there must be a huge loss somewhere. Most of the loss is in the condenser, which dumps about 40% of the input energy into the air or into an adjacent body of water. Steam drives the turbine that drives the electric generator. A few percent of the steam energy is lost in both of these components. However, the largest loss is in the cool low-pressure steam after it leaves the final turbine stage. This spent steam passes through a condenser that converts it back to water to feed the boiler and in the process, gives up about 1000 BTU per pound of steam to the condenser

Example 7-4

How much energy is required to operate a 150-megawatt (MW) power plant with a heat rate of 10,200 BTU/kw-hr? What is the overall thermal efficiency?

Solution:

Multiply the heat rate by the load (using consistent units) to get energy use.

$$150{,}000 \text{ kw} * 10{,}200 \text{ BTU/kw-hr} = 1530 \text{ mmBTU/hr}$$

The efficiency follows from the ratio the ideal energy to actual energy use:

$$3410/10{,}200 = 0.334 = 33.4\%$$

Knowing the energy input can be used to determine the amount of fuel used or to estimate the total emissions.

The newest combustion turbine power plants boast heat rates in excess of 7500 BTU/kw-hr. However, engine manufacturers compute heat rate using the lower heating value of the fuel (usually natural gas). By using the lower heating value the manufacturers can claim higher efficiency. Using the data from Table 3-4 (Fuel Heating Values), one may convert to a higher heating value basis, which gives about 8300 BTU/kw-hr. This can be compared directly to the heat rates reported by steam-electric power plants. New combined cycle power plants are considerably more efficient than simple cycle engines or steam power plants and some are now claiming thermal efficiencies above 60%, based on the LHV of the fuel.

7.2.5 CO_2 Emissions

Carbon is the principal constituent of all our common fuels and the resulting carbon dioxide is a greenhouse gas. The CO_2 emission rate depends on the type of fuel, and is directly proportional to the amount of heat released. The amount of CO_2 generated by burning fuel can be calculated in the same way as pollutant emissions (see Equation 5-1).

$$\frac{\text{lb } CO_2}{\text{mmBTU}} = \frac{\text{\% fuel C/100}}{\text{HHV}/10^6} \times \frac{44}{12} \qquad (7\text{-}5)$$

Where: % fuel C is the fuel % carbon content (ultimate analysis)
HHV is the fuel higher heating value –BTU/lb
44/12 is the molecular weight ration of CO_2/C

Table 7-2 lists some typical emission rates for various fuels.

Table 7-2. CO_2 Typical Emission Rates

Fuel	*CO_2 lb/mmBTU*
Natural Gas	120
No. 2 Oil, Diesel	165
No. 6 Oil	180
Bituminous Coal	185
Lignite	218
Carbon	260

Clearly, natural gas is the best fuel for minimizing CO_2 emissions because more than half its energy comes from burning hydrogen. Heavy oil or coal increases the emissions by 50%. Lignite has relatively high CO_2 emissions because, not only does most of the energy derives from burning carbon, but some energy must be used to evaporate all the water that is typical of lignite fuel. While natural gas is desirable, if used efficiently, any substantial gas leaks could offset the advantage because methane is a far more potent greenhouse gas than CO_2.

To compute the actual emissions, multiply the firing rate by the CO_2 emissions rate from Table 7-2.

Example 7-5.

From the last example of a 150 MW power plant that consumes 1530 mmBTU/hr of energy, assuming it is fired on No. 6 oil, what is the CO_2 emissions rate?

Solution:

Take the CO_2 emission rate for No. 6 oil from Table 7-2 and multiply by the heat input.

$$1530 \text{ mmBTU/hr} * 180 \text{ lb } CO_2\text{/mmBTU} = 275{,}400 \text{ lb } CO_2\text{/hr}$$

So this 150 MW power plant at full load will emit about 138 tons/hr of CO_2, or as much as 3300 tons/day. Switching the fuel to natural gas would reduce the potential emissions to about 2000 tons/day – still a substantial quantity.

7.3 EMISSIONS MONITORING

7.3.1 Emissions Variability

Source emission rates will vary for a variety of reasons. If mechanical breakdown and long term wear are excluded, other potential causes include:

- Load changes
- Operator implemented changes
- Natural short term fluctuations – particularly excess air level
- Changes in atmospheric conditions – specifically temperature and humidity
- Start up of cold equipment
- Fluctuations in fuel properties

Each of these factors has a different interpretation depending on the type of source and the type of emissions. However, the following discussion is only intended as an

overview. Table 7-3 attempts to organize the subject and provide a general indication of time scales and magnitudes.

Table 7-3. Typical Variation in Emission Rates

Source and Cause of Variation, Time Scale	*NOx*	*PIC*
Boiler - operator instigated changes (1 hr)	±15%	0 to Excessive
Boiler - natural draft fluctuations (15 sec.)	±5%	±50%
Reciprocating engine - atmospheric change (12 hr)	±5%	±10%
Gas Turbine - atmospheric changes (12 hr)	±10%	±10%
Waste combustor - waste properties (15 min)	±15%	±75%

The numbers here are illustrative and not to be used to predict the variations from any given source.

Note in Table 7-3, in nearly all cases, the fluctuation in NOx emissions is less than the fluctuation in PIC emissions. The reason for this is evident by examining Figure 5-9. NOx varies gradually and steadily as excess air changes. CO and smoke are either near zero or, they rise dramatically as excess air decreases. So small fluctuations in excess air can trigger large changes in PIC emissions, but only small changes in NOx emissions. In boilers and furnaces, the air flow is never perfectly steady, but fluctuates naturally by one or two percent. When the average excess air level is near the lowest practical level, air flow fluctuations are enough to generate spikes of CO and/or smoke. This is the reason that gray smoke from boilers is emitted in unsteady puffs and the trace from the opacity meter shows either nothing when there is plenty of excess air, or a series of spikes when the excess air is low. On boilers, the operators directly control the excess air level, so emissions can vary over a wide range depending on how the operator is running the boiler.

Engine emissions are usually very stable. Engine air flows experience much smaller and more rapid fluctuations than boilers, so excess air does not drive noticeable changes in engine emissions. A significant increase in air humidity will cause a noticeable decrease in NOx formation on either reciprocating or turbine engines. Ambient temperature has a strong effect on maximum engine load for either reciprocating or turbine engines and this can affect peak emissions.

Load always affects the total mass emissions (lb/hr) and usually affects the emission rate (concentration in units of ppm or lb/mmBTU) on all sources. Over the normal operating range, an increase in load generally means an increase in NOx emission rate. PIC are usually low and they may go up or down with load. Low or minimum load on many sources (boilers and engines) can be a higher emission point for both NOx and PIC. Boilers frequently have higher excess air levels at low load that increase NOx emissions. At idle, both reciprocating and turbine engines can be operating outside of their optimum envelope and both NOx and PIC emission rates can be higher. Start up generally means

higher emissions for all types of combustion sources. Start up times vary from a few minutes for some engines to many hours for large boilers.

7.3.2 Measurement Methods

This section is a brief introduction to emissions monitoring. There are three general methods of measuring emissions: (1) continuous emission monitors (CEMs), (2) federal reference method (FRM or RM) sampling trains, and (3) indirect or parametric emission monitoring (PEM). CEMs are used for most gas phase emissions. FRM sampling trains are required for particulate mass emissions and other pollutants that cannot be measured by continuous instruments, either because the appropriate instrument does not exist or the concentration levels are below the range of available instruments. Indirect (PEM) monitoring infers emissions on a specific source from other data such as fuel flow and exhaust temperature. An indirect monitoring system must be calibrated initially by one of the direct measurement methods. Indirect monitoring is generally less expensive than direct measurements and in some cases gives equivalent or better data.

Direct measurement methods determine the concentration of the pollutant, either in volume based units such as percent or parts per million (ppm), or in weight based units such as mg/m^3 or $grains/ft^3$. A direct measuring system must also record supporting data including one or more of the following:

- O_2 or CO_2 concentration
- Exhaust flow rate
- Exhaust moisture content
- Fuel flow rate or power output
- Ambient conditions (temperature, atmospheric pressure, humidity)

Some of this supplemental data is necessary to calculate and report data in units that may be compared to permit levels. Additional data may include ambient conditions, exhaust temperature and pressure, etc. that may be necessary for data reduction or to meet other permit requirements.

7.3.2.1 Continuous Emission Monitoring Systems (CEM)

The basic elements of a CEM system are shown in Figure 7-2. A gas sample is sucked from a probe in the stack, through an umbilical tube to an analysis cabinet. The analysis cabinet houses a sample gas pumping, drying and filtering system to supply clean dry gas to the analyzers. Instruments in the analysis cabinet measure the concentration of various species and report the results to a data acquisition system (DAS). Periodically, calibration gases from cylinders are sent through the system and the instruments are calibrated. These systems can either be set up temporarily and operated manually (similar to reference method test methods of 40 CFR 60, Appendix A), or they can be permanently installed in which case they operate automatically. On permanent CEM

systems there are one or more computers to (1) operate and calibrate the sampling system and (2) process and store the data (data acquisition system).

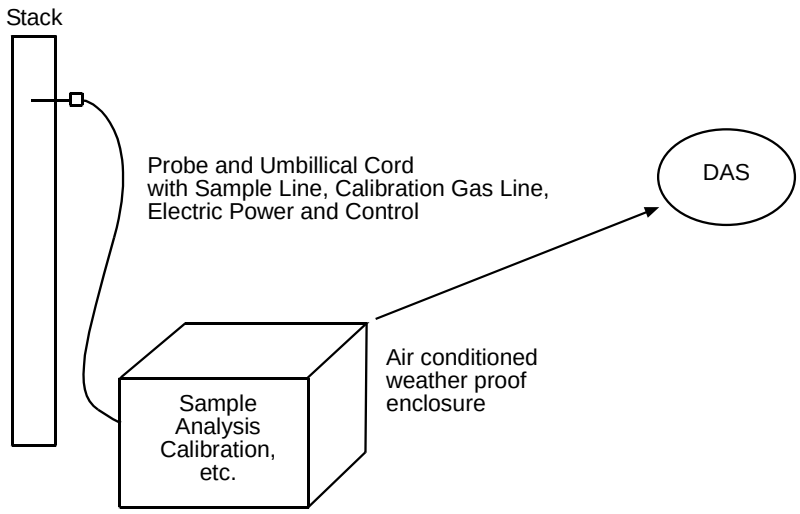

Figure 7-2. Elements of a Continuous Monitoring System

There are several types of CEM systems, each designed around a different method to handle one universal concern – water condensation in the sampling system. Liquid water in the sample stops or damages the instrument analyzers and absorbs some of the pollutants, such as NO_2 and SO_2. Flue gas moisture levels are typically 10% or more, which means the water condenses when the CEM sample gas temperature drops below about 120°-130°F. Drying the sample (by removing water or by dilution with dry air) changes its volume and alters the concentration of all pollutants. Water vapor in the flue gas introduces complex issues for both measurement and data reduction in the CEM. A brief description is provided about how the two most common systems work.

A *dry extractive CEM* sucks the gas sample through a heated system to the analysis cabinet. The gas is kept above the dew point temperature until it passes through a condenser that removes water with minimum contact between liquid water and the sample gas. The sample gas is analyzed and all the raw concentration data is obtained in units of ppm or percent concentration in dry exhaust gas (ppm or % on a dry basis). However, many of the regulations require measurement of total mass emissions – lb/hr. This typically requires stack flow rate data that is easy to measure, but reflects the flow of wet (total) flue gas. In order to combine the dry concentration data with the wet flow rate data, the system needs the exhaust gas moisture content, which requires additional data.

The *dilution extraction CEM* was developed to overcome the problem of correctly matching dry and wet data. As the exhaust sample is drawn from the stack it is diluted with a constant flow of dry air to give a sample with a known dilution ratio. Dilution

ratios of 100:1 are common. This reduces the water vapor concentration and drops the dew point temperature well below the ambient temperature. The diluted gas sample can be passed through the instruments without any water condensation. Since the sample contains the water and all the original pollutants it is still considered a "wet" sample. Calibration gases are also passed through the dilution system so the instruments are calibrated to stack concentration levels even though the sample concentrations at the instrument are a fraction of stack levels. So, for example, if the dilution rate was 100:1 and 50 ppm cal gas was passed through the system, the instrument would see 0.5 ppm. The data system would interpret the instrument reading as 50 ppm. Concentration data from the instruments in a dilution extraction system can be combined with stack flow data without the need for a water vapor correction. Perhaps the main drawback to the dilution extraction system emerges on certain new sources with NOx emission levels of a few ppm, resulting in extremely low concentrations reaching the instruments.

7.3.2.2 Federal Reference Method Sampling Trains

Reference method (RM) sampling trains are used to measure particulate emissions and other pollutants where acceptable continuous analyzers are not available. The sampling system is set up adjacent to the port(s) on the stack or duct that are used for sample extraction. Typically a sampling train draws sample for one hour and the resulting measurement is an average for that one-hour period. Usually three one-hour test runs are made and results are reported as the average. Figure 7-3 shows the components of a Method 5 particulate sampling train. Here particulate matter is collected on a filter and the volume of gas sampled is measured with a dry gas meter. The filter is weighed before and after the test giving a weight that can be combined with the sample volume to give a concentration – grams/m^3 or lb/ft^3. Impingers in an ice bath condense the water vapor, which is subsequently measured. The impingers can also be used to capture condensable particulate or certain gases, such as ammonia, formaldehyde, HCl, etc. Most reference method sample trains are similar to that shown in Figure 7-3. The difference is that the filter would be replaced by something like a canister of resin adsorbent, or there might be additional collection devices between or after the impingers. The collection devices are taken to a lab to analyze for specific substances.

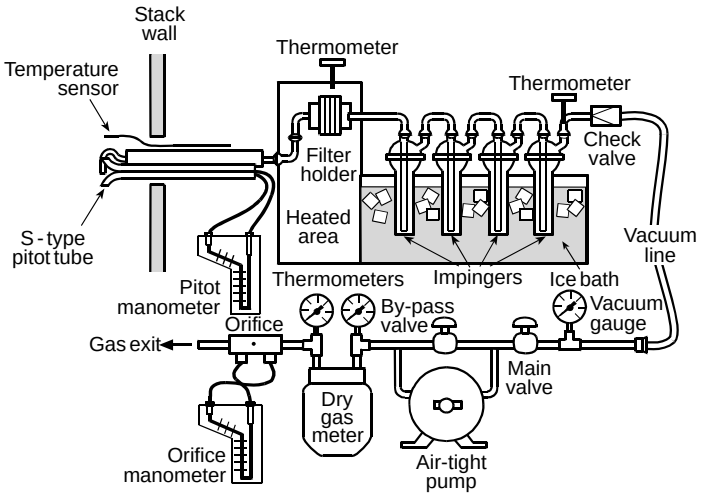

Figure 7-3. EPA Method 5 Sampling Train

Source: 40CFR60 Appendix A

7.3.2.3 Indirect or Parametric Emission Monitoring (PEM)

Indirect (PEM) monitoring is attractive primarily because it is much less expensive than a CEM and it gives continuous data. It is technically feasible to implement PEM on any source where the emissions can be accurately predicted from readily available data such as fuel flow, exhaust temperature, etc. PEM has been applied quite successfully to monitor NOx emissions from combustion turbines and reciprocating engines. It may also be used to monitor NOx emissions from small to medium size industrial boilers. Engine sources equipped with a SCR system are also candidates; although, catalyst deterioration would not be detected by a PEM system.

PEM systems are much less accurate when used to monitor CO emissions. As noted earlier, CO emissions are very sensitive to small changes in excess air and other combustor parameters, so CO does not lend itself well to indirect monitoring.

PEM systems usually rely on fuel flow or load and one or two other parameters as the primary basis for determining emissions. The algorithms used to convert this data to emissions rate can be set up to report emissions in pounds per hour or lb/mmBTU or both. Hence the issue of how to deal with exhaust moisture content is moot. PEM systems generally do not report either exhaust flow rate or moisture; although they could be programmed to do so.

7.3.3 Calculating Emissions

CEM instruments measure concentration in units of *parts per million by volume.* Depending on whether it is a dry extraction or a dilution extraction system the measured data could be ppmd (ppm by vol., dry basis) or ppmw (ppm by vol., wet basis).

A CEM system processes the measured data and typically reports emissions in units of:

- lb/hr,
- lb/mmBTU, or
- ppmd corrected for dilution

From these units, one can generally convert to other units using simple formulas and possibly some supporting data.

7.3.3.1 Correcting for Dilution

Exhaust gas is composed of the products of combustion plus a certain amount of excess air. Excess air in the stack gas may originate either in the combustion zone or from leaks in the ducts. Regardless of its origin, it dilutes the combustion gases and is present in the sample analyzed by the CEM. If emission standards were based on concentration as measured, then any source could reduce its emissions by simply diluting its flue gas with air. Sources with leaky ducts would have an advantage over sources with tight ducts. So to avoid this problem all emission concentrations are corrected for dilution and reported in forms such as:

- ppmvd corrected to 3% O_2, or
- ppmvd corrected to 12% CO_2

Measured O_2 or CO_2 are used to determine the amount of dilution air present in the sampled gas. The formula for correcting the measured emissions concentration is:

$$\text{ppm @ Y\%}O_2 = \text{ppm(meas.)} \times \frac{20.9 - Y}{20.9 - \%\,O_2\ \text{(meas.)}} \qquad \text{(7-6a)}$$

$$\text{ppm corrected to X\% } CO_2 = \text{ppm(meas.)} * \frac{x\%}{\%\,CO_2\ \text{(meas.)}} \qquad \text{(7-6b)}$$

Where: X and Y are percentages specified by the applicable emission standard for the source

Example 7-6.

If the measured data is NOx = 135 ppm, O_2 = 4.7%, what is the NOx concentration when corrected to 3% O_2?

Solution:

Inserting the data in equation (7-6a):

$$135\text{ppm} \times \frac{20.9 - 3}{20.9 - 4.7} = 149\text{ppm}$$

3%O_2 was used for this example; a number of other reference values are used in the Federal regulations, but the values are typical of the sources to which the standards apply. Note that O_2 or CO_2 must be measured at the same time and location as the emissions; standard practice is to divide the sample flow, sending part of it to each instrument.

Note that this is only a correction for air dilution of the flue gas and not a correction for the effect that the excess air in the combustion zone has on the amounts of pollutants formed. Changing combustion zone excess air will alter emission levels as well as changing the amount of air dilution.

7.3.3.2 Emissions in lb/mmBTU

One of the most common, and most useful, emission units is *pounds per million BTU* (lb/mmBTU). One particularly attractive feature of this dimension is that it is not necessary to measure the firing rate of the source to determine the emissions. All the necessary data can be acquired at the stack sampling location; the key measured parameters are the pollutant concentration and O_2 concentration. This means the reported emissions are not dependent on data, such as fuel flow rate, provided by the source operator. In fact, except for the use of the F-factor, *lb/mmBTU* uses the same data as *ppm (corrected)*. The formula is:

$$A\left[\frac{\text{lb}}{\text{mmBtu}}\right] = \frac{A\,(\text{ppmdv})}{1{,}000{,}000} * \frac{MW_A}{385} * F_d * \frac{20.9}{20.9 - \%O_2} \qquad (7\text{-}7)$$

Where:

ppmdv A	=	measured concentration of air pollutant A
MW_A	=	molecular weight of A, 46 for NO_2, 64 for SO_2, etc.
$\%O_2$	=	measured oxygen concentration, % by vol., dry basis
385	=	std ft^3 / lb-mole of ideal gas
F_d	=	dry F-factor, std ft^3 / mmBTU

bituminous coal	9780
oil	9190
natural gas	8710
wood	9240

Note that the measured values (ppm of pollutant and % O_2) are both based on dry flue gas. Neither gas flow rate nor source firing rate are needed. Since essentially the same data is used to calculate lb/mmBTU and ppm corrected, it makes little difference which dimensions are used unless the source switches fuels. Units of lb/mmBTU may be easier to use for computing emission inventories, etc.

7.3.3.3 Emissions in lb/hr

Mass emission rates in *pounds per hour* (lb/hr) can be determined either by multiplying the source firing rate (mmBTU/hr) by the emission concentration

(lb/mmBTU), or it can be determined entirely from stack data. The basic formula for computing lb/hr from measured data is:

$$A\left[\frac{lb}{hr}\right] = \text{exhaust flow}\left[\frac{scf}{hr}\right] * \frac{A\,(ppmw)}{1{,}000{,}000} * \frac{MW_A}{385} \qquad (7\text{-}8)$$

Where: A = pollutant species
MW_A = molecular weight of species A
exhaust flow is the total (wet) flue gas flow in standard cubic feet per hour
A is measured in a wet (not dried) sample
385 = the number of standard cubic feet of gas in a pound mole @ 68°F. (MW/385 = gas density in lb/^{3})

Note that there is no dilution correction here because the total flue gas flow is measured. However, the pollutant must be measured in a wet gas sample (dilution extraction system) or a dry measurement must be corrected back to its wet concentration. This same equation could be written with dry measurements; however, the trouble is that there is no simple instrument to measure dry flue gas flow rate.

As an alternative, mass emission rate can be determined without measuring stack flow if the firing rate of the source is known. The formula is:

$$\text{Emissions } {}^{lb}\!/_{hr} = \text{Emissions } {}^{lb}\!/_{mmBTU} \times \text{Firing Rate } {}^{mmBTU}\!/_{hr} \qquad (7\text{-}9)$$

In this case, the firing rate (mmBTU/hr) would be determined from fuel flow measurements and the emissions in lb/mmBTU from stack measurements and Equation 7-7. This method is applicable to gas and oil-fired sources where the fuel heating value is consistent and the fuel flow can be measured accurately. On a coal-fired source the fuel heating value can fluctuate over a considerable range, so this approach to emissions calculation is tenuous. On a solid waste-fired source the fuel analysis varies over such a wide range that this method of calculating emissions is not applicable.

7.4 RECIPROCATING ENGINES AND COMBUSTION TURBINES

7.4.1 Characteristics of Reciprocating Engines and Turbines

Combustion turbines are the prime mover in most new electric power plants in the U.S. The price and availability of natural gas is one of the reasons for this dominance. Most of these units run entirely on natural gas; although many can use distillate oil (No. 2, diesel or kerosene) as a backup fuel if the gas supply is shut off.

Many new installations are combined cycle or cogeneration systems that use the waste heat from the turbine or reciprocating engine to make hot water or steam for other uses. Without waste heat recovery turbines and reciprocating engines have about the same thermal efficiency as a steam electric power plant – about 35 -40%. The latest large combustion turbines are somewhat higher; however, small turbines may be considerably lower. Nonetheless, with waste heat recovery, all of these systems generally can exceed 50% in overall thermal efficiency. High efficiency, combined with the fact that they burn natural gas, means they emit considerably less carbon dioxide and almost no sulfur compared to traditional coal-fired steam-electric power plants.

7.4.2 Emissions and Control

Since most turbines and reciprocating engines run on natural gas or occasionally on clean oil, the only emission of serious concern is NOx. PIC are rarely high and in most new installations they are further controlled to very low levels with an oxidation catalyst. Low NOx combustion systems, based on premixing natural gas and air, have been developed for both turbines and reciprocating engines that reduce NOx dramatically from previous uncontrolled levels. In NOx sensitive areas, low NOx combustors are supplemented with SCR systems.

Uncontrolled NOx emissions from nearly all reciprocating engines are very high – in the range of 4 lb/mmBTU. On gas-fired engines, emissions can be reduced by about 90% if low NOx combustion chambers are available. Also on gas-fired engines emissions can be reduced dramatically by installing a non-selective catalytic reduction (NSCR) system and controlling the engine air flow to keep the air fuel-air ratio precisely stoichiometric. No low NOx combustion systems are yet available for diesel engines, but SCR controls can be installed on any reciprocating engine. Technology development is continuing on the development of emission controls for both gas and oil-fired engines.

On new installations it is fairly common practice to put an SCR NOx control system on the exhaust of either a reciprocating engine or a combustion turbine. At the present time the upper temperature limit for zeolite catalysts used in this application is about 1000°F. Higher temperatures decrease the life of the catalyst. Most turbines have exhaust temperatures that exceed 1000°F at full load, so the temperature needs to be reduced. When the turbine exhausts to a boiler (combined cycle or cogeneration), this is accomplished by locating the catalyst in the middle of the boiler after the gas temperature has been reduced. Figure 7-4 shows the general arrangement. The first section of the boiler reduces the temperature to a level acceptable to the catalyst.

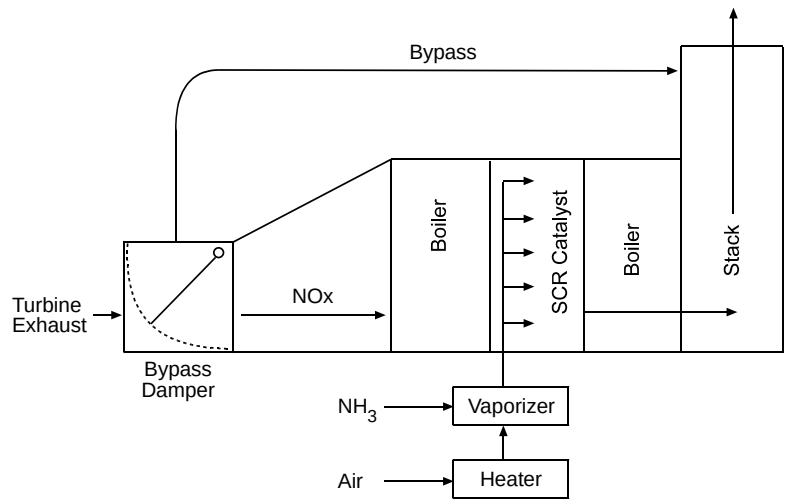

Figure 7-4. SCR Installation on a Combined Cycle System

Emissions during the startup of combustion turbines are higher than full load emissions, especially if the turbine is equipped with a low NOx combustor. Even large turbines can start up quickly and generally can achieve full load in about 20 minutes, so high startup emissions might not be a serious problem. However, if the turbine feeds a boiler (heat recovery steam generator or HRSG), the boiler requires several hours to warm up. Many of these systems are equipped with a bypass duct that allows the turbine to produce load while the boiler is warming up using perhaps 20% of the turbine exhaust. However, the exhaust flow through the bypass does not go through the SCR system. So even if the turbine load is high enough to put it into its low NOx operating mode, the additional NOx reduction of the SCR system will not be achieved until the boiler warms up and all the exhaust passes through the boiler.

CO and organic vapor emissions are relatively low, but sometimes significant from either combustion turbines or reciprocating engines. A simple way to deal with PIC emissions is to install an oxidation catalyst after the SCR system. CO and organic vapor emissions can be reduced to levels of a few ppm.

7.5 NATURAL GAS and OIL FIRED BOILERS

7.5.1 Characteristics of Boilers

Boilers are the most populous stationary source. They range in size from residential furnaces to utility boilers fired at thousands of mmBTU/hr. The focus of this course is with industrial and utility boilers that have firing rates higher than about 10 mmBTU/hr. Boilers can be designed to burn virtually any fuel from natural gas to low-grade coal mine waste. The emissions depend on the fuels used and on the design of air pollution control equipment. Small natural gas-fired boilers have little or no emissions control, while large coal- or waste-fired boilers have extensive air pollution control hardware.

Emissions from boilers, depending on the fuel, can include almost any air pollutant, but with rare exceptions the emissions do not include significant levels of organic compounds. Boiler CO emissions are generally quite low.

Boilers typically have long lives. They are easy to repair and boiler technology has not changed very much over the past 40 to 50 years. So many boilers built after about 1950 are not obsolete; they have not worn out and they are still operating. Thus much of the current boiler population predates all environmental regulation – other than rules to avoid excessive smoke. These boilers have been repaired and the burners and controls have probably been upgraded. But most of these upgrades have focused on improved reliability or efficiency, not on reduced emissions. So the current population of boilers include (1) some newer boilers built to meet varying levels of emission standards, and (2) many older boilers, with varying levels of combustion upgrade.

7.5.2 Nitrogen Oxides Control

At the beginning of the 21st Century, NOx is controlled on existing boilers largely by means of combustion or operational adjustments to reduce NOx formation. There are a few SNCR systems in service – mostly on municipal waste to energy boilers.

Combustion NOx controls consist of various combinations of the following elements:

- operating controls including low excess air and various burner adjustments
- staged combustion on large furnaces using specific combinations of burners
- low NOx burners
- overfired air
- flue gas recirculation.
- natural gas reburning
- switching fuel to natural gas or distillate oil

Aggressive use of combustion hardware adjustment/changes (the first five elements) can reduce NOx by 50% on most boilers and by 80%–90% on natural gas or distillate oil-fired boilers. The main cost of these changes is the initial capital cost of hardware changes. Fuel switching or natural gas reburning generally triggers significant operating costs because distillate oil is always more expensive than No. 6 oil, and natural gas can be more expensive than other fuels, depending on location and time of year. Fuel switching can be incremental, such as blending distillate and No. 6 oil, or seasonal such as switching to natural gas during summer months, or a combination.

NOx emissions are controlled to reduce ozone, which is a seasonal air pollution issue. Thus, depending on the jurisdiction, NOx reductions may be more important in the summer than in the winter. Most of the combustion hardware based controls can be operated year-round with little or no cost penalty, but fuel switching can be expensive and so it may be reserved for those times when additional NOx emission control is necessary.

Low NOx burner development is a continuing process and some further reduction from existing emission levels is likely. However, the largest reductions have probably already been achieved. Progress on large, multi-burner utility boilers is likely to be site specific rather than the result of new, low NOx burner technology.

Except for a few SNCR installations, primarily on municipal waste-to-energy boilers, SNCR or SCR controls have not been implemented on many boilers in the U.S. SCR systems may begin to appear on boilers as a result of regulatory pressure to reduce ozone levels in the eastern U.S. and some other areas.

7.5.3 Sulfur Oxides Control

Natural gas contains almost no sulfur and No. 2 oil contains low levels of sulfur – usually much less than the 0.5% permitted in ASTM specifications. So sulfur oxide emissions are an issue for boilers fired on No. 6 oil, coal, and some wastes. There are a few sulfur oxide scrubbers installed on coal-fired boilers in the U.S., but most sulfur reductions have been achieved by changing fuels. Coal and oil are sold on the basis of fuel heating value and fuel sulfur content, making it practical to control emissions by controlling the sulfur content of purchased fuel. When sulfur oxide scrubbers were first installed on a few large utility boilers in the 1980s there was little prior experience and these installations encountered a number of serious problems. In the intervening years, there have been significant advances in scrubber technology and the utility industry has accumulated operating experience. So the options for SO_2 emissions control can be evaluated with much more certainty about their cost and impact.

SO_3 (sulfuric acid) emissions are not directly controlled by regulations in most areas, but the emissions are indirectly controlled by prohibitions against visible plumes from the stack. When vapor phase sulfuric acid exceeds about 5 ppm, it can form a visible condensation plume that dissipates very slowly. This plume is most prevalent on No. 6 oil-fired boilers that use oil with 1% or higher sulfur content. Plumes have been observed from boilers firing 0.7% or even 0.5% sulfur oil, so reducing fuel sulfur content is not a sure path to invisible plumes. Coal-fired boilers usually don't emit visible acid plumes – usually because the fly ash absorbs enough acid to keep the amount of acid below the visible threshold. One or more of several approaches is used to reduce visible acid plumes from oil-fired boilers:

- reducing oil sulfur content may reduce the plume to acceptable levels
- keep the air heater and back end temperatures high enough to prevent condensed acid accumulation during low load operation
- operate at sufficiently low excess air levels that acid formation is reduced
- find a basic fuel additive, such as magnesium oxide, that reduces the amount of acid

Adequate control of visible acid plumes always requires some level of trial and error even when preceded by a perceptive diagnostic program to evaluate the causes.

7.5.4 Particulate Emissions

Particulate emissions should not be an issue with gas-fired boilers, although measurable emissions may be created as artifacts of the test procedure. Particulate emissions should not be significant from distillate oil-fired boilers unless the fuel has enough sulfur to form sulfuric acid and the test is run at low enough temperatures to capture the acid. Particulate emissions from No. 6 oil-fired boilers are significant and, as discussed earlier, they can exceed regulated levels if the oil atomization is poor or if the boiler generates a lot of sulfate and the emission limit is less than about 0.1 lb/mmBTU. Pulverized coal generates huge amounts of particulate and a high efficiency (>99%) dust collector is always required. Solid fuel stokers for wood or other fuels generate substantial amounts of particulate and some form of dust collector, either internal or external to the boiler, is always used. All new stoker boilers have a high efficiency dust collector in addition to an internal cyclone or multiclone collector.

Electrostatic precipitators have been added to a few large No. 6 oil-fired boilers with mixed results. They do reduce particulate emissions, but at considerable cost. Most large No. 6 oil-fired boilers can meet a particulate emission standard of about 0.05 lb/mmBTU in the absence of any dust collector. So the necessity and benefit of a high efficiency dust collector is often questionable. Oil-fired boiler ash levels are low enough and acid levels are high enough that the collected material becomes damp, sticky and highly corrosive unless the dust collector and its hoppers are maintained well above the acid dew point of about 260°F. This requires an adequate initial design and a concerted effort on the part of the operating staff. Then there is the problem of what to do with the collected ash. Some facilities inject all the ash back into the boiler where any carbon burns and the incombustible portion gradually accumulates in the boiler hopper(s). Some utilities are able to sell this bottom ash for its vanadium content. Other disposal routes generally must treat the ash as a hazardous waste because it is acidic and contains a number of water-soluble metallic compounds.

7.6 COAL FIRED BOILERS

Most of the preceding discussion of gas- and oil-fired boilers applies to pulverized coal boilers as well. We will limit the discussion here to additional features that are specific to coal-fired systems.

7.6.1 Characteristics of Pulverized Coal Boilers

Boilers designed for pulverized coal (PC) can also be fired on natural gas or oil, assuming the appropriate burner and fuel-handling hardware is in place. However, the converse is not true: boilers designed for oil or gas cannot fire pulverized coal without major changes and a substantial derating. PC boilers normally can fire only small amounts of gas or light oil to light off and warm up the boiler before the first

coal mill is started. The difference between PC and other types of boilers originates in the ash content of the coal, which is typically about 10%. So a power plant that burns several thousand tons of coal a day has to deal with several hundred tons of powdered rock passing through the boiler and duct work up to the dust collector. This has several affects on the design and operation of the boiler:

- Ash/dust accumulation on surfaces in the boiler reduces heat transfer, so a PC boiler needs more total heat transfer area.

- Different amounts of ash deposited in various boiler sections results in unbalanced heat transfer rates, and imbalances between steam generation and superheat and/or reheat, etc. Internal soot blowers are provided to allow operators to selectively clean sections and try to maintain balanced temperatures.

- If the dust is heated to its melting point, it will tend to agglomerate and will tend to stick tenaciously to surfaces. Dry ash (not molten) can be removed with soot blowers. However, slag accumulations in the boiler can block gas passageways or grow big enough to pose a physical hazard.

- The firebox in a PC boiler is large in order to (1) reduce wall temperatures, (2) provide more combustion residence time and (3) provide enough heat transfer area when the surfaces are partially fouled with ash.

- Operators use excess air and specific burner arrangements to control firebox temperatures and the tendency for ash to form slag accumulations.

So any combustion adjustments or changes on a PC boiler to improve emissions can have other affects that may be critically important to boiler operation.

Overall, PC boiler emissions are not substantially above those from a comparable residual oil-fired boiler. Combustion controlled NOx emissions are higher than oil-fired emissions because of the high nitrogen content of coal. Particulate emissions after a dust collector are equivalent to or lower than uncontrolled oil-fired particulate emissions. The particulate that is emitted from a coal boiler tends to be relatively insoluble silica and metal oxides, while that from an oil-fired boiler is mostly soluble sulfates with vanadium and other metals. Sulfuric acid emissions and visible plumes are less prevalent from properly operated PC boilers than from comparable residual oil-fired boilers.

7.6.2 Nitrogen Oxides Control

Combustion based NOx controls on a PC boiler are similar to those on an oil-fired boiler. One of the critical factors in NOx control on large boilers in general, and PC boilers in particular, is to achieve a uniform distribution of fuel and air to each burner. The burner-to-burner fuel and air distribution is never perfectly uniform, but the extent of the problem on individual boilers was never realized until attempts were

made to reduce NOx emissions. Engineers discovered that multiple low NOx burners did not reduce NOx emissions anywhere near as much as had been observed on single burners in a test furnace. Measuring fuel and air distribution to individual burners is both difficult and time consuming. But research on various boilers showed that PC blown from the coal grinding mills was not evenly divided between all the burners and that the coal flow could be highly non-uniform even within the coal pipe to an individual burner. Once these problems were identified and resolved, low NOx performance was usually achieved, and some of the problems with slag accumulation and non-uniform temperatures were resolved simultaneously. The point here is that the whole system has to be fine tuned to achieve low NOx performance, and some of the operating problems that might be attributed to new low NOx hardware could be existing problems that are brought to light by low NOx development work.

7.6.3 Sulfur Oxides and Particulate Matter

Reduced SO_2 emissions have frequently been achieved by switching to lower sulfur fuel. Any fuel change in a PC boiler requires some test firing and demonstration that the new coal will perform acceptably – mostly to be sure that the ash and slag do not trigger unmanageable accumulations in the boiler. On individual boilers the question comes down to this: Which low sulfur coals are acceptable?

Low sulfur coal can also trigger problems in an electrostatic precipitator. Low sulfur coal from the Powder River Basin has a very basic ash that combines with sulfuric acid. Eliminating the acid in the exhaust gas reduces corrosion problems, but it also raises the resistivity of the ash to the point that it is difficult to collect in an electrostatic precipitator. In some cases, this has been resolved by adding a few ppm of SO_3 to the exhaust to lower the dust resistivity and recover the performance of the precipitator.

There are many potential issues associated with changing coal to achieve an emissions goal. Anyone dealing with coal-fired boilers needs to be aware that they are complex and changes to one parameter can have a peripheral impact on a number of other parameters.

7.7 WOOD FIRING AND STOKER FURNACES

Up until about 1940 nearly all furnaces and boilers were stoker fired, mostly with coal and a few with wood. Today almost the only large stoker boilers are operating at forest products industries, burning waste wood, and at municipal waste-to-energy facilities. Most of the smaller boilers have been replaced by units that fire either natural gas or oil. But this is a relatively recent phenomenon. Residential coal delivery was still in vogue as late as the early 1940s in many major U.S. cities.

7.7.1 Characteristics of Stoker Furnaces

Combustion in a stoker occurs in two regions: (1) combustion of solid fuel in a fuel bed, and (2) combustion of gases above the bed. Bed combustion can be controlled by setting the thickness of the bed and by the amount of undergrate air fired through the bed. Above the bed combustion is controlled by the design of the overfire air ports and by the amount of overfire air. This arrangement limits the ability to tune the combustion in the same way that suspension-fired systems (i.e., PC boilers) are adjusted to control air emissions. A further limitation on older stokers with air-cooled grates (most of them) is that the undergrate air flow must be relatively high to keep the grate from overheating. This contributes to a high excess air requirement, characteristic of all stokers, and it limits the amount of air that can be blown through the overfire air ports to control emissions of smoke and CO. Overall, a stoker offers relatively few options for combustion tuning to reduce air pollutant formation.

7.7.2 Particulate Matter Emissions

Most of the fuel in a stoker burns on the grate and the resulting ash is then deposited, manually or automatically, in a bottom ash hopper. So most of the potential particulate emissions are kept in the boiler rather than being carried out by the exhaust gases. Retention can be anywhere from 50% to 90%. Ash retention depends primarily on two factors: (1) the size distribution of the fuel, and (2) feeder design – over-grate spreaders generate higher emissions.

Stokers will tend to emit any ash and fuel particles smaller than one to two millimeters that become airborne in the furnace. Most stokers include a multi-clone collector on the boiler to capture most of these particles. On older units, this is the only collector and the resulting emissions can be in the range of 0.3 to 0.7 lb/mmBTU. On newer units with a good dust collector, the multi-clone catches most of the burning particles and helps to protect the dust collector against fire.

7.7.3 Nitrogen Oxides Control

Nearly all the NOx from a stoker is formed during combustion in the fuel bed where there is no way to modify fuel mixing or stage combustion. Hence the combustion modifications used on PC or suspension-fired systems are inapplicable or relatively ineffective on a stoker. Flue gas recirculation (FGR) into the undergrate air may provide a modest NOx reduction. Reburning with natural gas is effective and it can be used simultaneously to improve a stoker's load response. NOx reductions in the range of 70% to 80% appear to be feasible. Several municipal waste-to-energy boilers have been designed and built with SNCR ammonia injection systems that reduce uncontrolled emissions by about 50%. A number of existing municipal waste-to-energy boilers have been retrofitted with SNCR urea injection systems that reduce NOx by somewhat more than 50%.

7.7.4 PIC and Dioxin-furans

Many stokers blow a significant amount of burning carbon particulate out of the combustion zone. This material can either be reinjected or discarded. On wood-fired boilers this can amount to several percent of the fuel input. For the most part this material is pure carbon with little or no organic content.

Combustion in the fuel bed on a stoker grate releases CO and organic gases that burn above the bed in the over-fired region. Most of the time the over-bed temperatures are high enough to destroy or decompose the organic gases, leaving CO and perhaps methane or other low molecular weight species. If the overfired air system is well designed and operated, it will burn up these combustible gases leaving only low levels of CO in the exhaust. Thus emissions of PIC gases depend almost entirely on the operation of the overfired air system. Tuning this system can usually get rid of smoke, but CO levels of a few hundred ppm are common on older stokers.

Older municipal waste-fired stokers were notorious for high emissions of dioxins, furans and other polycyclic organic species. This appears to be a consequence of several factors:

- grate and waste feeder designs that were inappropriate for municipal waste
- furnace temperatures that locally dipped to 1600°F or less
- inadequate overfired air design

Newer waste-to-energy facilities resolved these problems and the emissions of hazardous organic species from these units is very low.

Review Exercises

1. Which statement is false?
   a. When combustion efficiency is nearly 100%, PIC are near zero.
   b. Thermodynamics do not permit a thermal efficiency of 100%.
   c. Most electric power plants have thermal efficiencies less than 50%
   d. Very efficient combustion is the key to high overall (thermal) efficiency.

2. The energy loss associate with CO emissions of 320 ppm in a stack with O_2 = 6.2% is _____.
   a. 0.05%
   b. 0.12%
   c. 0.24%
   d. 1.15%

3. How much energy is wasted on a pulverized coal boiler when the fly ash contains an average of 7.1% carbon? The coal has 13.2% ash and HHV = 11,800 BTU/lb.
   a. 0.11%
   b. 1.00%
   c. 1.12%
   d. 2.24%

4. Most of the energy lost up a combustion source stack is in the form of _____.
   a. hot gas and water vapor
   b. smoke and unburned carbon
   c. carbon monoxide
   d. kinetic energy of the high velocity gas

5. Heat losses from uncondensed water vapor could be ignored in calculating thermal efficiency if the _____.
   a. moisture content of the fuel is very high.
   b. stack temperature is above the water dew point.
   c. fuel is dry and the lower heating value of the fuel is used in calculations.
   d. stack temperature is below 212°F.

6. What is the approximate thermal efficiency of a gas-fired boiler when stack measurements show T = 290°F, O_2 = 2.9%, water vapor = 14% by volume? Ambient temperature is 48°F.
   a. 78.1%
   b. 85.3%
   c. 88.6%
   d. 90.5%

7. What is the firing rate or fuel energy use of a 480-mw power plant with a heat rate of 9750 BTU/kw-hr?
   a. 4680 mmBTU/hr
   b. 4860 mmBTU/hr
   c. 5108 mmBTU/hr
   d. 5522 mmBTU/hr

8. What are the daily CO_2 emissions from a source that fires coal at a rate of 375 mmBTU/hr?
   a. 524,000 lb/day
   b. 1,450,000 lb/day
   c. 1,665,000 lb/day
   d. 69,400 lb/day

9. The dilution extraction CEM came into use as a result of _____.
   a. the need to measure pollutant concentration without drying the sample gas
   b. the inconsistency between measuring total gas flow and gas concentrations measured after water vapor is removed from the gas sample
   c. the need to measure and report SO_2 and NOx emissions in units of lb or tons/day
   d. All of the above

10. CO emissions are measured at 225 ppm in an exhaust gas with 5.3% oxygen. What would the concentration be if air dilution was reduced so that O_2 = 3%?
   a. 258 ppm
   b. 186 ppm
   c. 248 ppm
   d. Insufficient data to determine the answer.

Review Answers

1. d. Very efficient combustion is the key to high overall (thermal) efficiency

2. b. 0.12% energy loss

3. c. 1.12% energy loss

4. a. hot gas and water vapor

5. c. fuel is dry and the lower heating value of the fuel is used in calculations (see discussion in Section 3.3.2.1)

6. b. 85.3%

7. a. 4680 mmBTU/hr

8. c. 1,665,000 lb/day

9. d. All of the above

10. a. 258 ppm

References

1. Kitto, J.B. *Steam; Its Generation and Use*, (Babcock and Wilcox Company, Barberton, Ohio, 1992). A huge book with in depth coverage of large boiler furnaces, particularly coal-fired boilers. It also covers fluidized beds and refuse firing. The book has grown over the years and the material covered has changed.

2. Pritchard, R., Guy, J.J., and Conner, N.E. *Handbook of Industrial Gas Utilization*, (Van Nostrand Reinhold Co., 1977). The authors are/were at the University of Salford (GB) and the detail/clarity are typically British. The book covers all aspects of combustion hardware and furnace design for any system that fires gas or gas in combination with other fuels.

3. Reed, Richard J. and Schilster, Robert E. *North American Combustion Handbook*, (North American Manufacturing Company, Cleveland, OH, 1993). A good basic reference for small to medium size gas and oil-fired combustion systems.

4. Reed, Richard J. and Schilster, Robert E. *North American Combustion Handbook*, Volume II, (North American Manufacturing Company, Cleveland, OH, 1995). The book provides good detail on burner types, control systems, emissions, heat recovery and other special topics.

5. U.S. Code of Federal Regulations, Title 40, Part 60, Appendix A (Test Methods). These are the "reference" test methods that are the accepted procedures for virtually all emissions testing.

6. U.S. Environmental Protection Agency. John Richards. *Control of Gaseous Emissions*, APTI Course 415, Student Manual, NC State University, 1995. This manual has credible sections on incineration and NOx control as well as covering areas not related to combustion sources.

7. American Society of Mechanical Engineers. *Power Test Codes, PTC 4.1, Steam Generating Units* This gives methods, accepted by industry, for measuring boiler efficiency.