1.4 Natural Gas Combustion

1.4.1 General[1-2]

Natural gas is one of the major combustion fuels used throughout the country. It is mainly used to generate industrial and utility electric power, produce industrial process steam and heat, and heat residential and commercial space. Natural gas consists of a high percentage of methane (generally above 85 percent) and varying amounts of ethane, propane, butane, and inerts (typically nitrogen, carbon dioxide, and helium). The average gross heating value of natural gas is approximately 1,020 British thermal units per standard cubic foot (Btu/scf), usually varying from 950 to 1,050 Btu/scf.

1.4.2 Firing Practices[3-5]

There are three major types of boilers used for natural gas combustion in commercial, industrial, and utility applications: watertube, firetube, and cast iron. Watertube boilers are designed to pass water through the inside of heat transfer tubes while the outside of the tubes is heated by direct contact with the hot combustion gases and through radiant heat transfer. The watertube design is the most common in utility and large industrial boilers. Watertube boilers are used for a variety of applications, ranging from providing large amounts of process steam, to providing hot water or steam for space heating, to generating high-temperature, high-pressure steam for producing electricity. Furthermore, watertube boilers can be distinguished either as field erected units or packaged units.

Field erected boilers are boilers that are constructed on site and comprise the larger sized watertube boilers. Generally, boilers with heat input levels greater than 100 MMBtu/hr, are field erected. Field erected units usually have multiple burners and, given the customized nature of their construction, also have greater operational flexibility and NO_x control options. Field erected units can also be further categorized as wall-fired or tangential-fired. Wall-fired units are characterized by multiple individual burners located on a single wall or on opposing walls of the furnace while tangential units have several rows of air and fuel nozzles located in each of the four corners of the boiler.

Package units are constructed off-site and shipped to the location where they are needed. While the heat input levels of packaged units may range up to 250 MMBtu/hr, the physical size of these units are constrained by shipping considerations and generally have heat input levels less than 100 MMBtu/hr. Packaged units are always wall-fired units with one or more individual burners. Given the size limitations imposed on packaged boilers, they have limited operational flexibility and cannot feasibly incorporate some NO_x control options.

Firetube boilers are designed such that the hot combustion gases flow through tubes, which heat the water circulating outside of the tubes. These boilers are used primarily for space heating systems, industrial process steam, and portable power boilers. Firetube boilers are almost exclusively packaged units. The two major types of firetube units are Scotch Marine boilers and the older firebox boilers. In cast iron boilers, as in firetube boilers, the hot gases are contained inside the tubes and the water being heated circulates outside the tubes. However, the units are constructed of cast iron rather than steel. Virtually all cast iron boilers are constructed as package boilers. These boilers are used to produce either low-pressure steam or hot water, and are most commonly used in small commercial applications.

Natural gas is also combusted in residential boilers and furnaces. Residential boilers and furnaces generally resemble firetube boilers with flue gas traveling through several channels or tubes with water or air circulated outside the channels or tubes.

1.4.3 Emissions[3-4]

The emissions from natural gas-fired boilers and furnaces include nitrogen oxides (NO_x), carbon monoxide (CO), and carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), volatile organic compounds (VOCs), trace amounts of sulfur dioxide (SO_2), and particulate matter (PM).

Nitrogen Oxides -

Nitrogen oxides formation occurs by three fundamentally different mechanisms. The principal mechanism of NO_x formation in natural gas combustion is thermal NO_x. The thermal NO_x mechanism occurs through the thermal dissociation and subsequent reaction of nitrogen (N_2) and oxygen (O_2) molecules in the combustion air. Most NO_x formed through the thermal NO_x mechanism occurs in the high temperature flame zone near the burners. The formation of thermal NO_x is affected by three furnace-zone factors: (1) oxygen concentration, (2) peak temperature, and (3) time of exposure at peak temperature. As these three factors increase, NO_x emission levels increase. The emission trends due to changes in these factors are fairly consistent for all types of natural gas-fired boilers and furnaces. Emission levels vary considerably with the type and size of combustor and with operating conditions (e.g., combustion air temperature, volumetric heat release rate, load, and excess oxygen level).

The second mechanism of NO_x formation, called prompt NO_x, occurs through early reactions of nitrogen molecules in the combustion air and hydrocarbon radicals from the fuel. Prompt NO_x reactions occur within the flame and are usually negligible when compared to the amount of NO_x formed through the thermal NO_x mechanism. However, prompt NO_x levels may become significant with ultra-low-NO_x burners.

The third mechanism of NO_x formation, called fuel NO_x, stems from the evolution and reaction of fuel-bound nitrogen compounds with oxygen. Due to the characteristically low fuel nitrogen content of natural gas, NO_x formation through the fuel NO_x mechanism is insignificant.

Carbon Monoxide -

The rate of CO emissions from boilers depends on the efficiency of natural gas combustion. Improperly tuned boilers and boilers operating at off-design levels decrease combustion efficiency resulting in increased CO emissions. In some cases, the addition of NO_x control systems such as low NO_x burners and flue gas recirculation (FGR) may also reduce combustion efficiency, resulting in higher CO emissions relative to uncontrolled boilers.

Volatile Organic Compounds -

The rate of VOC emissions from boilers and furnaces also depends on combustion efficiency. VOC emissions are minimized by combustion practices that promote high combustion temperatures, long residence times at those temperatures, and turbulent mixing of fuel and combustion air. Trace amounts of VOC species in the natural gas fuel (e.g., formaldehyde and benzene) may also contribute to VOC emissions if they are not completely combusted in the boiler.

Sulfur Oxides -

Emissions of SO_2 from natural gas-fired boilers are low because pipeline quality natural gas typically has sulfur levels of 2,000 grains per million cubic feet. However, sulfur-containing odorants are added to natural gas for detecting leaks, leading to small amounts of SO_2 emissions. Boilers combusting unprocessed natural gas may have higher SO_2 emissions due to higher levels of sulfur in the natural gas. For these units, a sulfur mass balance should be used to determine SO_2 emissions.

Particulate Matter -

Because natural gas is a gaseous fuel, filterable PM emissions are typically low. Particulate matter from natural gas combustion has been estimated to be less than 1 micrometer in size and has filterable and condensable fractions. Particulate matter in natural gas combustion are usually larger molecular weight hydrocarbons that are not fully combusted. Increased PM emissions may result from poor air/fuel mixing or maintenance problems.

Greenhouse Gases -[6-9]

CO_2, CH_4, and N_2O emissions are all produced during natural gas combustion. In properly tuned boilers, nearly all of the fuel carbon (99.9 percent) in natural gas is converted to CO_2 during the combustion process. This conversion is relatively independent of boiler or combustor type. Fuel carbon not converted to CO_2 results in CH_4, CO, and/or VOC emissions and is due to incomplete combustion. Even in boilers operating with poor combustion efficiency, the amount of CH_4, CO, and VOC produced is insignificant compared to CO_2 levels.

Formation of N_2O during the combustion process is affected by two furnace-zone factors. N_2O emissions are minimized when combustion temperatures are kept high (above 1475°F) and excess oxygen is kept to a minimum (less than 1 percent).

Methane emissions are highest during low-temperature combustion or incomplete combustion, such as the start-up or shut-down cycle for boilers. Typically, conditions that favor formation of N_2O also favor emissions of methane.

1.4.4 Controls[4,10]

NO_x Controls -

Currently, the two most prevalent combustion control techniques used to reduce NO_x emissions from natural gas-fired boilers are flue gas recirculation (FGR) and low NO_x burners. In an FGR system, a portion of the flue gas is recycled from the stack to the burner windbox. Upon entering the windbox, the recirculated gas is mixed with combustion air prior to being fed to the burner. The recycled flue gas consists of combustion products which act as inerts during combustion of the fuel/air mixture. The FGR system reduces NO_x emissions by two mechanisms. Primarily, the recirculated gas acts as a dilutent to reduce combustion temperatures, thus suppressing the thermal NO_x mechanism. To a lesser extent, FGR also reduces NO_x formation by lowering the oxygen concentration in the primary flame zone. The amount of recirculated flue gas is a key operating parameter influencing NO_x emission rates for these systems. An FGR system is normally used in combination with specially designed low NO_x burners capable of sustaining a stable flame with the increased inert gas flow resulting from the use of FGR. When low NO_x burners and FGR are used in combination, these techniques are capable of reducing NO_x emissions by 60 to 90 percent.

Low NO_x burners reduce NO_x by accomplishing the combustion process in stages. Staging partially delays the combustion process, resulting in a cooler flame which suppresses thermal NO_x formation. The two most common types of low NO_x burners being applied to natural gas-fired boilers are staged air burners and staged fuel burners. NO_x emission reductions of 40 to 85 percent (relative to uncontrolled emission levels) have been observed with low NO_x burners.

Other combustion control techniques used to reduce NO_x emissions include staged combustion and gas reburning. In staged combustion (e.g., burners-out-of-service and overfire air), the degree of staging is a key operating parameter influencing NO_x emission rates. Gas reburning is similar to the use of overfire in the use of combustion staging. However, gas reburning injects additional amounts of natural gas in the upper furnace, just before the overfire air ports, to provide increased reduction of NO_x to NO_2.

Two postcombustion technologies that may be applied to natural gas-fired boilers to reduce NO_x emissions are selective noncatalytic reduction (SNCR) and selective catalytic reduction (SCR). The SNCR system injects ammonia (NH_3) or urea into combustion flue gases (in a specific temperature zone) to reduce NO_x emission. The Alternative Control Techniques (ACT) document for NO_x emissions from utility boilers, maximum SNCR performance was estimated to range from 25 to 40 percent for natural gas-fired boilers.[12] Performance data available from several natural gas fired utility boilers with SNCR show a 24 percent reduction in NO_x for applications on wall-fired boilers and a 13 percent reduction in

NO_x for applications on tangential-fired boilers.[11] In many situations, a boiler may have an SNCR system installed to trim NO_x emissions to meet permitted levels. In these cases, the SNCR system may not be operated to achieve maximum NO_x reduction. The SCR system involves injecting NH_3 into the flue gas in the presence of a catalyst to reduce NO_x emissions. No data were available on SCR performance on natural gas fired boilers at the time of this publication. However, the ACT Document for utility boilers estimates NO_x reduction efficiencies for SCR control ranging from 80 to 90 percent.[12]

Emission factors for natural gas combustion in boilers and furnaces are presented in Tables 1.4-1, 1.4-2, 1.4-3, and 1.4-4.[11] Tables in this section present emission factors on a volume basis (lb/10^6 scf). To convert to an energy basis (lb/MMBtu), divide by a heating value of 1,020 MMBtu/10^6 scf. For the purposes of developing emission factors, natural gas combustors have been organized into three general categories: large wall-fired boilers with greater than 100 MMBtu/hr of heat input, boilers and residential furnaces with less than 100 MMBtu/hr of heat input, and tangential-fired boilers. Boilers within these categories share the same general design and operating characteristics and hence have similar emission characteristics when combusting natural gas.

Emission factors are rated from A to E to provide the user with an indication of how "good" the factor is, with "A" being excellent and "E" being poor. The criteria that are used to determine a rating for an emission factor can be found in the Emission Factor Documentation for AP-42 Section 1.4 and in the introduction to the AP-42 document.

1.4.5 Updates Since the Fifth Edition

The Fifth Edition was released in January 1995. Revisions to this section are summarized below. For further detail, consult the Emission Factor Documentation for this section. These and other documents can be found on the Emission Factor and Inventory Group (EFIG) home page (http://www.epa.gov/ttn/chief).

Supplement D, March 1998

- Text was revised concerning Firing Practices, Emissions, and Controls.
- All emission factors were updated based on 482 data points taken from 151 source tests. Many new emission factors have been added for speciated organic compounds, including hazardous air pollutants.

July 1998 - minor changes

- Footnote D was added to table 1.4-3 to explain why the sum of individual HAP may exceed VOC or TOC, the web address was updated, and the references were reordered.

Table 1.4-1. EMISSION FACTORS FOR NITROGEN OXIDES (NO_x) AND CARBON MONOXIDE (CO) FROM NATURAL GAS COMBUSTION[a]

Combustor Type (MMBtu/hr Heat Input) [SCC]	NO_x[b]		CO	
	Emission Factor ($lb/10^6$ scf)	Emission Factor Rating	Emission Factor ($lb/10^6$ scf)	Emission Factor Rating
Large Wall-Fired Boilers (>100) [1-01-006-01, 1-02-006-01, 1-03-006-01]				
Uncontrolled (Pre-NSPS)[c]	280	A	84	B
Uncontrolled (Post-NSPS)[c]	190	A	84	B
Controlled - Low NO_x burners	140	A	84	B
Controlled - Flue gas recirculation	100	D	84	B
Small Boilers (<100) [1-01-006-02, 1-02-006-02, 1-03-006-02, 1-03-006-03]				
Uncontrolled	100	B	84	B
Controlled - Low NO_x burners	50	D	84	B
Controlled - Low NO_x burners/Flue gas recirculation	32	C	84	B
Tangential-Fired Boilers (All Sizes) [1-01-006-04]				
Uncontrolled	170	A	24	C
Controlled - Flue gas recirculation	76	D	98	D
Residential Furnaces (<0.3) [No SCC]				
Uncontrolled	94	B	40	B

[a] Reference 11. Units are in pounds of pollutant per million standard cubic feet of natural gas fired. To convert from $lb/10^6$ scf to $kg/10^6$ m^3, multiply by 16. Emission factors are based on an average natural gas higher heating value of 1,020 Btu/scf. To convert from $lb/10^6$ scf to lb/MMBtu, divide by 1,020. The emission factors in this table may be converted to other natural gas heating values by multiplying the given emission factor by the ratio of the specified heating value to this average heating value. SCC = Source Classification Code. ND = no data. NA = not applicable.

[b] Expressed as NO_2. For large and small wall fired boilers with SNCR control, apply a 24 percent reduction to the appropriate NO_X emission factor. For tangential-fired boilers with SNCR control, apply a 13 percent reduction to the appropriate NO_X emission factor.

[c] NSPS=New Source Performance Standard as defined in 40 CFR 60 Subparts D and Db. Post-NSPS units are boilers with greater than 250 MMBtu/hr of heat input that commenced construction modification, or reconstruction after August 17, 1971, and units with heat input capacities between 100 and 250 MMBtu/hr that commenced construction modification, or reconstruction after June 19, 1984.

TABLE 1.4-2. EMISSION FACTORS FOR CRITERIA POLLUTANTS AND GREENHOUSE GASES FROM NATURAL GAS COMBUSTION[a]

Pollutant	Emission Factor ($lb/10^6$ scf)	Emission Factor Rating
CO_2[b]	120,000	A
Lead	0.0005	D
N_2O (Uncontrolled)	2.2	E
N_2O (Controlled-low-NO_X burner)	0.64	E
PM (Total)[c]	7.6	D
PM (Condensable)[c]	5.7	D
PM (Filterable)[c]	1.9	B
SO_2[d]	0.6	A
TOC	11	B
Methane	2.3	B
VOC	5.5	C

[a] Reference 11. Units are in pounds of pollutant per million standard cubic feet of natural gas fired. Data are for all natural gas combustion sources. To convert from $lb/10^6$ scf to $kg/10^6$ m^3, multiply by 16. To convert from $lb/10^6$ scf to 1b/MMBtu, divide by 1,020. The emission factors in this table may be converted to other natural gas heating values by multiplying the given emission factor by the ratio of the specified heating value to this average heating value. TOC = Total Organic Compounds. VOC = Volatile Organic Compounds.

[b] Based on approximately 100% conversion of fuel carbon to CO_2. $CO_2[lb/10^6 scf] = (3.67)(CON)(C)(D)$, where CON = fractional conversion of fuel carbon to CO_2, C = carbon content of fuel by weight (0.76), and D = density of fuel, $4.2x10^4$ $lb/10^6$ scf.

[c] All PM (total, condensible, and filterable) is assumed to be less than 1.0 micrometer in diameter. Therefore, the PM emission factors presented here may be used to estimate PM_{10}, $PM_{2.5}$ or PM_1 emissions. Total PM is the sum of the filterable PM and condensible PM. Condensible PM is the particulate matter collected using EPA Method 202 (or equivalent). Filterable PM is the particulate matter collected on, or prior to, the filter of an EPA Method 5 (or equivalent) sampling train.

[d] Based on 100% conversion of fuel sulfur to SO_2. Assumes sulfur content is natural gas of 2,000 grains/10^6 scf. The SO_2 emission factor in this table can be converted to other natural gas sulfur contents by multiplying the SO_2 emission factor by the ratio of the site-specific sulfur content (grains/10^6 scf) to 2,000 grains/10^6 scf.

TABLE 1.4-3. EMISSION FACTORS FOR SPECIATED ORGANIC COMPOUNDS FROM NATURAL GAS COMBUSTION[a]

CAS No.	Pollutant	Emission Factor ($lb/10^6$ scf)	Emission Factor Rating
91-57-6	2-Methylnaphthalene[b, c]	2.4E-05	D
56-49-5	3-Methylchloranthrene[b, c]	<1.8E-06	E
	7,12-Dimethylbenz(a)anthracene[b,c]	<1.6E-05	E
83-32-9	Acenaphthene[b,c]	<1.8E-06	E
203-96-8	Acenaphthylene[b,c]	<1.8E-06	E
120-12-7	Anthracene[b,c]	<2.4E-06	E
56-55-3	Benz(a)anthracene[b,c]	<1.8E-06	E
71-43-2	Benzene[b]	2.1E-03	B
50-32-8	Benzo(a)pyrene[b,c]	<1.2E-06	E
205-99-2	Benzo(b)fluoranthene[b,c]	<1.8E-06	E
191-24-2	Benzo(g,h,i)perylene[b,c]	<1.2E-06	E
207-08-9	Benzo(k)fluoranthene[b,c]	<1.8E-06	E
106-97-8	Butane	2.1E+00	E
218-01-9	Chrysene[b,c]	<1.8E-06	E
53-70-3	Dibenzo(a,h)anthracene[b,c]	<1.2E-06	E
25321-22-6	Dichlorobenzene[b]	1.2E-03	E
74-84-0	Ethane	3.1E+00	E
206-44-0	Fluoranthene[b,c]	3.0E-06	E
86-73-7	Fluorene[b,c]	2.8E-06	E
50-00-0	Formaldehyde[b]	7.5E-02	B
110-54-3	Hexane[b]	1.8E+00	E
193-39-5	Indeno(1,2,3-cd)pyrene[b,c]	<1.8E-06	E
91-20-3	Naphthalene[b]	6.1E-04	E
109-66-0	Pentane	2.6E+00	E
85-01-8	Phenanathrene[b,c]	1.7E-05	D
74-98-6	Propane	1.6E+00	E

TABLE 1.4-3. EMISSION FACTORS FOR SPECIATED ORGANIC COMPOUNDS FROM NATURAL GAS COMBUSTION (Continued)

CAS No.	Pollutant	Emission Factor ($lb/10^6$ scf)	Emission Factor Rating
129-00-0	Pyrene[b, c]	5.0E-06	E
108-88-3	Toluene[b]	3.4E-03	C

[a] Reference 11. Units are in pounds of pollutant per million standard cubic feet of natural gas fired. Data are for all natural gas combustion sources. To convert from $lb/10^6$ scf to $kg/10^6$ m^3, multiply by 16. To convert from $1b/10^6$ scf to lb/MMBtu, divide by 1,020. Emission Factors preceeded with a less-than symbol are based on method detection limits.

[b] Hazardous Air Pollutant (HAP) as defined by Section 112(b) of the Clean Air Act.

[c] HAP because it is Polycyclic Organic Matter (POM). POM is a HAP as defined by Section 112(b) of the Clean Air Act.

[d] The sum of individual organic compounds may exceed the VOC and TOC emission factors due to differences in test methods and the availability of test data for each pollutant.

TABLE 1.4-4. EMISSION FACTORS FOR METALS FROM NATURAL GAS COMBUSTION[a]

CAS No.	Pollutant	Emission Factor ($lb/10^6$ scf)	Emission Factor Rating
7440-38-2	Arsenic[b]	2.0E-04	E
7440-39-3	Barium	4.4E-03	D
7440-41-7	Beryllium[b]	<1.2E-05	E
7440-43-9	Cadmium[b]	1.1E-03	D
7440-47-3	Chromium[b]	1.4E-03	D
7440-48-4	Cobalt[b]	8.4E-05	D
7440-50-8	Copper	8.5E-04	C
7439-96-5	Manganese[b]	3.8E-04	D
7439-97-6	Mercury[b]	2.6E-04	D
7439-98-7	Molybdenum	1.1E-03	D
7440-02-0	Nickel[b]	2.1E-03	C
7782-49-2	Selenium[b]	<2.4E-05	E
7440-62-2	Vanadium	2.3E-03	D
7440-66-6	Zinc	2.9E-02	E

[a] Reference 11. Units are in pounds of pollutant per million standard cubic feet of natural gas fired. Data are for all natural gas combustion sources. Emission factors preceeded by a less-than symbol are based on method detection limits. To convert from $lb/10^6$ scf to $kg/10^6$ m^3, multiply by l6. To convert from $lb/10^6$ scf to 1b/MMBtu, divide by 1,020.

[b] Hazardous Air Pollutant as defined by Section 112(b) of the Clean Air Act.

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