Chapter 6 Overview of Sources of the Air Pollutants

6.1 Stationary Combustion Facilities

6.1.1 Introduction

The combustion is the rapid oxidation reaction accompanied with light and heat. The combustibles of which the heat generated could be utilized economically is called fuel. It is classified into solid fuels such as coal and coke, liquid fuels such as heavy oil and light oil, and gas fuels such as natural gas and oil gas. The stationary combustion facilities are the major source of air pollutants besides automobiles. When 12 kg of carbon burns, 22.4 m_N^3 of carbon dioxide will be produced as shown in Eq. (1), and 4 kg of hydrogen will generate 2×22.4 m_N^3 of water vapor as shown in Eq. (2). In this way, there are theoretical relationships between the amount of element composing fuels and the amount of air required for its combustion or the amount of exhaust gas produced from combustion. The amount of air theoretically required for the complete combustion is called the theoretical amount of air, and that of exhaust gas the theoretical amount of combustion gas.

$$C + O_2 = CO_2 \qquad \cdots\cdots (1)$$

$$2\,H_2 + O_2 = 2\,H_2O \qquad \cdots\cdots (2)$$

As an example, the theoretical amount of air and the theoretical amount of combustion gas will be calculated when 1 kg of heavy oil composed of 87% carbon, 12% hydrogen and 1% sulfur is burnt. Oxygen required to burn 12 kg of carbon is 22.4$m^3{}_N$, and the same volume of exhaust gas is produced by this reaction. Therefore, the volume of oxygen required to burn 0.87 kg of carbon contained in 1 kg of heavy oil is $22.4 \times 0.87/12 = 1.624$ m_N^3 and the same volume of the exhaust gas, that is carbon dioxide, will be produced. Also, 0.12 kg of hydrogen is contained in the heavy oil and the volume of oxygen required for its combustion is $22.4 \times 0.12/4 = 0.672$ m_N^3 and twice that volume, 1.344 m_N^3, of water vapor is produced. As the molecular weight of sulfur is 32, 32 kg of sulfur will react with 22.4 m_N^3 of oxygen, and the same volume of sulfur dioxide is generated. Accordingly, the volume of oxygen required to burn 0.01 kg of sulfur contained in the heavy oil is $22.4 \times 0.01/32 = 0.007$ m_N^3 and the same volume of sulfur dioxide will be produced. Thus, the volume of oxygen required for the combustion of heavy oil becomes to $1.624 + 0.672 + 0.007 = 2.303$ m_N^3. If we convert it to the amount of air, the theoretical amount of air of $2.303 \times 1/0.21 = 10.97 \fallingdotseq 11$ m_N^3 is obtained by assuming the content of oxygen in the air as 21%. Also, in addition to the volume of reaction product gases, that is $1.624 + 1.344 + 0.007 = 2.975$ m_N^3, the volume of nitrogen, $2.303 \times 0.79/0.21 = 8.66$ m_N^3, which will not participate in the combustion reaction, should be added to obtain the volume of the theoretical burnt gas, and it is calculated as $2.975 + 8.66 = 11.635$ m_N^3. This is the wet theoretical amount of combustion gas containing water vapor, and the volume of dry theoretical amount of combustion gas is obtained by subtracting the amount of water vapor from the last value as $11.635 - 1.344 = 10.291$ m_N^3. Generally, the combustion requires a larger amount of air than the theoretical amount of air, and the ratio between actually used air and the theoretical air amount of is called the air fuel ratio. The combustion will be more ideal as this ratio is as near as 1. Incidentally, the theoretical amount of air is, for instance, about 10-13 m_N^3/kg for fuel oil, and the combustion of 1 dl of fuel oil requires about 1-1.3 m_N^3 of air.

The calorific value of fuel is different for each fuel, and it is 4,500-8,000 Kcal/Kg for coal and 11,000-11,500 Kcal/Kg for kerosene or gasoline. In order to realize combustion, there must be a combustion field where fuels and air are supplied and mixed with each other and the combustion temperature is maintained. However, the combustion would not proceed with those conditions alone. It will stop unless the heat of combustion and the burnt gas are removed from the combustion field. Thus the combustion furnace has been used, and it utilizes heat and releases exhaust gas through stacks to the atmosphere to cause air pollution problems.

6.1.2 Formation of Major Air Pollutants

(1) Sulfur Oxides [2)]

Sulfur existing in crude oil as organic polymer compounds of sulfur is largely transferred to heavy oil during the oil refinery process and desulfurized by hydrogenation technique. However, some sulfur will remain in heavy oil and oxidized to sulfur dioxide in the flame of combustion facilities. A part of it will oxide to anhydrous sulfuric acid, and both enter into the exhaust gas and will be released in the atmosphere. Also, sulfur exists in coal as sulfides of iron, organic sulfur compounds, or gypsum, and when they burn, the former two will be transformed to sulfur oxides and some will remain in the coal ash.

(2) Soot and Dust [2)]

Inorganic compounds are contained in the coal and transformed to ash by combustion, and a part of it will enter in the burnt gas. Particularly, fine flyash generated by the combustion of pulverized coal has been attracting much attention. Small amount of inorganic compounds is also existing in crude oil and transformed to ash when burned. Also, soot and dust will be formed in the process of combustion which causes black smoke which has been attracting people's attention. The smoke includes the soot, which is formed when the combustible gas component generated by the combustion process burns in gas phase, and the carbon remained cenosphere, which is a carbonaceous material formed by condensation polymerization reaction of thermally decomposed fuel droplets in the furnace. The soot is spherical in shape with diameter of 0.02-0.05 μ m and very fine, and the cenosphere is also almost spherical in shape with 10-300 μ m diameter, but has bumpy surfaces. The chemical composition of soot and dust is generally considered to be carbonaceous material, and actually it is an aggregate of hydrocarbon of mostly around $C_{40}H_{16}$, and contains many condensed multi-cyclichydro carbons. The mechanism of soot and dust formation is very complex, and they are considered to be formed through processes such as the dehydration of hydrocarbons, thermal decomposition, polymerization, unsaturated bonds, and formation of aromatic rings in case of gas combustion. In the case of liquid spray combustion, tar is formed in the oil droplet by thermal decomposition. Then high order hydrocarbons are formed which finally forms the carbon remained dust by releasing gases.

(3) Carbon Monoxide

Carbon monoxide is generated by incomplete combustion of fuels, and could be possibly released from industries such as gas work, steel mill and carbonyl compounds manufacturing.

(4) Nitrogen compounds [2]

Air is a gas mixture of one volume of oxygen and four volumes of nitrogen. In the combustion reaction, those two elements react mainly in the flame to form nitrogen oxides which are attracting attention as the air pollutant. Also, nitrogen containing compounds such as aniline and quinoline are existing in the fuel, and become as a cause of the generation of nitrogen oxides. Incidentally, the formation rate of nitrogen oxides is faster for the latter reaction (fuel NOx) than for the former reaction (thermal NOx).

Furthermore, nitrous oxide (N_2O) which, like fluorocarbon, will destroy ozone layer in the stratosphere is generated from facilities such as fluidized bed coal boilers and sludge incinerator where fuels with high nitrogen content is burned at low temperature.

(5) Dioxins

The formation mechanism of dioxins in the combustion process is complex, and is not understood fully. The release of dioxins from incinerator of domestic and industrial wastes is becoming a big problem.

(6) Other Pollutants

The kind of air pollutants and their volume formed in the combustion process are different with different fuels, facilities, or combustion equipment. In addition to pollutants described above, various air pollutants including heavy metals and multi-cyclic aromatic hydrocarbons can be released from the combustion furnaces such as coal or incinerator and glass furnace, which introduce industrial materials into the field of combustion.

6.1.3 Thermal Power Station [3]

(1) Overview

The thermal power station is the important facility to support our civilization, but is also causing air pollution. The technology of thermal power generation includes the steam power station which makes electricity by rotating the electrical generator via steam turbines that are driven by high pressure steam generated by the boiler, the electric generation which uses internal combustion engines, and that which combines the former two technologies. Fig.6.1.1 shows an example of the system of steam power station, which is composed of internal combustion engine, combustion system, steam system, water supply system, and electrical system [3]. The sources of air pollutant are the former two systems which use coal, oil and natural gas as a fuel.

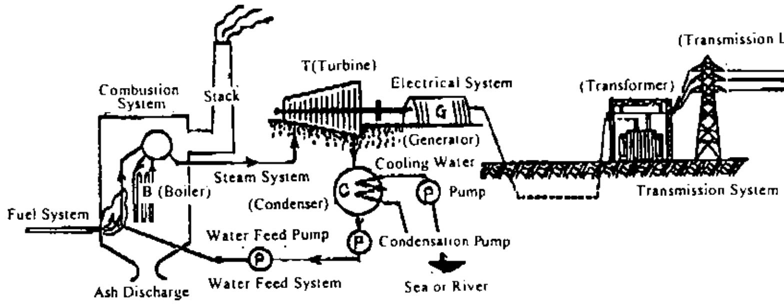

Fig.6.1.1 An Example System of Steam Power Station

(2) Steam Power Station

Combustion Equipment and Formation Mechanisms of Air Pollutants

The stoker-type combustion equipment is used which delivers coal to the furnace core by moval grates and burns it there. In the stoker combustion, the coal is heated and its combustible components are evaporated and ignited to heat it further, and the coal burns as it gets softer. Therefore, the surface in contact with air is small and much soot is generated, and also the combustion efficiency is low. As a result, the pulverized coal combustion is devised to make the contact area of fuel and air larger and to increase the combustion efficiency by enhancing their mixing. In this method, 70-80% of the coal is crushed to a fine powder of about 200 mesh pass, and then transferred by air to the burner. It is applied in the recent power stations which burns only coal. Incidentally, the type of pulverized coal burner includes the injection burner which injects the mixture of pulverized coal and in the center and introduces the secondary air in parallel around it, and the swirl burner which mixes and burns the pulverized coal, mixed by central rotation blades with primary air, with secondary air introduced around it. In the pulverized coal combustion facility, a part of ash enters into an ash collector as slug. Inorganic materials contained in coal is melted and evaporated in the flame, and then is solidified when they exit from the flame as temperature drops. In this process, they are transformed into very fine flyash as surface areas tend to be maximized and uniform pressure is exerted. The major component of flyash is silica, and the particle size of this fine glassy powder is 0.1-100 μ m with average diameter of about 15 μ m. Its content in the exhaust gas is about 15 g/m_N^3. Presently, more than about 99% of flyash is recovered by the electrostatic precipitator. In the combustion of heavy oil, it is warmed to the temperature of 85-105℃ from about 35℃ in the storage tank to reduce viscosity, so that the spraying power required for delivering it to the burner could be reduced. The burner is designed to completely mix air and fuel, which it makes into a spray of heavy oil allowing a larger area of fuel and air to come into contact and to obtain complete combustion. The type of heavy oil burner includes; the pressure injected burner, in which either a spray is formed by pressurizing the heavy oil and injecting it through small holes to give high speed swirling motion, or the heavy oil is injected and burned as swirling motion is applied; the steam spray burner in which heavy oil is sprayed by a jet of steam; the air injection burner in which compressed air, instead of steam, is used for injecting heavy oil through a spiral passage to make a rotating spray; and the injection rotation burner in which a thin layer of heavy oil is made by injecting it into a cylindrical cup rotated at high speed and fine particles of heavy oil are made. Among those, the pressure injected burner and the steam injection burner are commonly used in large capacity boilers. The type of thermal power station includes the heavy oil burning station that burns only heavy oil, the station that burns kerosene, naphtha, etc. to reduce air pollution, the one that burns the mixture of heavy oil and pulverized coal, and the one that burns either heavy oil or pulverized oil or COM (Coal Oil Mixture), which is a suspension of pulverized coal, mixed at equal calorific value, in the heavy oil. Also, the station that burns imported natural gas is increasing since the technology of sea transportation of liquefied natural gas by tanker has been developed. The number of natural gas thermal power station is increasing because the amount of air pollutants contained in its burnt gas is smaller. Natural gas is burned in the gas burner, and its combustion efficiency is high because its mixing with air is better.

Boiler [3)]

The boiler is a facility to generate high pressure steam for driving the turbine, and is an important facility in the steam power station along with the generator and the turbine. Fig.6.1.2 is a schematic of the boiler, and it has an overhead drum that contains water delivered from the water supply system. Many water tubes, drawn from this drum, are arranged on the front and rear surface and a part of the side surface of the fire furnace. These tubes absorb thermal radiation generated by the combustion. The feed water to the boiler is heated by the combustion burnt gas in the economizer, and enters into the boiler drum. From here, it flows down through the descending water tube to absorb heat, and returns to the drum, as its temperature rises, through the water tubes in a state of mixed steam and saturated water. Then, the water is removed by a steam separator in the drum, and only steam is delivered to the turbine after heated by a super heater.

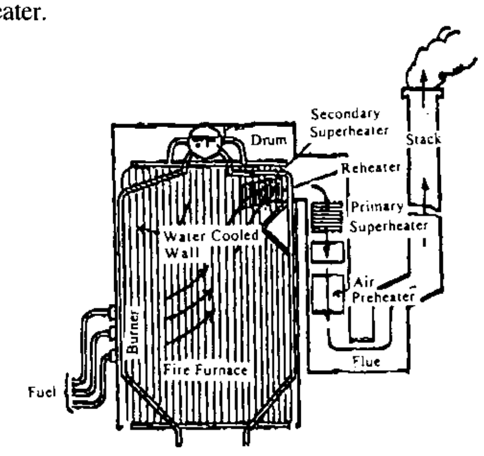

Fig.6.1.2 Schematic Diagram of Boiler

Steam Turbine [3)]

The steam turbine corresponds to a hydraulic turbine in the hydraulic power plant. High pressure, high temperature steam generated in the boiler is introduced in the turbine blade to obtain power by its high speed rotation. Depending on the working mechanism, it is classified into an impulse turbine and a reaction turbine. Generally, the former is suitable for high pressure steam and the latter for low pressure steam, and therefore they are used in combination with each other. Furthermore, when classified by the use of steam, it is divided into a condensation turbine, a back pressure turbine, a extraction turbine, etc. In the condensation turbine, the steam discharged through turbine is entirely introduced into a condenser to reduce the pressure to near vacuum state and to make the pressure head large so that the heat of steam could be used efficiently only in the turbine system. In the back pressure turbine, the discharged steam is used for process steam without reducing the pressure so much. In the extraction turbine, the steam for factory process is taken out from the middle of the steam path.

Generation Status of Air Pollutants [4)]

The concentration of air pollutants exhaust from the stack of steam power station is dependent on the type of fuel, and the amount discharged depends on the amount of fuel consumed or power generated.

Most of the sulfur oxides (more than 95%) is released in the atmosphere as sulfur dioxide, and its amount can be calculated from the amount of fuel used and the content of sulfur in the fuel. Further, its concentration in the exhaust gas can be calculated from the composition of fuel and the condition of combustion, or air fuel ratio (excess air ratio). Also, in the case of pulverized coal combustion, the concentration of solid particles, such as soot and dust, corresponds to that of flyash, and is about 15 g/m_N^3 as mentioned previously, although it is quite variant. In the heavy oil combustion, the solid particle generated is mostly soot, and there are data that its concentration is 0.02-0.038 g/m_N^3 for the combustion of Class C heavy oil [4)].

Accordingly, in the case of mixed combustion of coal and heavy oil, the concentration of solid particle increases roughly in proportion to the mixture ratio of coal. In the case of natural gas combustion, solid particles are scarcely found in the exhaust gas. As for the nitrogen oxides, they are generated and discharged mostly as a form of nitrogen monoxide, but some nitrogen dioxide is also discharged. Therefore, it is a common practice to obtain their combined amount and to convert it into the amount of nitrogen dioxide, with expressing the amount in mass and the concentration in volumetric ratio (ppm).

Considering the formation mechanism of those pollutants, the discharged amount is dependent on the fuel and facility. Particularly, more fuel NOx, which originates from organic nitrogen compounds contained in the fuel, is generated in the coal combustion. Furthermore, the concentration of thermal NOx, which is formed by the oxidation of nitrogen contained in the air, increases as the flame temperature increases. Accordingly, the concentration of thermal NOx increases in the steam power station in which the air for combustion is heated by the air heater. As a result, the concentration of nitrogen oxides tends to be higher in the coal combustion, and then in the oil combustion, while the lowest value is found in the gas combustion. For example, there are data that, in the steam power station, its concentration is 545 ppm for the coal combustion when the oxygen in exhaust gas is converted to 0%, similarly 122-372 ppm for the oil combustion, and 173-672 ppm for the Class C heavy oil combustion [4)].

(3) Other Thermal Power Station

Other types of thermal power station now in operation include, the station operated by diesel engine or gas turbine and the one that operated by the combined system which drives the generator by a gas turbine and a steam turbine, which uses the exhaust of the former as the boiler's heat source, placed in tandem. Particularly, the combined power system is getting much attention as its thermal efficiency reaches to more than 60% even if the energy is used mostly for electric power generation.

Also, the MHD power generation, which generates electricity by flowing high temperature combustion gas plasma through magnetic field, is promising as a large scale direct power generation technology of high thermal efficiency, and its development is attracting much attention.