

OBJECTIVES**Terminal Learning Objective**

At the end of this chapter, the student will understand the basics of oxidation systems.

Enabling Learning Objectives

- 6.1 Distinguish among the various types of oxidation systems.
- 6.2 Identify the principles of operation for oxidation systems.
- 6.3 Determine the factors that influence the capability and sizing of an oxidation system.
- 6.4 Identify the operating parameters that need to be evaluated in an oxidation system.

Oxidation

Oxidation systems are used to destroy organic compounds classified as volatile organic compounds (VOCs) and/or air toxic compounds. At sufficiently high temperatures and adequate residence times, essentially all organic compounds can be oxidized to form carbon dioxide and water vapor. The oxidation products of organic compounds containing chlorine, fluorine, or sulfur are HCl, HF, Cl₂ or SO₂.

Oxidation air pollution control systems are based on mature technology that has been used successfully for more than 40 years. However, there have been a number of recent developments that have increased the types of commercially-available oxidizer systems. Oxidizer systems for VOC and air toxic compound control can be categorized into two main groups and a number of subgroups:

High-Temperature, Gas-Phase Oxidation Processes

- Recuperative thermal oxidizers
- Regenerative thermal oxidizers
- Process boilers used for thermal oxidation
- Flares used for thermal oxidation

Catalytic Oxidation Processes

- Recuperative catalytic oxidizers
- Regenerative catalytic oxidizers

High-temperature, gas-phase oxidation processes use temperatures in the range of 1,000°F to 2,000°F (540°C to 1,100°C). Thermal oxidizers and process boilers handle gas streams with inlet organic vapor concentrations less than 25% to 50% of their Lower Explosive Limit (LEL). (Refer to Chapter 2 for discussion on explosive limits.) Flares are used for the combustion of organic vapor waste streams that have concentrations greater than 100% of the Upper Explosive Limit (UEL). Catalytic oxidation processes operate at temperatures ranging from

400°F to 1,000°F (200°C to 540°C) and are designed for gases containing less than 25% of the LEL.

The terms *recuperator* and *regenerator* refer to the type of heat exchanger used to increase system efficiency. A recuperator is a tubular or plate heat exchanger where heat is transferred through the metal surface. A regenerator uses a set of refractory packed beds that store heat. Both types reduce the amount of supplement fuel needed to oxidize the contaminants in the combustion chamber. With sufficiently high organic concentration, the energy released during oxidation may be sufficient to maintain the necessary temperature without the addition of supplemental fuel.

6.1 Types and Components of Oxidizer Systems

High-Temperature, Gas-Phase Oxidation Systems

This section describes the characteristics of the four main categories of high-temperature, gas-phase oxidation processes.

- Recuperative thermal oxidizers
- Regenerative thermal oxidizers
- Boilers
- Flares

The emphasis is on the design and performance characteristics that determine their applicability to various types of air pollution sources.

All four of these process types use very high gas temperatures to oxidize the organic pollutants to carbon dioxide, water, and other combustion products. These processes usually operate at gas temperatures ranging from 1,000°F to more than 2,000°F (540°C to 1,100°C), and should be at least 200°F to 300°F (110°C to 170°C) above the auto-ignition temperature of the most difficult-to-oxidize organic compound in the gas stream.¹

A proper oxidizer design is achieved by considering the three “Ts” of combustion—time, temperature, and turbulence. Large residence times, high temperatures, and highly turbulent flow all contribute to the complete destruction of the organic pollutant. Figure 6-1 shows the interplay between time and temperature for a hypothetical compound. With a residence time of 1 sec, 100% destruction can be achieved at a temperature of about 1200°F. However, with a residence time of 0.01 sec, a temperature of about 1500°C is required.

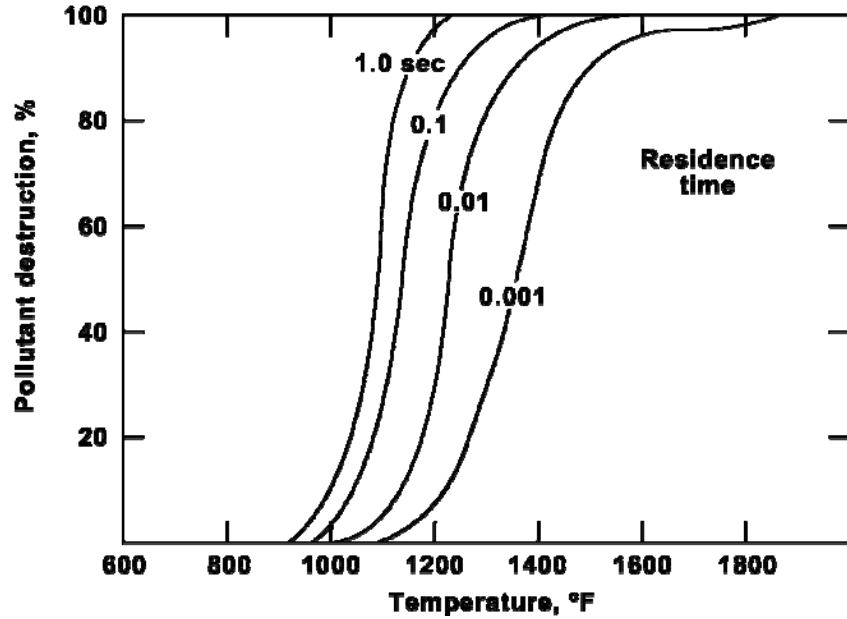


Figure 6-1. The effects of time and temperature on pollutant destruction efficiency.

Turbulent flow is needed to ensure that the oxidizer feed is well-mixed with the products from the supplemental fuel burners and that none of the pollutants are allowed to bypass the zone of maximum temperature. As shown in Figure 6-2, mixing can be promoted by the proper use of baffles within the oxidization chamber.

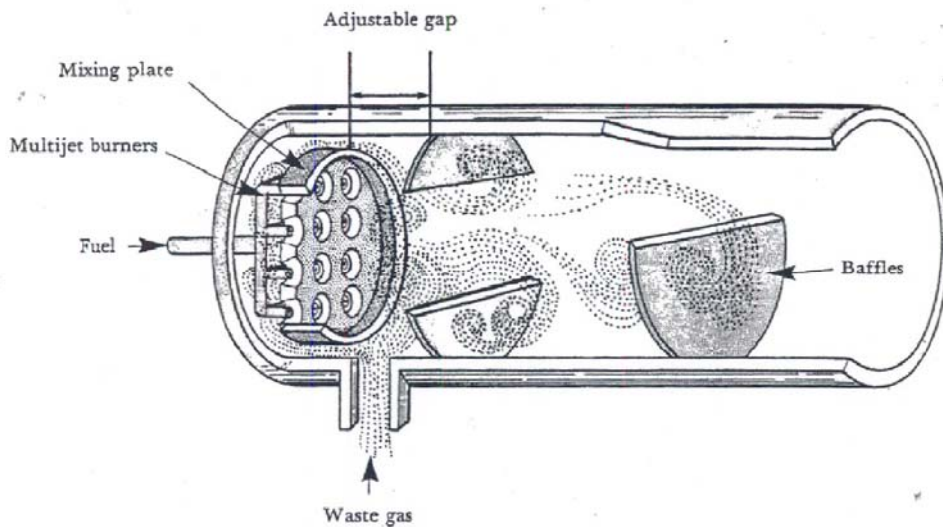


Figure 6-2. Thermal oxidizer using multi-jet burners and baffles to promote mixing.

Recuperative Thermal Oxidizers

A recuperative thermal oxidizer consists of a refractory-lined chamber equipped with one or more gas- or oil-fired burners. As shown in Figure 6-3, the contaminant-laden gas stream is mixed with the hot combustion gases from the burner flame in order to achieve the desired operating temperature. The contaminated gas stream does not necessarily pass through the burner itself.

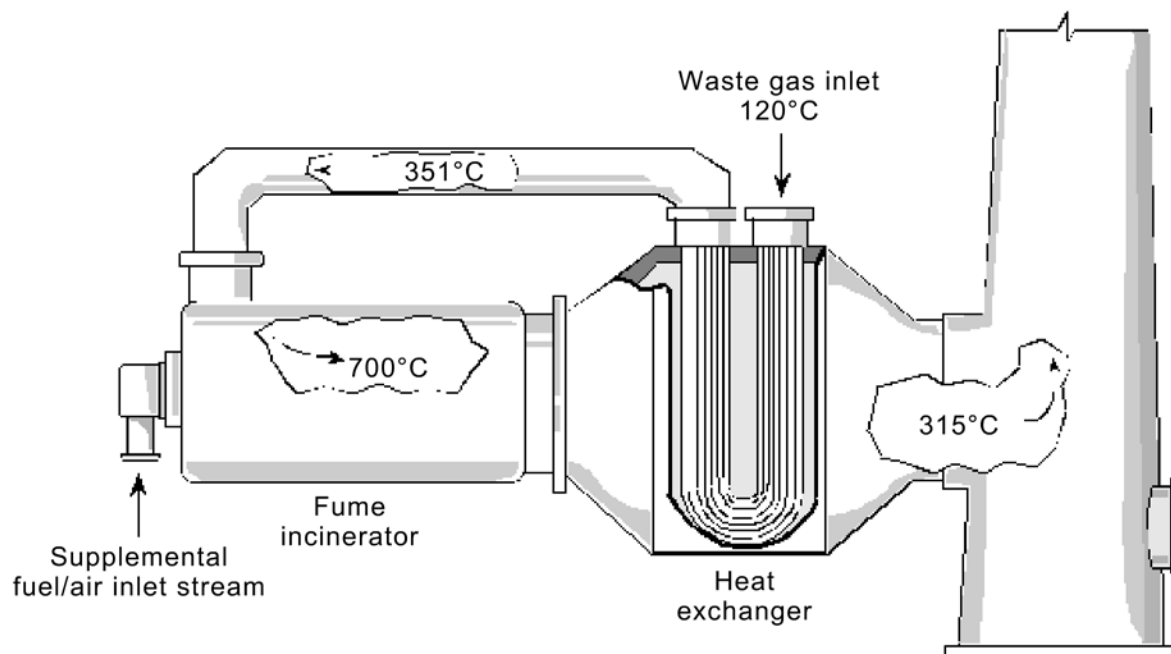


Figure 6-3. Oxidizer equipped with a double-pass recuperative heat exchanger.

The combustion chamber is sized to provide sufficient residence time to complete the oxidation reactions, typically from approximately 0.3 to more than 2 seconds. The time needed for high-efficiency destruction is strongly dependent on the operating temperature and the mixing within the chamber.

The unit depicted in Figure 6-3 includes a recuperative heat exchanger (recuperator) to recover a portion of the sensible heat generated by the combustion of the burner fuel and by the oxidation of the organic vapors in the gas stream. A recuperator is a tubular or plate-type heat exchanger. The hot gas stream passes on one side of the tube bank, and the cold inlet gas stream passes on the other side. Heat recoveries range from approximately 40% to 65% of the total heat released in the combustion chamber. Typical temperatures at key locations in the system are included.

Because of the presence of the recuperative heat exchanger, particulate matter in the inlet gas stream must be minimized to prevent fouling the surface of the tubes and reducing heat-transfer efficiency. Some recuperative units include clean-out ports and access hatches to facilitate cleaning.

Thermal oxidizers are relatively heavy units because of the refractory lining required to protect the metal shell from the high temperatures within the

chamber. Because of their weight, thermal oxidizers are often placed on the ground rather than on roofs or other elevated areas.

A simplified flowchart of a recuperative thermal oxidizer system is shown in Figure 6-4. The instrumentation used to evaluate the performance of the oxidizer includes temperature monitors on the incinerator products (before and after the recuperator) and the solvent-laden gas exiting the recuperator, and the inlet LEL concentration monitor. Recuperative and regenerative thermal oxidizers are usually designed for inlet concentrations less than 25% of the LEL, but in some cases, the oxidizers have been operated with concentrations as high as 50% of the LEL. Because of safety-related LEL limits, the inlet concentrations of thermal oxidizers are usually in the 1,000 to 10,000 ppm range.

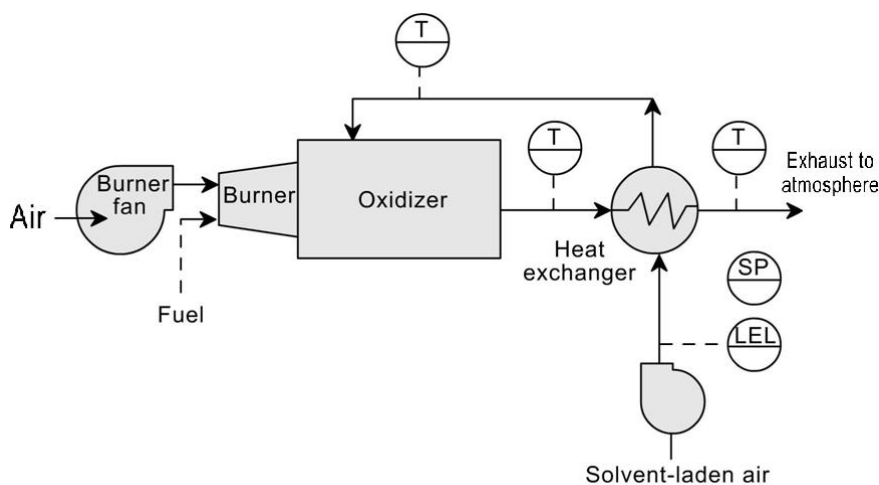


Figure 6-4. Flowchart of a recuperative heat exchanger.

The burner normally operates continuously unless the organic vapor concentration in the inlet gas stream is sufficiently high to maintain the desired temperature without supplemental fuel. The outlet temperature monitor downstream of the heat exchanger is used to shut down the burner (pilot flame remains on) in the event of excessively high gas temperatures.

A burner master controller is used to maintain proper air-fuel ratios. A pilot flame igniter system and a flame scanner system (not shown on Figure 6-2) ensure that the burner operates safely.

These types of oxidizers usually do not have flashback protection devices, because flashback through the gas handling system is not a major safety concern with the low organic vapor concentrations of the inlet gas stream. The LEL monitor on the inlet gas stream is used to activate the atmospheric discharge vent and to shut down the entire process that generates the organic-vapor-containing gas stream if the concentrations exceed the safe level.

The static pressure gauge, while rarely present in recuperative thermal oxidizers, can be used to monitor the gas flow resistance through the recuperator.

Regenerative Thermal Oxidizers

Regenerative thermal oxidizers have heat recovery efficiencies as high as 95%, much higher than recuperative units.² Because of the high inlet gas temperatures created by the heat recovery, burner fuel is required only if the organic vapor concentrations in the gas stream are very low. At moderate-to-high concentrations, the heating value of the organic contaminants is sufficient to maintain the necessary temperatures in the combustion chamber.

High-efficiency heat recovery is achieved by passing the inlet gas stream through a large packed bed containing ceramic packing that has been previously preheated by passing the outlet gases from the combustion chamber through the bed. At least two beds are required, and gas flow dampers are used to switch the inlet and outlet gas streams to the appropriate beds.

Three beds are commonly used in a regenerative system. One of the beds is used to preheat the inlet gas stream, the second is used to transfer the heat of combustion from the treated gas stream, and the third is in a purge cycle. Without a purge cycle, emission spikes would occur as a portion of the untreated gas stream would be released immediately after each flow reversal.²

An example of a commercial system is shown in Figure 6-5. This unit has three parallel beds with an overhead refractory-lined combustion chamber equipped with two gas-fired burners.

Another type of regenerative thermal oxidizer, a “flameless” oxidizer, is shown in Figure 6-6. In this case, the burner is used only for preheating the packed ceramic bed prior to the introduction of organic vapor.³ The contaminated gas stream enters a gas distribution chamber near the bottom of the unit and is mixed with air. The ceramic bed temperature is maintained above the auto-ignition temperature of the most difficult-to-oxidize compound being treated. One of the advantages of this type of combustion system is the low NO_x generation rate due to the limited peak gas temperatures in the packed bed.

Packed-bed (flameless) oxidizer systems are not used for gas streams containing organometallic or organophosphorus compounds, as these contaminants can form particulate matter that accumulates in the packed bed.

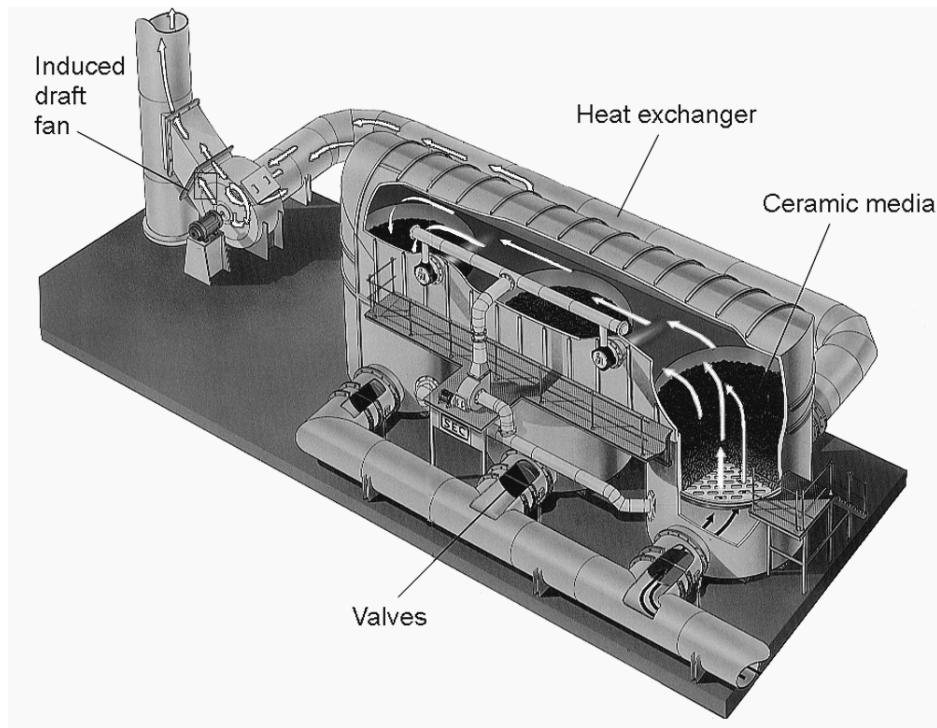


Figure 6-5. Regenerative thermal oxidizer.
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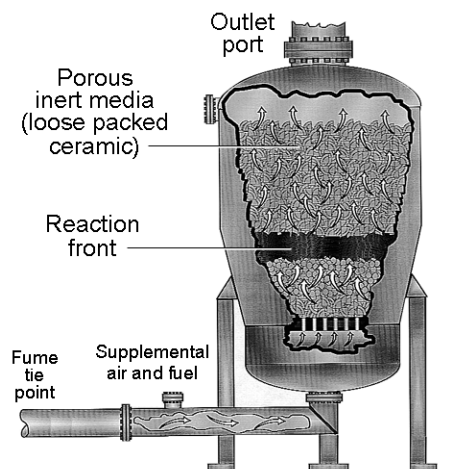


Figure 6-6. Flameless thermal oxidizer.
(Reprinted courtesy of Thermax, Inc., San Jose, CA.)

All of the regenerative units are vulnerable to particulate matter in the inlet gas stream that can plug the packed bed and increase the static pressure drop. Therefore, regenerative units are used only on sources with very low particulate loadings (i.e., < 0.015 gr/ACF) or on sources where it is safe and practical to remove the particulate matter upstream of the oxidizer.

Regardless of the type of thermal oxidizer used, the oxidation of halogenated compounds results in the formation of compounds such as hydrochloric acid and hydrofluoric acid, which are regulated air toxic compounds. Accordingly, it is necessary to include absorbers downstream of the oxidizer in order to reduce the emission of these compounds.

Process Boilers Used for Thermal Oxidation

An alternative to installing a thermal oxidizer is to burn the waste gases in an existing plant or process boiler, thus avoiding the capital cost of new equipment. Process and plant boilers are normally designed to operate with combustion chamber temperatures in excess of 1,800°F (980°C) and with flue gas residence times in excess of 1 to 2 seconds, conditions similar to those of thermal oxidizers.

The waste gas stream is usually injected into the boiler at an elevation close to the main burners and overfire air nozzles (Figure 6-7). In some cases, the waste gas stream may be used as part of the combustion air supply for the burners in the boiler. Regardless of the injection location, the temperatures in this area are well above the auto-ignition temperatures of most organic compounds. Oxidation must be completed before the combustion products pass through the furnace area and reach the main heat exchange surfaces (convective superheaters, reheaters, economizers) where the gas temperature drops quickly.

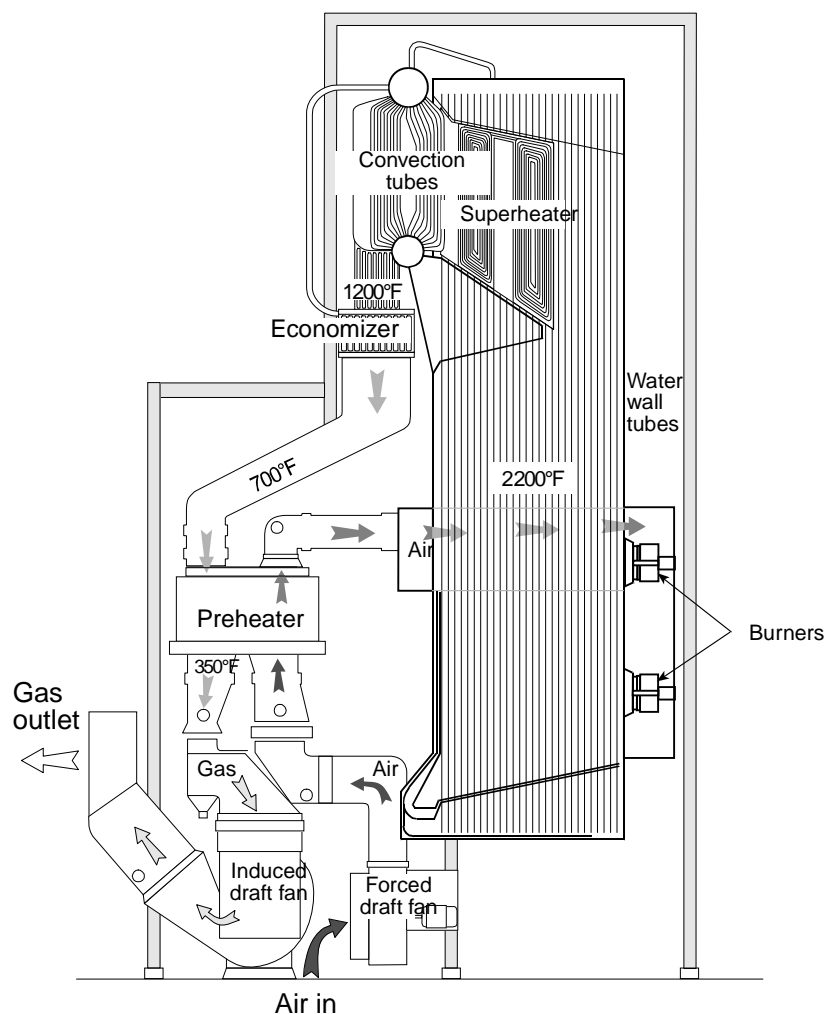


Figure 6-7. Oil-fired boiler.

The flow rate of the organic-contaminated stream must not overwhelm the gas-handling capability of the boiler-induced draft fans. The volume of combustion gas generated by the oxidation of the waste gas stream should be only a small fraction of the total combustion gas flow rate of the unit to avoid exceeding the allowable gas velocities and gas temperatures throughout the boiler.

The combustion of the organic vapor in the waste stream must not create high-temperature zones in the furnace areas of boilers with temperature-sensitive selective noncatalytic reduction systems (SNCR) for NO_x control. SNCR systems are discussed in a later chapter.

The operating schedules of the boiler and the process generating the gas stream are one of the main constraints to using a boiler for organic vapor oxidation. The boiler must operate within a normal load range of approximately 40% to 100% of design load in order to have the necessary temperatures for organic vapor combustion. If the boiler firing rate varies greatly, it may be

necessary to operate auxiliary burners in the boiler to maintain the temperatures necessary for oxidization.

Another factor limiting the usefulness of process boilers is the long ducts often needed to transport the organic--containing gas stream from the process area to the boiler area. Ducts can be expensive, and some of the organic vapor may condense and accumulate in the ducts.

Flares Used for Thermal Oxidation

Flaring is used for the destruction of intermittent or emergency emissions of combustible gases from industrial sources that otherwise would create safety and health hazards at or near the plant. As such, they are more properly classified as safety devices instead of pollution-control devices. Flares are used mainly at oil refineries and chemical plants that handle large volumes of combustible gases, and can have organic compound destruction efficiencies exceeding 98%.⁴

Flares, which are simply burners designed to handle varying rates of fuel while burning smokelessly, may be elevated or at ground level. Flares are elevated to eliminate potential fire hazards at ground level. Ground-level flares must be completely enclosed to conceal the flame. Either type of flare must be capable of operating over a wide range of waste gas flow rates in order to handle all plant emergencies. The range of waste gas flows within which a flare can operate and still burn efficiently is referred to as the *turndown ratio*. Flares are expected to handle turndown ratios of up to 1,000:1, while most industrial boilers seldom handle more than a 10:1 turndown ratio.

Although the flares are designed to eliminate waste gas stream disposal problems, they can present safety and operational problems of their own.

- **Thermal radiation.** Heat given off to the surrounding area may be unacceptable.
- **Light.** Luminescence from the flame may be a nuisance if the plant is located in an urban area.
- **Noise.** Jet venturis are used for mixing at the flare tip. They can cause excessive noise levels in nearby neighborhoods.
- **Smoke.** Incomplete combustion can result in toxic or obnoxious emissions.
- **Energy consumption.** Flares waste energy because of (1) the need to maintain a constant pilot flame and (2) the loss of the heating value of the chemicals burned.

Flares are usually used for waste gas streams having organic vapor concentrations above the upper explosive limit. The heat content of the organic compounds in the waste gas stream must usually be in the range of 100 Btu/SCF to 150 Btu/SCF to sustain efficient combustion; otherwise supplemental fuel must be added. This type of system is referred to as a *fired* or *endothermic* flare.

Elevated Flares

A typical elevated flare is composed of a system that first collects the waste gases and then passes the gases through a knockout drum to remove any liquids. Flame

arrestors are placed between the knockout drum and the flare stack to prevent flashback of flames into the collection system. The elevated flare stack (Figure 6-8) is essentially a hollow pipe that may extend to heights exceeding 150 feet. The diameter of the flare stack determines the volume of waste gases that can be handled.

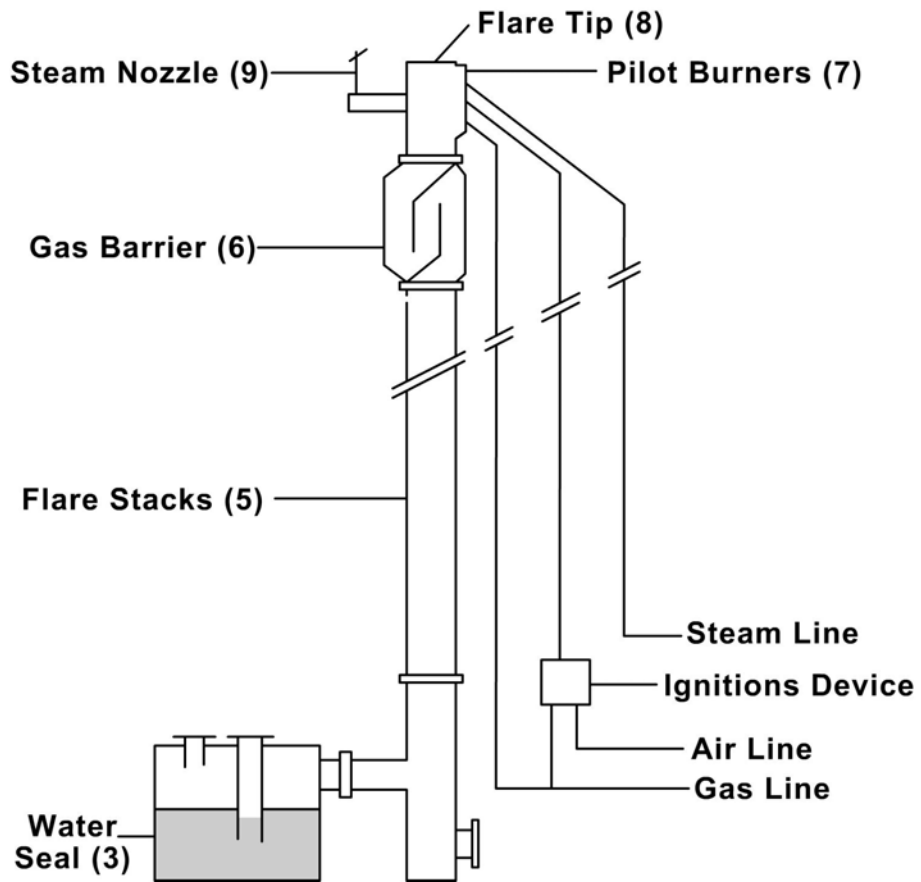


Figure 6-8. Steam-assisted Elevated Flare System.

The smokeless flare tip using steam injection shown in Figure 6-9 is at the top of the stack. It is comprised of the burners and a system to mix the air and fuel.

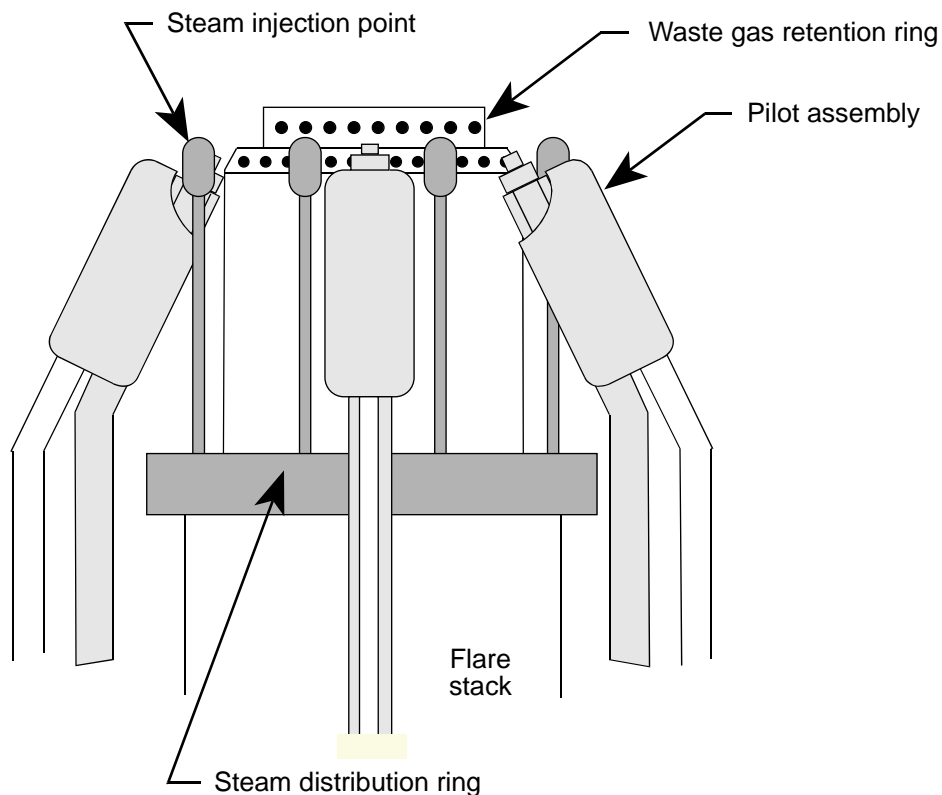


Figure 6-9. Smokeless flare tip of an elevated flare.

A number of flare tip designs provide good mixing characteristics over a wide range of waste gas flow rates while maintaining excellent flame-holding capabilities. Steam jets have proven to be one of the most effective ways to mix air and waste gases. In addition to increasing turbulence, the steam reacts with the gases to produce oxygenated intermediate compounds that burn readily at lower temperatures and reduce polymerization of organic compounds in the waste gas stream. For these reasons, steam injection is used for waste gases that are difficult to burn. Compounds with a hydrogen-to-carbon weight ratio less than 0.3, which includes most organics, are difficult to burn and usually require steam injection.¹ Steam requirements range between 0.05 and 0.3 kg of steam per kg of waste gas.⁵ The steam is automatically injected at a rate proportional to the flow rate of the waste gases.

Shields are often used on elevated flares to protect the flame from atmospheric conditions. These shields also help reduce noise and visibility problems associated with flares.

Enclosed Ground Flares Used for Thermal Oxidation

A number of ground flares are available commercially. The term *ground flare* refers to locating the flare tip at or near ground level. Most ground flares consist of multiple burners enclosed within a refractory shell that encloses the flame to eliminate noise, luminescence, and safety hazards. The waste gas is introduced through a jet or venturi to provide turbulent mixing, and a stack is still required for the proper release of the combustion gases. Figure 6-10 shows a ground flare that has two chambers.

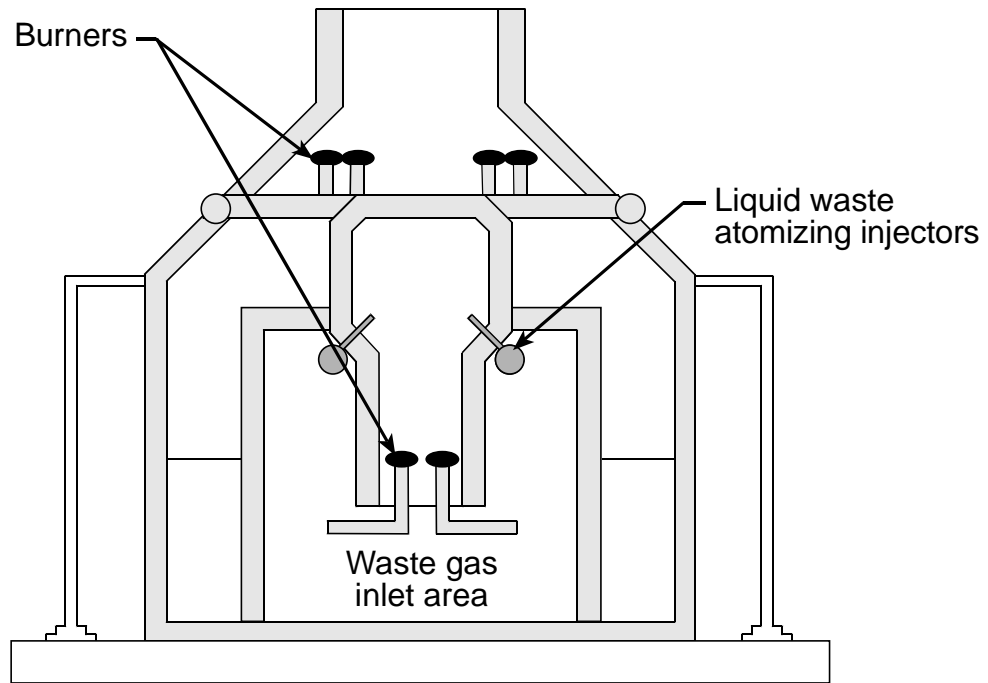


Figure 6-10. Enclosed ground flare.

The size of a ground flare is directly proportional to the volume of vapors it must handle. Ground flares can require more than twice the steam injection rates as elevated flares. Some plants have incorporated both designs: a ground flare used for normal or intermittent operation, and a large elevated flare used only to control emergency releases of large quantities of gases.

Catalytic Oxidation Systems

Catalytic oxidation systems are designed with both regenerative and recuperative heat exchangers to minimize fuel consumption. The advantages and limitations of the recuperators and regenerators are identical to those of thermal oxidizers. Accordingly, this section emphasizes only the characteristics of catalytic oxidation.

A catalyst is a substance that accelerates a chemical reaction without undergoing a change itself. In catalytic oxidation, a waste gas is passed through a

catalyst bed. The catalyst causes the oxidation reactions to proceed at a much lower temperature than is possible in gas-phase thermal oxidation. A catalytic oxidizer operating in the 600°F to 850°F (320°C to 450°C) range can achieve the same efficiency as a thermal oxidizer operating between 1,000°F and 2,000°F (540°C and 1,100°C). Because of the lower operating temperatures, it is often possible for catalytic oxidizers to operate without supplemental fuel except during start-up.

Advantages and Disadvantages

Catalytic oxidizers, which can achieve organic compound destruction efficiencies of more than 95%,⁶ can be used with inlet organic concentrations ranging from approximately 100 ppm to more than 10,000 ppm. The upper concentration limit depends on the lowest LEL for the compounds present in the gas stream. The principle advantages of catalytic oxidizers over thermal oxidizers are the lower temperatures and the reduced supplemental fuel requirements. In addition, because of the low operating temperatures, refractory-lined combustion chambers are usually not needed, which reduces the weight of the unit.

The primary disadvantages of catalytic oxidizers are the cost of the catalyst and performance problems related to the physical and chemical deterioration of catalyst activity. Some chemicals react irreversibly with the catalyst, while other materials mask the catalyst surface. Both problems result in the need to regenerate or replace the catalyst at frequent intervals.

Catalytic units have start-up times similar to thermal units. The time needed to heat the catalyst bed is approximately equal to the time necessary to preheat the refractory of a thermal oxidizer. Accordingly, both types of oxidizers are subject to emission problems from processes that have frequent start-up/shut-down cycles.

Operation

A cutaway of a conventional catalytic oxidizer is shown in Figure 6-11. The inlet gas stream passes through a recuperative-type heat exchanger to recover a portion of the sensible heat from the hot exhaust gases. The preheated gas stream then enters a chamber where it is distributed across the inlet face of the catalyst bed. If the inlet gas temperature and concentration are too low to sustain the catalytic reactions, a preheat burner is used to raise the temperature to the range of 500°F to 900°F (260°C to 480°C).⁶ The preheat burner is also operated during start-up.

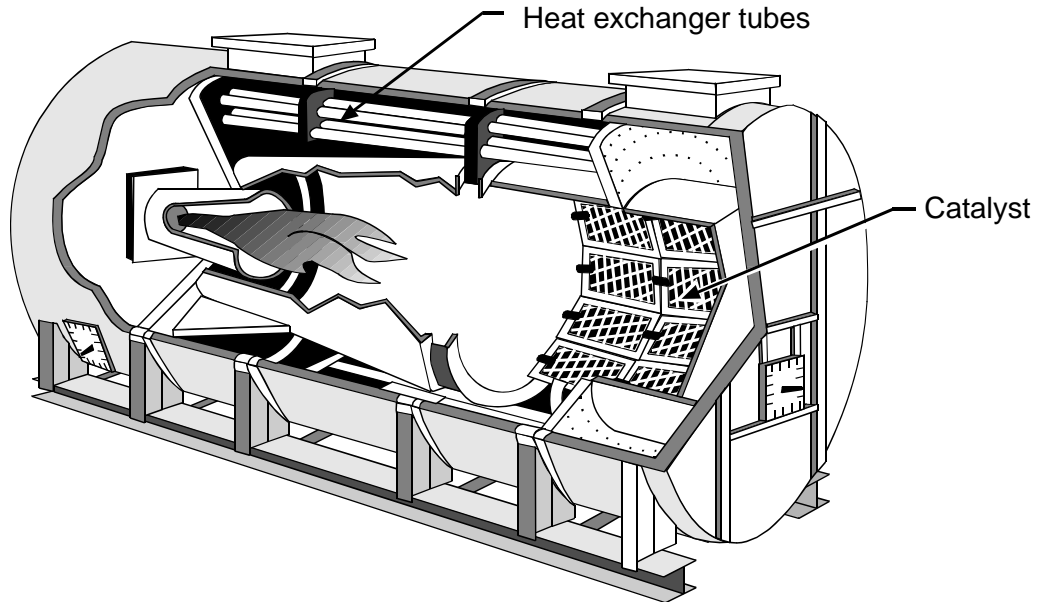


Figure 6-11. Cutaway of a catalytic oxidizer.

The exothermic combustion reactions that occur as the gas stream passes through the catalyst bed increase the gas temperature by 50°F to 300°F (10°C to 150°C), depending on organic concentration. The gas stream then passes through the hot-gas-side of the recuperative heat exchanger and is exhausted to the atmosphere.

The active catalyst is deposited onto the surface of a carrier, such as alumina, that is bonded to a support structure. The support material is arranged in a matrix shape to provide high geometric surface area, low pressure drop, and uniform flow of the waste gas through the catalyst bed. Structures that provide these characteristics are honeycomb matrices (Figure 6-12), grids, or mesh pads.

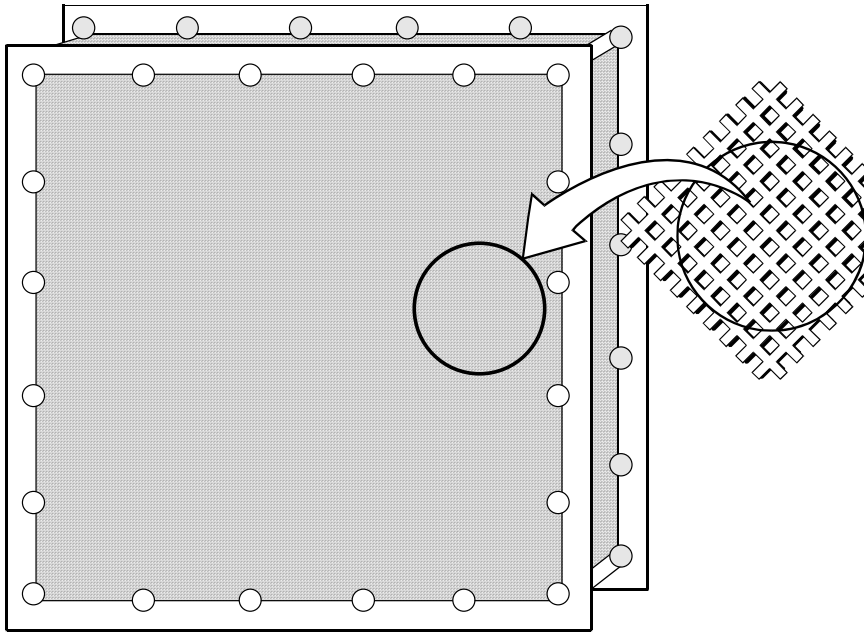


Figure 6-12. Catalyst bed honeycombs.

A close-up cross-section view of a honeycomb-type catalyst is shown in Figure 6-13. The walls of the honeycomb are metallic. The catalyst is precipitated uniformly over the entire surface of the carrier to maximize the surface area available for the catalytic reactions.

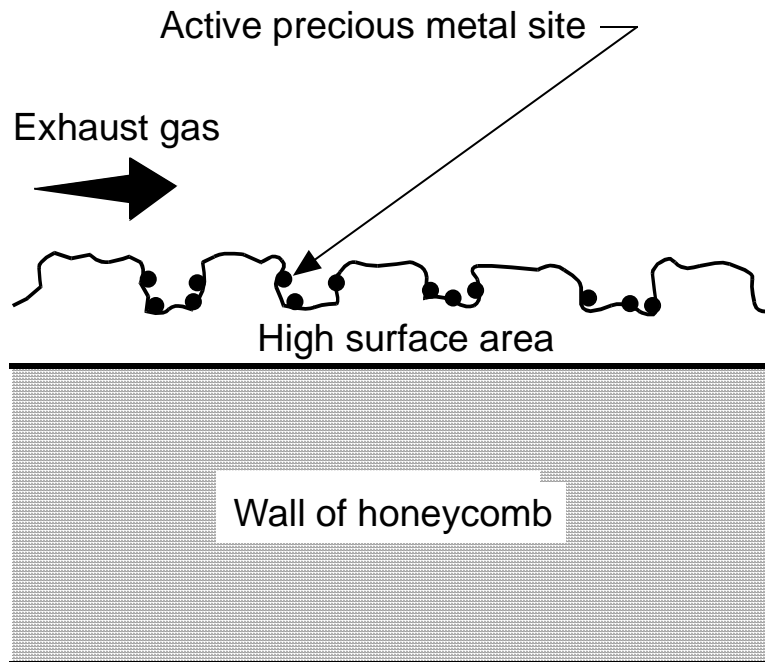


Figure 6-13. Close-up cross-section of a catalyst on a honeycomb. (Reprinted courtesy of Engelhard Corporation, Ontario, CA.)

The geometry of a honeycomb catalyst bed is described in terms of the cell (gas-passage) density. Typical values range from 100 to 600 cells per square inch.⁶ The catalyst surface area is proportional to the number of cells per square inch.

The operation of the catalytic oxidizer is often described in terms of the space velocity which has units of reciprocal time. The space velocity is calculated by dividing the gas flow rate entering the bed (actual volumetric flow rate) by the volume of the bed. Normal values are between 20,000 hour⁻¹ to 100,000 hour⁻¹. High space velocities correspond to high gas volumetric flow rates and/or low catalyst quantities. At a given operating temperature, decreasing space velocity results in increased residence time and provides increased destruction efficiency.⁷ The catalyst bed is the main contributor to the static pressure drop across the oxidizer. Normal static pressure drops are between 2 and 8 in. W.C. (0.5 and 2.0 kPa).

Catalytic oxidizers usually cannot be used on waste gas streams containing high concentrations of particulate matter. The particulate matter deposits on the surface of the catalyst and blocks the access of the organic compounds. Oil droplets can also block access to the catalyst bed unless they are vaporized in the preheat section. By periodically cleaning and washing the catalyst, much of the activity can be restored. Blocking access to the catalyst surface in this manner is referred to as *fouling*.

Masking and fouling problems can sometimes be minimized by using a fluidized-bed arrangement. In this type of system, the catalyst is prepared as small spherical particles supported on a grid. The catalyst particles are fluidized by the upward flow of gas. Particle-to-particle abrasion continually cleans the catalyst surfaces to minimize the effect of masking. One disadvantage of this type of system is the need to collect and dispose of the fine particulate matter generated by physical attrition in the fluidized bed.

Catalyst Material

The active catalyst material typically consists of:

Noble metals

- Platinum
- Palladium
- Rhodium

Metal oxides

- Chromium oxide
- Manganese oxide
- Cobalt oxide

The metal oxides are used when halogenated compounds are present, because the chlorine and fluorine will deactivate the noble metal catalysts.

Catalyst Poisoning

Certain metals react irreversibly with or alloy to the catalyst, thereby making it inactive. Deactivation in this manner is called *catalyst poisoning*. Catalyst poisons can be divided into two categories:

Fast-Acting Poisons

- Phosphorus
- Bismuth
- Arsenic
- Antimony
- Mercury

Slow-Acting Poisons

- Iron
- Lead
- Tin
- Silicones

Catalysts are more tolerant of the slow-acting poisons, particularly at temperatures below 1,000°F (540°C). At sufficiently high temperatures (i.e., 1,000°F), even copper and iron are capable of alloying to noble metals such as platinum, thereby reducing their activity.

Sulfur and halogen compounds act as masking agents and thereby inhibit the oxidation reactions. Their interaction with the catalyst is reversible, and once the halogen or sulfur compound is removed, catalyst activity is restored.

Catalyst Service Life

All catalysts deteriorate with normal use. Gradual loss of the catalyst material can occur from erosion, attrition, and vaporization. High temperatures can also accelerate catalyst deactivation through the process referred to as *thermal aging*. This is caused by the sintering or densification of the catalyst support material, which results in the loss of active catalyst surface area.

The average service life of a catalyst is 2 to 5 years, with low operating temperature generally resulting in longer service life.

6.2 Operating Principles

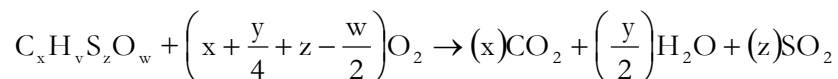
The operating principles for high-temperature, gas-phase oxidation systems and catalytic systems are discussed in this section. This material provides a basis for the later information presented concerning the capability and sizing of new oxidizer systems.

High-Temperature, Gas-Phase Oxidation Systems

Combustion Products and Gas Volumes

In all high-temperature combustion processes, a complex set of several hundred to several thousand chemical reactions occur simultaneously. The result of these reactions is represented by the following generalized stoichiometric reaction. The main reaction products are carbon dioxide and water vapor.

(Reaction 6-1)



Usually, sulfur dioxide is the dominant reaction product formed from sulfur present in the fuel or waste stream. However, 0.5% to 2% of the total sulfur can also form sulfur trioxide, which ultimately forms vapor phase sulfuric acid once the gas stream cools below approximately 600°F (320°C). To estimate the oxygen requirement, it is assumed that all of the sulfur forms sulfur dioxide. The reactions involving the formation of nitrogen oxides (NO_x) are ignored when making material balance calculations involving the total volume of reaction products and the amount of oxygen needed. If chlorine or fluorine atoms are present in the organic compound being burned, hydrochloric acid (HCl) and hydrofluoric acid (HF) will usually be formed. However, if the compounds being burned have only a limited number of hydrogen atoms per molecule, chlorine gas (Cl₂) can also form in the combustion chamber.¹

Nitrogen atoms in the organic compounds (i.e., cyanides or amines) being oxidized can form nitrogen oxides (NO and NO₂), or they can be chemically reduced to molecular nitrogen. The quantity of nitrogen oxides formed from the organic wastes is usually small compared to the nitrogen oxides formed in the burner flame of the thermal oxidizer. Nitrogen oxides are also generally neglected when making material balance calculations.

The concentrations of the pollutants generated by thermal oxidation can be calculated by using the stoichiometry of the combustion reactions and information concerning the quantity of supplemental fuel being burned in the unit.

The combustion reactions go to completion if the following conditions exist:

- The gas temperature is sufficiently high.
- The combustible materials and the air are well-mixed (turbulence).
- There is sufficient oxygen (air).
- The residence time within the combustion chamber is relatively long.

Temperature

The necessary gas temperature is based primarily on the auto-ignition temperature of the most difficult-to-oxidize organic compound contained in the waste stream.¹ The auto-ignition temperature of various fuels and compounds

can be found in combustion handbooks such as the *North American Combustion Handbook*.⁸ Table 6-1 provides a list of the auto-ignition temperatures of some common organic compounds present in waste gas streams.

Table 6-1. Auto-ignition temperatures.	
Compound	Auto-Ignition Temperature (°F)
Acetone	870
Acetonitrile	970
Isopropyl Alcohol (IPA)	780
Methanol	878
Methyl Ethyl Ketone (MEK)	759
Toluene	896
Xylene	867

Most oxidizers operate at temperatures 200°F to 300°F (110°C to 170°C) above the auto-ignition temperature of the organic compound being burned. Thermal destruction of most organic compounds occurs between 1,100°F and 1,200°F (590°C and 650°C). Therefore, most thermal oxidizers operate at 1,300°F to 1,600°F (700°C to 870°C).

Turbulence

Proper mixing is important in combustion processes for two reasons. First, mixing the burner fuel with air ensures complete combustion of the fuel. Second, thoroughly mixing the organic-containing waste gases with the burner combustion gases ensures that the entire waste gas stream reaches the necessary combustion temperatures.

A number of methods are available to improve the mixing of the air and combustion streams, including the use of refractory baffles, swirl-fired burners, or baffle plates. It is difficult to obtain complete mixing. Unless properly designed, many of these mixing devices may create “dead spots” and reduce operating temperatures. Inserting obstructions to increase turbulence may not be sufficient.

Combustion Air Requirements

The combustion air requirements for the supplemental fuel burner used in thermal oxidizers must be taken into account when sizing the burner system and the combustion chamber. To achieve complete combustion of the fuel (e.g., natural gas, propane, No. 2 oil), a sufficient supply of oxygen must be present in the burner flame to convert all of the carbon to CO₂. This quantity of oxygen is referred to as the *stoichiometric* (or theoretical) *amount*. The stoichiometric amount of oxygen is determined from a balanced chemical equation summarizing the oxidation reactions. For example, 1 mole of methane (the major component of natural gas) requires 2 moles of oxygen for complete combustion (Reaction 6-2).



If a sub-stoichiometric amount of oxygen is available (not enough oxygen to completely oxidize the fuel), the mixture is referred to as *fuel-rich*. Incomplete combustion occurs under these conditions. This reduces the peak flame temperature and results in the formation of CO and other partially-oxidized compounds.

If more than the stoichiometric amount of oxygen is supplied, the mixture is referred to as *lean*. The unreacted oxygen and nitrogen entering with the combustion air carry away a portion of the heat released by the combustion reactions, and the peak flame temperature is reduced. The high oxygen levels in the flame can also contribute to generating nitrogen oxides.

In order to maximize the flame temperature and minimize pollutant generation, the burner should be operated with a slight excess of oxygen, i.e., slightly lean. Burners firing natural gas, propane, and No. 2 oil usually operate with excess air rates in the range of 10% to 30%. This means that the combustion air supplied to the burner has 1.1 to 1.3 times the amount of the necessary oxygen based on the balanced stoichiometric reactions of the fuel. In Problem 6-1 below, the calculated (stoichiometric) oxygen requirement is 1.56 pound moles per minute. Because the burner was operating at a 25% excess air rate, the total amount of oxygen supplied to the burner was 1.25 times this amount, or 1.95 pound moles per minute. This additional oxygen is needed simply to ensure complete combustion and to account for the non-ideal factors, such as incomplete mixing, that affect fuel combustion.

At high excess air rates, the total flow rate of the combustion products is high. This is due primarily to the large amount of nitrogen that enters with the oxygen, and, in part, to the excess oxygen that is part of the flue gas stream. Nitrogen comprises approximately 79% of ambient air. Therefore, when the oxygen requirement increases, a large quantity of nitrogen enters with the combustion air and is included in the exhaust gas stream. In Problem 6-1, the combustion air supply to the burner included 7.34 pound moles per minute of nitrogen, all of which exits with the combustion products. The residence time of the combustion products in the combustion chamber is reduced because of the additional quantity of nitrogen present. Therefore, the fuel-firing rate must be increased slightly to account for the heat lost with the additional nitrogen.

The reduction in combustion chamber residence time associated with high excess air levels can be minimized by using oxygen present in the waste gas stream. Most waste streams have oxygen concentrations between 16% and 20.9%, so that by using this source of oxygen, the combustion air rate to the burner can be reduced, and the residence time can be increased.

Residence Time

The residence time needed to complete the oxidation reactions in the combustion chamber depends both on the rate of the reactions at the prevailing temperature and on the mixing of the waste stream and the hot combustion gases from the supplemental burner or burners. Residence times are usually between 0.3 and 2 seconds.

The residence time of gases in the combustion chamber may be calculated as the ratio of the volume of the refractory-lined combustion chamber and the volumetric flow rate of combustion products through the chamber.

$$\text{(Eq. 6-1)} \quad t = \frac{V}{Q}$$

Where: t = residence time (sec)
 V = chamber volume (ft³)
 Q = actual gas volumetric flow rate at combustion conditions (ft³/sec)

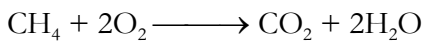
Q is the total flow of hot gases in the combustion chamber. Adjustments to the flow rate must include any outside air added for combustion. Problem 6-1 illustrates how to determine residence time from the volumetric flow rate of gases.

Problem 6-1

A thermal oxidizer controls emissions from a paint-baking oven. The cylindrical unit has a diameter of 5 feet and a length of 12 feet, with all combustion air supplied by an auxiliary source. The exhaust from the oven is 8,000 SCFM. The oxidizer uses 300 SCFM of natural gas and operates at a temperature of 1,400°F. What is the residence time in the combustion chamber? Assume that the fuel is 100% methane and that the burner is operated at 125% of the stoichiometric requirement.

Solution:

Step 1. Write the combustion reaction.



The stoichiometric oxygen requirement is two moles of oxygen for every mole of methane burned to completion.

Step 2. Calculate the total amount of O₂ at stoichiometric conditions.

$$300 \text{ SCFM} \left(\frac{\text{lb mole CH}_4}{385.4 \text{ ft}^3} \right) = 0.778 \frac{\text{lb mole CH}_4}{\text{min}}$$

$$\text{Stoichiometric O}_2 = 2 \times (\text{lb mole CH}_4)$$

$$\frac{2 \text{ lb mole O}_2}{\text{lb mole CH}_4} \left(0.778 \frac{\text{lb mole CH}_4}{\text{min}} \right) = 1.56 \frac{\text{lb mole O}_2}{\text{min}}$$

Step 3. Calculate air sent to burner (125% of stoichiometric requirement).

Total O₂ requirement = 1.25 × (stoichiometric requirement)

$$= 1.25 \left(1.56 \frac{\text{lb mole O}_2}{\text{min}} \right) = 1.95 \frac{\text{lb mole O}_2}{\text{min}}$$

$$\text{Total N}_2 = \frac{0.79 \text{ lb mole N}_2}{0.209 \text{ lb mole O}_2} \left(1.95 \frac{\text{lb mole O}_2}{\text{min}} \right)$$

$$= 7.34 \text{ lb mole N}_2/\text{min}$$

Step 4. Calculate the total flue gas flow rate.

Total flue gas flow rate = Exhaust gas heated (a) + Products of combustion (b) + Nitrogen and excess oxygen (c)

a. Exhaust gas heated = 8,000 SCFM

b. Products of combustion = CO₂ + H₂O

$$\text{CO}_2 = 1 \frac{\text{lb mole CO}_2}{\text{lb mole CH}_4} \left(0.778 \frac{\text{lb mole CH}_4}{\text{min}} \right) = 0.778 \text{ lb mole CO}_2/\text{min}$$

$$\text{H}_2\text{O} = 2 \frac{\text{lb mole H}_2\text{O}}{\text{lb mole CH}_4} \left(0.778 \frac{\text{lb mole CH}_4}{\text{min}} \right) = 1.56 \text{ lb mole H}_2\text{O}$$

$$\text{CO}_2 + \text{H}_2\text{O} = 2.34 \text{ lb mole}/\text{min}$$

$$2.34 \frac{\text{lb mole}}{\text{min}} \left(\frac{385.4 \text{ SCF}}{\text{lb mole}} \right) = 902 \text{ SCFM}$$

c. Nitrogen and excess oxygen = total N₂ + O₂ remaining

$$= 7.34 \text{ lb mole N}_2/\text{min} + 0.39 \text{ lb mole O}_2/\text{min} = 7.73 \text{ lb mole}/\text{min}$$

Amount of oxygen consumed = stoichiometric required

$$= 1.56 \text{ lb mole}/\text{min}$$

Amount of oxygen remaining = total – consumed

$$= 1.95 \text{ lb mole}/\text{min} - 1.56 \text{ lb mole}/\text{min}$$

$$= 0.39 \text{ lb mole}/\text{min}$$

$$7.73 \frac{\text{lb mole}}{\text{min}} \left(\frac{385.4 \text{ SCF}}{\text{lb mole}} \right) = 2,980 \text{ SCFM}$$

$$\begin{aligned} \text{Total flue gas flow rate} &= 8,000 \text{ SCFM} + 902 \text{ SCFM} + 2,980 \text{ SCFM} \\ &= 11,880 \text{ SCFM} \end{aligned}$$

Step 5. Convert the flue gas flow rate to actual conditions.

$$\text{Total ACFM} = 11,880 \text{ SCFM} \left(\frac{1,400 + 460 \text{ }^\circ\text{R}}{528 \text{ }^\circ\text{R}} \right) = 41,850 \text{ ACFM}$$

Step 6. Calculate the volume of the combustion chamber.

$$\text{Combustion Chamber Vol.} = \pi(r)^2 L = 3.14 (2.5 \text{ ft})^2 12 \text{ ft} = 235.5 \text{ ft}^3$$

Step 7. Calculate the residence time.

$$\begin{aligned} \text{Residence Time} &= \frac{\text{chamber volume}}{\text{volumetric flow rate}} = \frac{235.5 \text{ ft}^3}{41,850 \text{ ACF/min}} = 0.00562 \text{ minutes} \\ &= 0.00562 \text{ min} \left(\frac{60 \text{ sec}}{\text{min}} \right) = 0.337 \text{ seconds} \end{aligned}$$

The residence time of the combustion gas in the thermal oxidizer described in Problem 6-1 is 0.337 seconds.

Problem 6-2

What would be the residence time for the thermal oxidizer described in Problem 6-1 if all of the combustion air is supplied by the waste gas stream? Assume that the waste gas stream has an oxygen concentration of 16%, a carbon dioxide concentration of 1%, a moisture concentration of 1%, and a nitrogen concentration of 82% (volume).

Solution:

Step 1. Determine if there is sufficient oxygen in the waste gas stream.

$$\begin{aligned} \text{O}_2 &= 8,000 \text{ SCFM} \left(\frac{\text{lb mole gas}}{385.4 \text{ SCF}} \right) \left(\frac{0.16 \text{ lb mole O}_2}{\text{lb mole gas}} \right) \\ &= 3.32 \text{ lb mole O}_2/\text{min} \end{aligned}$$

This is more than the 1.56 lb mole O₂/min calculated in Problem 6-1. Therefore, there is sufficient O₂. (However, there may be flame-stability limits that are more restrictive than the simple stoichiometric requirements used in this example.)

Step 2. Calculate flue gas flow rate.

Flue gas = (Waste gas stream - reacted oxygen) + (Products of combustion)

$$\text{Waste gas stream} = 8000 \text{ SCFM} \left(\frac{\text{lb mole}}{385.4 \text{ SCF}} \right) = 20.76 \text{ lb mole/min}$$

$$\text{Waste gas stream - reacted O}_2 = (20.76 - 1.56) = 19.20 \text{ lb mole/min}$$

$$\text{Products of combustion} = (\text{CO}_2 + \text{H}_2\text{O}) = 2.34 \text{ lb mole/min (from Problem 6-1, step 4)}$$

$$\text{Flue gas} = (19.20 \text{ lb mole/min} + 2.34 \text{ lb mole/min}) = 21.54 \text{ lb mole/min}$$

Step 3. Calculate total volumetric flow rate (ACFM).

$$\text{Vol. Flow rate} = (21.54 \text{ lb mole/min}) \left(\frac{385.4 \text{ SCF}}{\text{lb mole}} \right) \left(\frac{1,400 + 460^\circ \text{R}}{528^\circ \text{R}} \right)$$

$$\text{Vol. Flow rate} = 29,240 \text{ ACFM}$$

Step 4. Calculate residence time.

$$\text{Residence time} = \frac{\text{chamber volume}}{\text{volumetric flow rate}}$$

$$= \frac{235.5 \text{ ft}^3}{29,240 \text{ ft}^3/\text{min}} = 0.008054 \text{ minutes}$$

$$= 0.008054 \text{ min} \left(\frac{60 \text{ sec}}{\text{min}} \right) = 0.483 \text{ sec}$$

This is substantially longer than the 0.337-second residence time calculated in Problem 6-1. It illustrates the change that results when the waste gas stream is used as the source of oxygen instead of having a separate combustion air supply for the burner.

Despite the apparent advantage, thermal oxidizers often use a separate air supply rather than obtaining all or part of the needed oxygen from the waste gas stream. One of the main problems with using the waste gas stream is that nonvolatile organic compounds or particulate matter in the waste gas stream may potentially foul the burner. There can also be variations in the waste gas stream composition that affect the ability to maintain a stable flame, especially when the oxygen concentration drops below approximately 16%.

Inlet Organic Vapor Concentration

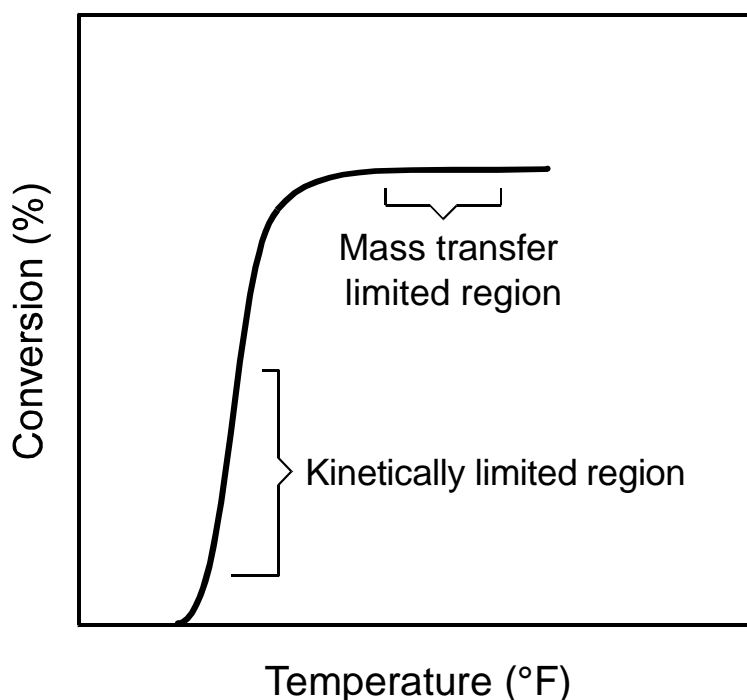
Thermal oxidizers and boilers usually operate at organic vapor concentrations below 25% of the LEL. Since combustion does not occur readily in this range, the waste gas stream can be transported safely to the combustion device, and the

risk of flashback from the oxidizer to the process equipment is minimized. The VOC inlet concentration is usually determined by an LEL detector, which determines the approximate total concentration of oxidizable organic compounds.

However, explosive limits are not absolute values that apply at all temperatures, pressures, and other conditions. At high temperatures, there is sufficient energy to overcome the activation energy for the organic molecules to begin oxidation, and the exothermic energy released by the oxidation reaction is not quickly lost to the surrounding molecules.

Catalytic Oxidation Systems

The general factors that control the rate of catalytic oxidation are illustrated in Figure 6-14. At low temperatures, the rate of oxidation is limited by the kinetics of the oxidation reactions, while at high temperatures the rate is limited by the rate of mass transfer. The temperature of the catalytic oxidizer is set at a level at which the controlling factor is the rate of mass transfer of oxygen and organic compounds to and from the catalyst surface.



**Figure 6-14. Importance of temperature in catalytic systems.
(Reprinted courtesy of Engelhard Corporation, Ontario, CA.)**

The temperature necessary for catalytic oxidation depends on the compounds present in the waste gas stream and the characteristics of the catalyst bed. An example of destruction efficiency curves for typical compounds is shown in Figure 6-15.

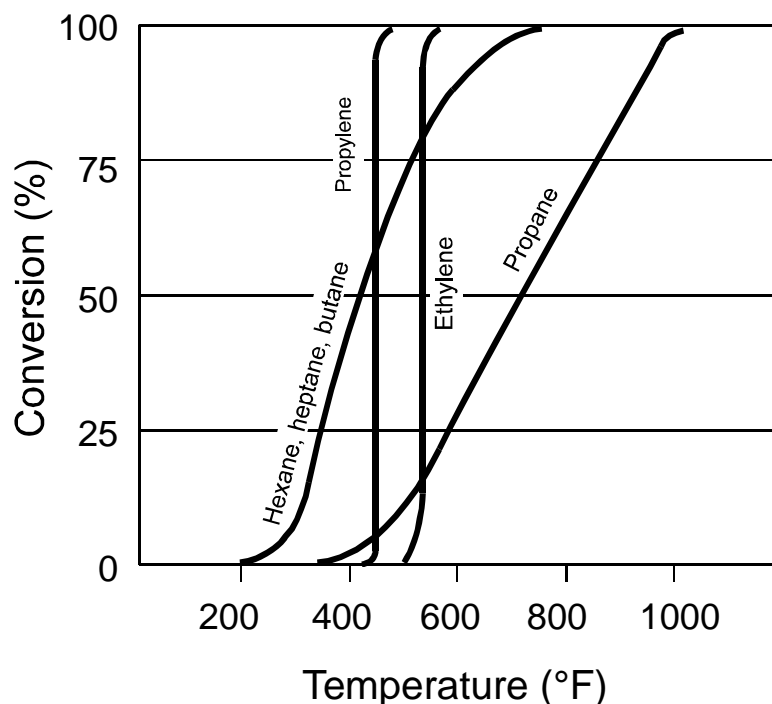


Figure 6-15. Destruction efficiency curves for selected organic compounds. (Reprinted courtesy of Engelhard Corporation, Ontario, CA.)

The minimum operating temperature is the left side of the destruction efficiency temperature curve where the controlling factor is the mass transfer rate, i.e., about 600°F for ethylene but about 1000°F for propane. It is not necessary to operate the supplemental fuel burner when the waste gas contains moderate to high concentrations of organics. The heat released during catalytic oxidation and recovered in the recuperative heat exchanger is sufficient to maintain the required oxidation temperature. Accordingly, catalytic oxidizers are generally more energy-efficient than high-temperature flame oxidizers.

6.3 Capability and Sizing

Destruction Efficiency

There are two primary means for estimating the organic compound destruction efficiency of high-temperature, gas-phase oxidation systems and catalytic oxidation systems: (1) empirical evaluation based on previous applications and (2) pilot plant tests.

Most units are selected based on empirical data available to the oxidizer manufacturer and/or the facility owner. The destruction efficiency data determined by testing procedures, such as the U.S. EPA reference methods, provide useful databases for evaluating the capability of new units. Destruction

efficiency data from other units must be evaluated on a compound-specific basis to predict the differences in the oxidation rates.

Pilot plant tests can be conducted when there is insufficient data on a specific compound or group of compounds in the waste gas stream. These tests involve the treatment of a 100 to 2,000 ACFM slipstream from the operating process unit for approximately one to four weeks. One or more reference method tests are usually conducted as part of these test programs. One of the advantages of the pilot plant tests is that data directly relevant to the process equipment is obtained prior to the design of the full-scale system. The primary disadvantage of the pilot tests is the cost. However, an improperly conducted pilot test can also give erroneous results. For example, the condensation of nonvolatile organic vapor in the slipstream duct upstream of the pilot oxidizer can give lower-than-actual emission rates. Also, short-term tests may not fully reveal long-term problems that could affect catalyst beds.

Fuel Requirements

The supplemental fuel requirement is one of the main parameters of concern in oxidation systems. If insufficient supplemental fuel is supplied or if combustion is not complete, the oxidizer temperature will not be sufficiently high to destroy all the organic contaminants.

The supplemental fuel requirement can be estimated based on a simple heat balance around the unit coupled with information on the waste gas stream. Figure 6-16 shows a simplified oxidation system that serves as the basis for the heat balance.

From the 1st Law of Thermodynamics:

(Eq. 6-2) Heat in = Heat out + Heat loss

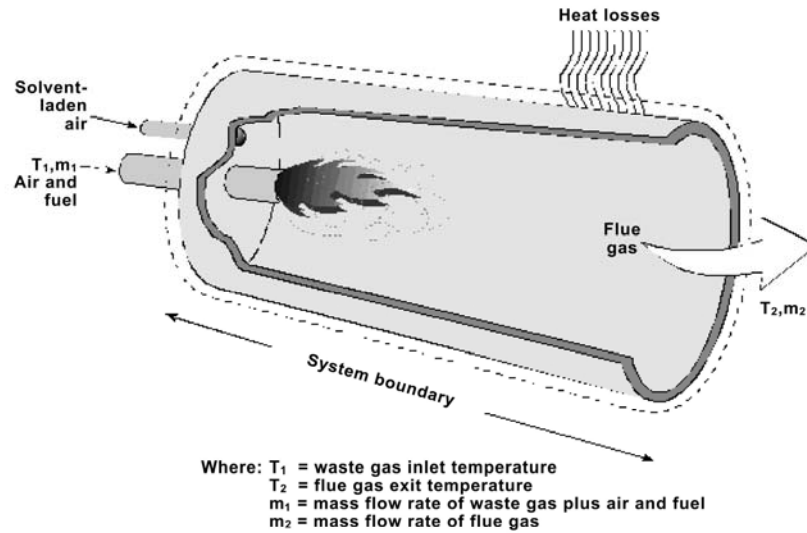
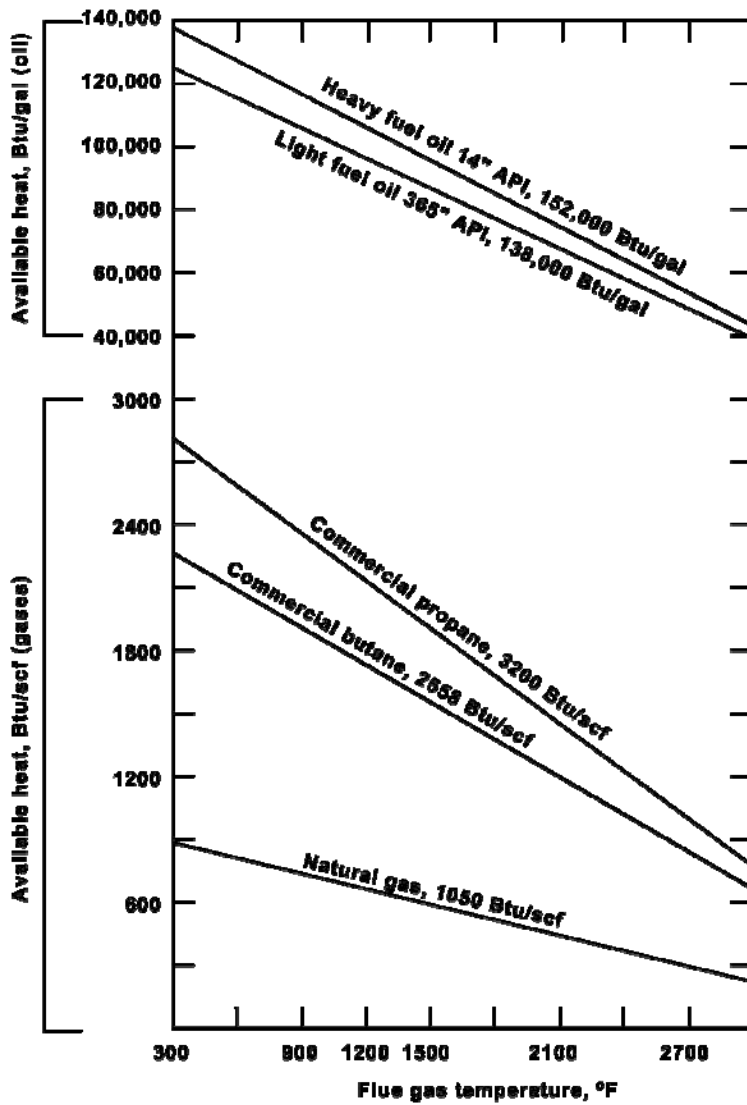


Figure 6-16. Heat balance around an oxidizer.

Energy is supplied by the combustion of the waste organics and the supplemental fuel. Some of this energy is used to heat the products of combustion (CO_2 , H_2O , excess O_2 , combustion air N_2) to the outlet gas temperature. The remainder of the energy generated by the burner is used to heat the waste gas stream to the outlet gas temperature. This quantity of heat that remains is called the available heat. The available heat is highest at low oxidizer temperatures (because less of the total heat is needed to heat the combustion products) and decreases as the oxidizer temperature increases. This is illustrated in Figure 6-17.



Source: North American Combustion Handbook, 1968.

Figure 6-17. Available heat of common fuels.

The available heat approaches the gross heating value (also known as the higher heating value) of the fuel at 60°F (16°C) if the products of combustion are also at 60°F.

When the available heat value is used to evaluate oxidizers, it is not necessary to take separate account of the heat lost with the combustion products, because this is automatically included in the available heat value for the temperature being evaluated. However, there are cases where it is more convenient to use the gross heating value and then take into account the heat loss associated with the combustion products and the waste gases separately.

In order to calculate the heat that exits the oxidizer with the waste gas stream, the enthalpies of the inlet and outlet waste gas streams must be determined. *Enthalpy* is a thermodynamic term whose numerical value can be read from tables such as those below. Table 6-2a presents the enthalpies of combustion gases in units of Btu/SCF, while Table 6-2b presents the same data in units of Btu/lb_m. Enthalpy is a relative term that is compared to some reference temperature. 60°F is chosen as the reference temperature in these tables, and the enthalpy of all components is arbitrarily set to be zero at that temperature. It is important to note, particularly for H₂O, that the tabulated values apply only to gases. Thus, if for some reason liquid H₂O is injected into the oxidizer, it would also be necessary to include the latent heat of vaporization of water in the calculation. The latent heat of vaporization represents the heat required to evaporate a liquid at its boiling temperature.

Gas Temp. (°F)	O₂	N₂	CO₂	H₂O	Air
60	0.00	0.00	0.00	0.00	0.00
100	0.74	0.74	0.39	0.36	0.74
200	2.61	2.58	0.94	0.85	2.58
300	4.50	4.42	3.39	2.98	4.42
400	6.43	6.27	5.98	5.14	6.29
500	8.40	8.14	8.69	7.33	8.17
600	10.40	10.02	14.44	11.81	10.07
700	12.43	11.93	17.45	14.11	12.00
800	14.49	13.85	20.54	16.45	13.95
900	16.59	15.80	23.70	18.84	15.92
1000	18.71	17.77	26.92	21.27	17.92
1100	20.85	19.78	30.21	23.74	19.94
1200	23.02	21.79	33.55	26.26	21.98
1300	25.20	23.84	36.93	28.82	24.05
1400	27.40	25.90	40.36	31.42	26.13

1500	29.62	27.98	43.85	34.08	28.24
2000	40.90	38.65	61.71	47.91	38.99
2500	52.43	49.67	80.15	62.60	50.07

Table 6-2b. Enthalpies of combustion gases, Btu/lb _m .					
Gas Temp. (°F)	O ₂	N ₂	CO ₂	H ₂ O	Air
60	0.0	0.0	0.0	0.0	0.0
100	8.8	6.4	5.8	17.8	9.6
200	30.9	34.8	29.3	62.7	33.6
300	53.4	59.8	51.3	108.2	57.8
400	76.2	84.9	74.9	154.3	82.1
500	99.5	110.1	99.1	201.0	106.7
600	123.2	135.6	124.5	248.7	131.6
700	147.2	161.4	150.2	297.1	156.7
800	171.7	187.4	176.8	346.4	182.2
900	196.5	213.8	204.1	396.7	211.4
1000	221.6	240.5	231.9	447.7	234.1
1100	247.0	267.5	260.2	499.7	260.5
1200	272.7	294.9	289.0	552.9	287.2
1300	298.5	326.1	318.0	606.8	314.2
1400	324.6	350.5	347.6	661.3	341.5
1500	350.8	378.7	377.6	717.6	369.0
2000	484.5	523.0	531.4	1003.1	509.5
2500	621.0	672.3	690.2	1318.1	654.3

Source of Tables 6-2a and 6-2b: U.S. EPA, *Air Pollution Engineering Manual*, 2nd ed., 1973.

In addition to using tables such as those above, the enthalpy of the combustion gas component at the outlet temperature, T, can also be computed from Equation 6-3.

(Eq. 6-3)
$$H = C_p(T - T_o)$$

Where: H = enthalpy (Btu/lb_m)
 C_p = specific heat at temperature T (Btu/lb_m °F)
 T = temperature of the component (°F)

T_o = reference temperature ($^{\circ}\text{F}$)

The change in enthalpy of a component between the oxidizer's entering and exit temperatures is obtained by subtracting the enthalpy of the component entering the oxidizer from that of the component exiting, which is also the amount of that must be supplied by the fuel. Using Equation 6-3, the enthalpy entering at T_1 is subtracted from the enthalpy exiting at T_2 , giving:

$$\text{(Eq. 6-4)} \quad \Delta H = C_{p2}(T_2 - T_o) - C_{p1}(T_1 - T_o)$$

Where: ΔH = change in enthalpy (Btu/lb_m)
 C_{p2} = average specific heat between T_o and T_2
 C_{p1} = average specific heat between T_o and T_1

To simplify this calculation, an average specific heat value, C_p between T_1 and T_2 , can be used. This reduces Equation 6-4 to:

$$\text{(Eq. 6-5)} \quad \Delta H = C_p (T_2 - T_1)$$

The specific heat varies with the temperature and composition of the gas stream. Therefore, Equation 6-5 is used to obtain an approximate value. For most incineration systems, the waste gases are considered to be essentially air, for which an average specific heat value, C_p , is 0.26 Btu/lb_m $^{\circ}\text{F}$ (1086 J/kg $^{\circ}\text{C}$) for typical temperature ranges normally encountered in high-temperature, gas-phase oxidation systems.

Equation 6-5 depicts the amount of heat required to increase unit mass of gas from T_1 to T_2 . The total heat requirement is then determined by multiplying both sides of Equation 6-5 by the mass flow rate (m) of the waste gas stream. The total heat rate required is given by:

$$\text{(Eq. 6-6)} \quad q = m\Delta H = mC_p(T_1 - T_2)$$

Where: q = total heat rate (Btu/hr)
 m = mass flow rate of waste gases (lb_m/hr)

Equation 6-6 can be used to compute the heat rate required to raise the gas temperature from T_1 to T_2 . Problem 6-3 illustrates the use of Equation 6-6 and Table 6-2.

These equations are simple heat balances, equating heat in to heat out. They do not account for any heat losses in the system. Heat losses from refractory or ducting are usually accounted for by assuming that a fixed percent of the total theoretical heat input with the fuel is lost. For example, if an oxidizer is required to supply heat at the rate of 1×10^6 Btu/hr, and there is a 10% heat loss from the combustion chamber, the total heat rate would have to be 1.1×10^6 Btu/hr to account for the losses. Heat is also lost to the system from the latent heat associated with vaporization of water or organic liquid droplets entrained in the waste gas stream.

Problem 6-3 illustrates a method that can be used to roughly estimate the fuel requirement for an oxidizer.

Problem 6-3

The exhaust from a meat smokehouse contains obnoxious odors and fumes. The company plans to oxidize the 5,000 ACFM exhaust stream. What quantity of natural gas is required to raise the waste gas stream from a temperature of 90°F to the required temperature of 1,200°F? The gross heating value of natural gas is 1,059 Btu/SCF. The exhaust gas can be considered to be air. Assume no heat losses.

Solution:

Step 1. All calculations are based on a 1-hour time period. First, the volume of waste gas must be corrected to standard conditions (68°F and 1 atm).

$$G = \frac{5,000 \text{ ACF}}{\text{min}} \left(\frac{460^\circ \text{R} + 68}{460^\circ \text{R} + 90} \right) \left(\frac{60 \text{ min}}{\text{hr}} \right) = 288,000 \text{ ft}^3/\text{hr}$$

Step 2. The volumetric flow rate is then converted to a mass flow rate by multiplying by the density.

$$m = \left(\frac{288,000 \text{ SCF}}{\text{hr}} \right) \left(\frac{\text{lb mole}}{385.4 \text{ SCF}} \right) \left(\frac{29 \text{ lb}_m}{\text{lb mole}} \right) = 21,700 \text{ lb}_m/\text{hr}$$

Recall that the average molecular weight of air is 29 lb_m/lb mole.

Step 3. The heat rate can be determined by two methods.

- a. By using the enthalpy values in Table 6-2b:

$$H \text{ for air at } 1,200^\circ\text{F} = 287.2 \text{ Btu/lb}_m$$

H for air at 90°F is obtained by interpolating:

$$= 9.6 - [9.6 (10/40)] = 7.2 \text{ Btu/lb}_m$$

$$q = m \Delta H = m (H_{\text{air}@1,200} - H_{\text{air}@90})$$

$$= (21,700 \text{ lb}_m/\text{hr})(287.2 - 7.2 \text{ Btu/lb}_m)$$

$$= 6,070,000 \text{ Btu/hr}$$

- b. By using Equation 6-6:

For air $C_p = 0.26 \text{ Btu/lb}_m^\circ\text{F}$:

$$q = m C_p \Delta T$$

$$= (21,700 \text{ Btu/hr})(0.26 \text{ Btu/lb}_m)(1,200-90^\circ\text{F})$$

$$= 6,260,000 \text{ Btu/hr}$$

This value is less accurate because it was calculated using an average value for C_p .

Step 4. To compute the amount of natural gas required from the heating rate, the available heat of the fuel (H_A) must be computed using Figure 6-17.

In Figure 6-17, the flue gas temperature is located on the x-axis ($1,200^\circ\text{F}$). Read up from this point to the line for natural gas with a heating value of 1,059 Btu/SCF. The heat available is read from the y-axis as approximately 690 Btu/SCF.

The amount of natural gas needed is:

$$Q_{\text{gas}} = \frac{q}{H_A} = \frac{6,070,000 \text{ Btu/hr}}{690 \text{ Btu/SCF}}$$

$$Q_{\text{gas}} = 8,780 \text{ SCF natural gas/hr}$$

Acid Gas Emissions

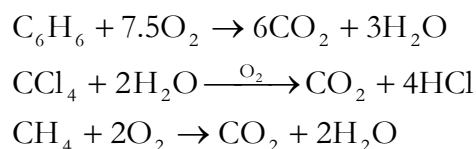
The oxidation of halogenated organic compounds generates compounds such as HCl and HF. The emission rates of these compounds must be calculated to determine if an absorption system is needed after the oxidizer. The calculation is a straightforward application of the combustion stoichiometry in the oxidizer. Problem 6-4 illustrates these procedures.

Problem 6-4

A thermal oxidizer is treating a 5,000 SCFM gas stream containing 500 ppm benzene and 120 ppm carbon tetrachloride. The oxidizer uses 300 SCFM of natural gas and operates at a temperature of $1,400^\circ\text{F}$. What is the concentration of HCl formed in the oxidizer's effluent gas stream? Assume that the oxidizer fuel is 100% methane, and that the burner is operated at 125% of the stoichiometric requirement.

Solution:

Step 1. Write the combustion reactions.



Step 2. Calculate the required amount of O_2 at stoichiometric conditions.

$$300 \text{ SCFM} \frac{\text{lb mole CH}_4}{385.4 \text{ SCF}} = 0.778 \text{ lb mole CH}_4/\text{min}$$

$$\text{Stoichiometric O}_2 = 2 \times (\text{lb mole CH}_4)$$

$$\frac{2 \text{ lb mole O}_2}{\text{lb mole CH}_4} \left(0.778 \frac{\text{lb mole CH}_4}{\text{min}} \right) = 1.56 \text{ lb mole O}_2/\text{min}$$

Step 3. Calculate air sent to the burner (125% of stoichiometric requirement).

$$\text{Total O}_2 \text{ requirement for methane fuel} = 1.25 \times (\text{stoichiometric requirement})$$

$$= 1.25 \left(\frac{1.56 \text{ lb mole O}_2}{\text{min}} \right) = 1.95 \text{ lb mole O}_2/\text{min}$$

$$\text{Total N}_2 = \frac{0.79 \text{ lb mole N}_2}{0.21 \text{ lb mole O}_2} \left(1.95 \frac{\text{lb mole O}_2}{\text{min}} \right)$$

$$= 7.34 \text{ lb mole N}_2/\text{min}$$

Step 4. Calculate the total flue gas flow rate:

Flue gas flow rate = Exhaust gas heated (a) + Products of combustion (b) + Excess oxygen & nitrogen (c)

- a. Exhaust gas heated = 5,000 SCFM – benzene and carbon tetrachloride oxidized

$$\text{C}_6\text{H}_6 = 5000 \text{ SCFM} \left(\frac{0.000500 \text{ lb mole C}_6\text{H}_6}{\text{lb mole total}} \right) = 2.5 \text{ SCFM}$$

$$\text{CCl}_4 = 5000 \text{ SCFM} \left(\frac{0.000120 \text{ lb mole CCl}_4}{\text{lb mole total}} \right) = 0.6 \text{ SCFM}$$

$$\text{Exhaust gas heated} = 5,000 \text{ SCFM} - (2.5 \text{ SCFM} + 0.6 \text{ SCFM})$$

$$= 4,996.9 \text{ SCFM (could have neglected change with negligible error)}$$

$$\text{Exhaust gas heated} = (4,996.9 \text{ SCFM}) \left(\frac{\text{lb mole}}{385.4 \text{ SCF}} \right)$$

$$= 12.97 \text{ lb mole/min}$$

- b. Products of combustion = CO₂ + H₂O + HCl

Amount of oxygen needed for carbon tetrachloride = 0 (no net oxygen consumption)

$$\begin{aligned} \text{Amount of oxygen remaining} &= \text{total} - \text{consumed} \\ &= 1.95 \text{ lb mole/min} - (1.56 \text{ lb mole/min} + 0.0487 \text{ lb mole/min}) \\ &= 0.34 \text{ lb mole/min} \end{aligned}$$

$$\begin{aligned} \text{Excess oxygen and nitrogen} &= 0.34 \text{ lb mole/min} + 7.34 \text{ lb mole/min} \\ &= 7.68 \text{ lb mole/min} \end{aligned}$$

Flue gas flow rate = Exhaust gas heated (a) + Products of combustion (b) + Excess oxygen & nitrogen (c)

$$\begin{aligned} &= 12.97 \text{ lb mole/min} + 2.41 \text{ lb mole/min} + 7.68 \text{ lb mole/min} \\ &= 23.06 \text{ lb mole/min} \end{aligned}$$

Step 5. Calculate the lb mole of HCl formed per minute.

$$\begin{aligned} &(5,000 \text{ SCFM}) \left(\frac{\text{lb mole total}}{385.4 \text{ SCF}} \right) \left(\frac{0.00012 \text{ lb mole CCl}_4}{\text{lb mole total}} \right) \left(\frac{4 \text{ lb mole HCl}}{\text{lb mole CCl}_4} \right) \\ &= 0.00623 \text{ lb mole/min} \end{aligned}$$

Step 6. Calculate the HCl concentration.

$$= \left(\frac{0.00623 \text{ lb mole HCl}}{23.06 \text{ lb mole total}} \right) (10^6 \text{ ppm}) = 270 \text{ ppm}$$

6.4 Instrumentation

High-Temperature, Gas-Phase Oxidation Systems

The thermal oxidizer system flowchart shown in Figure 6-18 includes the instrumentation commonly used to evaluate performance. These instruments are used to detect the onset of one or more of the following performance problems:

- Low gas temperatures
- Burner combustion problems
- Short-circuiting through the heat exchanger
- Reduced pollutant destruction due to restricted gas flow through the oxidizer
- Fouling and/or plugging of the heat exchanger
- Generation of additional pollutants in the oxidizer

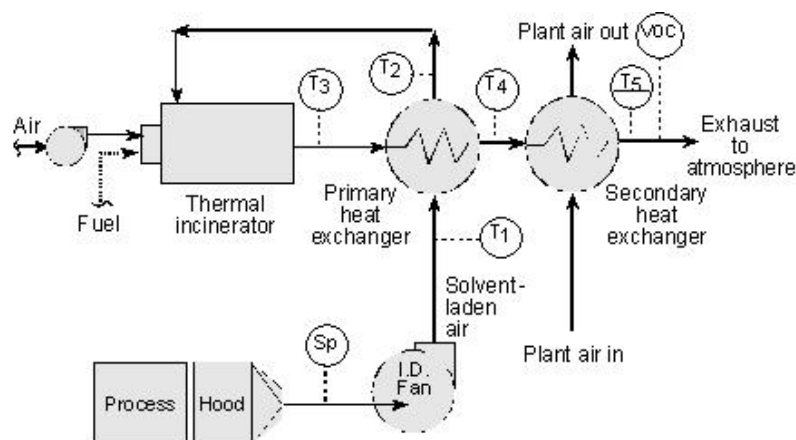


Figure 6-18. Flowchart of a thermal oxidizer system.

Gas Temperatures

The most important operating parameter used to evaluate the operation of thermal oxidizers is the outlet gas temperature (T_3). As stated earlier, this temperature should be 200°F to 300°F (110°C to 170°C) above the auto-ignition temperature of the most difficult-to-oxidize compound in the waste gas stream.

The outlet gas temperature should be monitored carefully during start-up of the unit. The combustion chamber should be preheated before introducing the waste gas stream to ensure that the gas temperatures will be sufficiently high. This preheat period also allows the oxidizer components, such as the refractory lining, to thermally expand at acceptable rates. For these reasons, thermal oxidizers do not usually go from cold off-line conditions to full on-line waste gas oxidation service on an immediate basis.

The inlet gas stream temperature increase across the recuperative or regenerative heat exchanger ($T_2 - T_1$) provides a useful indicator of its physical condition. The accumulation of particulate matter on either side of the unit reduces the heat transfer efficiency, resulting in increased fuel requirements.

The temperature of the exhaust to the atmosphere (T_5) should be monitored to ensure that it is well above the dew point temperature of the exhaust gas to prevent moisture condensation and the formation of artificial rain in the vicinity of the exhaust stack.

VOC Concentration

The outlet VOC concentration can be measured using portable VOC analyzers. The normal monitoring location is downstream of the secondary heat exchanger (Figure 6-18) so that the temperature is relatively low.

The VOC concentration measured by the portable instruments provides only a qualitative indication of the outlet concentration since the instruments respond differently to each organic compound. There is also some inevitable uncertainty regarding (1) the presence of partial oxidation products in the burner flame and (2) the incomplete combustion of the waste gas stream organic compounds.

Furthermore, thermal oxidizers often handle waste gas streams containing numerous organic compounds, and it is impractical to calibrate portable VOC analyzers for the exact mixture. Nevertheless, these instruments provide a very useful qualitative indicator of performance.

High outlet VOC concentrations could be due to low combustion chamber temperatures or the short-circuiting of inlet gas through the heat exchanger.

Catalytic Oxidation Systems

The instrumentation used with catalytic oxidizers is somewhat more extensive than that used for thermal oxidizers because of the presence of the vulnerable catalyst. Figure 6-19 illustrates the type of instrumentation used to support performance evaluation of catalytic oxidizers.

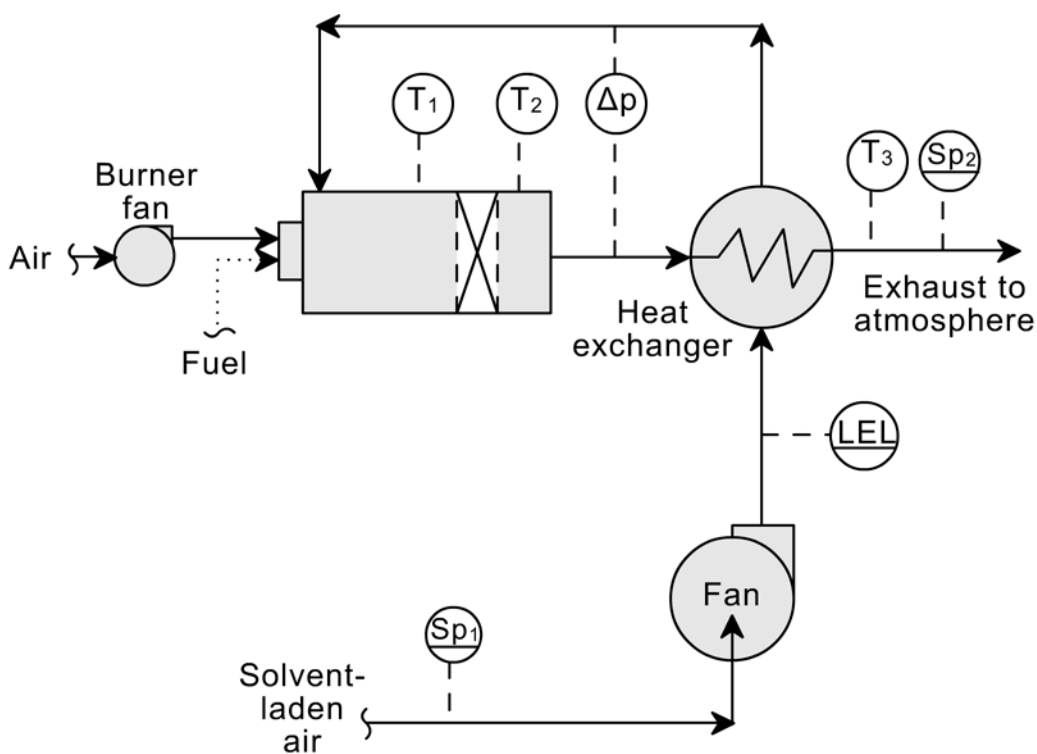


Figure 6-19. Flowchart of a catalytic oxidizer system.

Gas Temperatures

The inlet and outlet gas temperatures (Figure 6-19) of the catalyst bed provide useful indirect indicators of the performance of the system. The inlet gas temperature should be above the minimum level necessary for high-efficiency destruction of the organic compounds being treated. During routine operation, the bed outlet temperature should be 50°F to 200°F (30°C to 110°C) higher than the inlet temperature, because the oxidation reactions are exothermic. If the catalyst bed has become fouled, masked, or poisoned, the gas temperature increase across the bed will not be as high as baseline levels.

The gas temperature rise across the catalyst bed is also related to the concentration of organic vapor in the waste gas stream. A decrease in the inlet VOC concentration will also cause a decrease in the temperature rise across the catalyst bed. Accordingly, changes in the inlet VOC concentration should be evaluated along with the temperature data. The inlet VOC concentration is usually monitored by an LEL detector. During start-up periods, the oxidizer should be preheated to the operating temperature using the supplemental burner. If the organic vapor-laden waste gas stream is directed to the oxidizer before it is hot, many of the organics will not be destroyed, and contaminants could condense on the catalyst surfaces.

High oxidizer outlet gas temperatures can damage the recuperative heat exchanger. In extreme cases, it is also possible to volatilize a portion of the catalyst. Accordingly, the outlet temperature should be monitored. High outlet temperatures can be caused by short-term, high-concentration surges of organics in the waste gas stream or may be due to the ignition of carbonaceous deposits on a portion of the catalyst bed.

Outlet VOC Concentration

A portable VOC analyzer can be used to qualitatively monitor the outlet organic concentration from the oxidizer. Outlet concentrations considerably higher than baseline levels indicate the need to evaluate the catalyst activity.

Review Exercises

Types and Components of Oxidizer Systems

1. A recuperative heat exchanger is composed of _____.
 - a. packed beds of ceramic material
 - b. tube banks
 - c. rotating cylinder with heat exchange baskets
 - d. n one of the above

2. Regenerative heat exchangers are capable of heat recoveries up to ____ efficiency.
 - a. 40% to 65%
 - b. 65% to 90%
 - c. 90% to 95%
 - d. 95% to 99%

3. Recuperative heat exchangers are capable of heat recoveries up to ____ efficiency.
 - a. 40% to 65%
 - b. 65% to 90%
 - c. 90% to 95%
 - d. 95% to 99%

4. Regenerative heat exchangers are vulnerable to _____.
 - a. plugging due to particulate matter
 - b. poisoning due to phosphorus
 - c. deactivation due to sulfur compounds
 - d. None of the above

5. What type of air pollution control system is generally used to collect acid gases formed during the oxidation of halogenated organic compounds?
 - a. Absorbers
 - b. Adsorbers
 - c. Condensers
 - d. None of the above

6. What is the typical operating temperature range (bed inlet) of a catalytic oxidizer?
 - a. 200°F to 500°F
 - b. 500°F to 900°F
 - c. 900°F to 1400°F
 - d. 1400°F

7. What is the typical operating temperature range (bed inlet) of a thermal oxidizer?
 - a. 200°F to 800°F
 - b. 800°F to 1200°F
 - c. 1200°F to 1800°F
 - d. >1800°F

8. When is the burner operated in a catalytic oxidizer? Select all that apply.
 - a. During start-up and shutdown
 - b. When the concentration of the contaminant is too low to provide sufficient heat for the oxidation reactions in the catalyst bed
 - c. When the heat exchanger has too low of an efficiency to increase inlet gas temperature sufficiently for the necessary oxidation temperature
 - d. All of the time

9. When is the burner operated in a thermal oxidizer? Select all that apply.
 - a. During start-up and shutdown
 - b. When the concentration of the contaminant is too low to provide sufficient heat for the oxidation reactions in the oxidizer chamber
 - c. When the heat exchanger has too low of an efficiency to increase inlet gas temperature sufficiently for the necessary oxidation temperature
 - d. All of the time

10. What is the typical inlet contaminant concentration for thermal and catalytic oxidizers?
 - a. < 5% of the LEL of the gas mixture
 - b. < 25% of the LEL of the gas mixture
 - c. < 50% of the LEL of the gas mixture
 - d. < 75% of the LEL of the gas mixture

Operating Principles of Oxidizer Systems

11. What is the typical operating temperature of a thermal oxidizer?
 - a. The average auto-ignition temperature of the gas mixture
 - b. 200°F to 300°F above the average auto-ignition temperature of the gas mixture
 - c. The auto-ignition temperature of the most difficult-to-oxidize major gas stream contaminant
 - d. 200°F to 300°F above the auto-ignition temperature of the most difficult-to-oxidize major gas stream contaminant

12. What is the typical residence time for gas streams in the combustion chamber of a thermal oxidizer?
 - a. Up to 0.3 seconds

- b. 0.3 to 2 seconds
 - c. 2 to 5 seconds
 - d. Greater than 5 seconds
13. What are some of the consequences of a high-temperature gas surge in a catalytic oxidizer? Select all that apply.
- a. The catalyst could volatilize and be lost to the gas stream.
 - b. A recuperative heat exchanger could warp and develop leaks.
 - c. The catalyst could sinter.
 - d. There are no consequences of high-temperature surges.

Capability and Sizing of Oxidizer Systems

14. How many lb moles of combustion air are needed to burn 1 SCF of methane (CH_4) if the burner operates with 15% excess air?
15. The preheated waste gas stream of 4,000 ACFM enters a thermal oxidizer. The waste gas stream temperature is 1000°F , and the pressure is +6 in W.C. How much natural gas is needed to incinerate this gas stream at a temperature of $1,500^\circ\text{F}$? Use an air concentration of 21% oxygen and 79% nitrogen in solving the problem.

Review Answers

Types and Components of Oxidizer Systems

1. A recuperative heat exchanger is composed of _____.
 - b. tube banks
2. Regenerative heat exchangers are capable of heat recoveries up to ____ efficiency.
 - c. 90% to 95%
3. Recuperative heat exchangers are capable of heat recoveries up to ____ efficiency.
 - a. 40% to 65%
4. Regenerative heat exchangers are vulnerable to _____.
 - a. plugging due to particulate matter
5. What type of air pollution control system is generally used to collect acid gases formed during the oxidation of halogenated organic compounds?
 - a. Absorbers
6. What is the typical operating temperature range (bed inlet) of a catalytic oxidizer?
 - b. 500°F to 900°F
7. What is the typical operating temperature range (bed inlet) of a thermal oxidizer?
 - c. 1200°F to 1800°F
8. When is the burner operated in a catalytic oxidizer? Select all that apply.
 - a. During start-up and shutdown
 - b. When the concentration of the contaminant is too low to provide sufficient heat for the oxidation reactions in the catalyst bed
 - c. When the heat exchanger has too low of an efficiency to increase inlet gas temperature sufficiently for the necessary oxidation temperature
9. When is the burner operated in a thermal oxidizer? Select all that apply.
 - a. During start-up and shutdown
 - b. When the concentration of the contaminant is too low to provide sufficient heat for the oxidation reactions in the oxidizer chamber
 - c. When the heat exchanger has too low of an efficiency to increase inlet gas temperature sufficiently for the necessary oxidation temperature
10. What is the typical inlet contaminant concentration for thermal and catalytic oxidizers?

- b. < 25% of the LEL of the gas mixture

Operating Principles of Oxidizer Systems

11. What is the typical operating temperature of a thermal oxidizer?
 d. 200°F to 300°F above the auto-ignition temperature of the most difficult-to-oxidize major gas stream contaminant
12. What is the typical residence time for gas streams in the combustion chamber of a thermal oxidizer?
 b. 0.3 to 2 seconds
13. What are some of the consequences of a high-temperature gas surge in a catalytic oxidizer? Select all that apply.
 a. The catalyst could volatilize and be lost to the gas stream.
 b. A recuperative heat exchanger could warp and develop leaks.
 c. The catalyst could sinter.

Capability and Sizing of Oxidizer Systems

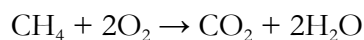
14. How many lb moles of combustion air are needed to burn 1 SCF of methane (CH₄) if the burner is operating with 15% excess air?

Solution:

Step 1. Calculate the lb mole of CH₄ burned.

$$\begin{aligned} \text{Pound mole of methane} &= \\ \left(\frac{1.0 \text{ lb mole}}{385.4 \text{ SCF}} \right) 1.0 \text{ SCF CH}_4 &= 0.00259 \text{ lb mole CH}_4 \end{aligned}$$

Step 2. Write the combustion reaction.



Step 3. Calculate the O₂ and N₂ required.

$$\begin{aligned} \text{Pound mole of O}_2 \text{ needed} &= (0.00259 \text{ lb mole CH}_4) \left(\frac{2 \text{ lb mole O}_2}{1 \text{ lb mole CH}_4} \right) \\ &= 0.00519 \text{ lb mole O}_2 \end{aligned}$$

$$\begin{aligned} \text{At 15\% excess air, lb mole of air} &= 1.15 (0.00519 \text{ lb mole O}_2) \\ &= 0.0060 \text{ lb mole O}_2 \end{aligned}$$

$$\begin{aligned} \text{Pound mole N}_2 \text{ fed} &= \left(\frac{0.79 \text{ lb mole N}_2}{0.21 \text{ lb mole O}_2} \right) (0.0060 \text{ lb mole O}_2) \\ &= 0.0226 \text{ lb mole N}_2 \end{aligned}$$

Step 4. Calculate the air fed for 15% excess air.

$$\begin{aligned} \text{Air needed} &= 0.0060 + 0.0226 \\ &= 0.0286 \text{ lb mole air} \end{aligned}$$

15. The preheated waste gas stream of 4,000 ACFM enters a thermal oxidizer. The waste gas stream temperature is 1000°F, and the pressure is +6 in. W.C. How much natural gas is needed to incinerate this gas stream at a temperature of 1,500°F? Use an air concentration of 21% oxygen and 79% nitrogen in solving the problem.

Solution:

Step 1. Determine the enthalpy change for 1 SCF of air based on data in Table 6-2a.

$$\text{Enthalpy of air @ } 1000^\circ\text{F} = 17.92 \text{ Btu/SCF}$$

$$\text{Enthalpy of air @ } 1500^\circ\text{F} = 28.24 \text{ Btu/SCF}$$

$$\begin{aligned} \text{Change in enthalpy} &= 28.24 \text{ Btu/SCF} - 17.92 \text{ Btu/SCF} \\ &= 10.32 \text{ Btu/SCF} \end{aligned}$$

Step 2. Convert the gas flow rate to SCFM.

$$\text{SCFM} = 4000 \text{ ACFM} \left(\frac{528^\circ\text{R}}{1000^\circ\text{F} + 460^\circ\text{R}} \right) \left(\frac{407 + 6 \text{ in. W.C.}}{407 \text{ in. W.C.}} \right) = 1470 \text{ SCFM}$$

Step 3. Calculate the total change in enthalpy of the gas stream heated to 1500°F.

$$(1470 \text{ SCF/min})(10.32 \text{ Btu/SCF}) = 15,170 \text{ Btu/min}$$

Step 4. Calculate the natural gas requirement using the available heat at 1500°F (data in Figure 6-14).

$$\left(15,170 \frac{\text{Btu}}{\text{min}} \right) \left(\frac{\text{SCF of gas}}{600 \text{ Btu available heat}} \right) = 25.3 \text{ SCF/min of gas}$$

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