B.7 CATALYTIC OXIDIZERS$^{1,2,16,17}$

B.7.1 Background

Catalytic oxidizers are oxidation systems (similar to thermal oxidizers) that control VOC and volatile HAP emissions. Catalytic oxidizers use a catalyst to promote the oxidation of VOCs to CO$_2$ and water (i.e., increase the kinetic rate).

The design of the oxidation system is dependent on the pollutant concentration in the waste gas stream, type of pollutant, presence of other gases, level of oxygen, stability of processes vented to the system, and degree of control required. Important design factors include temperature (an operating temperature high enough to oxidize the waste gas on the catalyst), residence time (sufficient residence time in the catalyst bed for the oxidation reaction to occur), turbulence or mixing of combustion air with the waste gas, VOC concentration and species, catalyst characteristics, and the presence of masking agents in the waste gas that can reduce the effectiveness of the catalyst bed. Time, temperature, degree of mixing, and sufficient O$_2$ govern the completeness of the combustion reaction. Of these, only the temperature and the oxygen can be significantly controlled after construction. Residence time and mixing are fixed by incinerator design, and flow rate can be controlled only over a limited range.

The rate at which VOC compounds and volatile HAP are oxidized is greatly affected by temperature; the higher the temperature, the faster the oxidation reaction proceeds. The operating temperature needed to achieve a particular VOC control efficiency depends on the species of pollutants, concentration, and the catalyst type. Each pollutant has a temperature which must be reached to initiate the catalytic oxidation reaction. The initiation temperature is also dependent on the type of catalyst. The use of the catalyst allows the combustion reaction to occur at a lower temperature than the autoignition temperature. Catalytic oxidizers generally operate between 650°F and 1000°F.

The catalyst support and bed geometry influence the size and shape of the catalyst bed and affect the pressure differential across the bed. The catalyst typically lasts 2 to 5 years. Thermal aging over the lifetime of the catalyst and the presence of PM and catalyst poisons in the inlet gas streams reduce the catalyst’s ability to promote the oxidation reaction by masking and coating the catalyst, thereby preventing contact between VOC and the catalyst surface.

Thorough mixing is necessary to ensure that all waste and fuel come in contact with oxygen. Because complete mixing generally is not achieved, excess air/oxygen is added (above stoichiometric or theoretical amount) to ensure complete combustion. For catalytic oxidizers, good mixing of the waste gas and oxygen promotes uniform oxidation in the catalyst bed and avoids localized heating of bed sections.

Normal operation of a catalytic oxidizer is characterized by a fixed inlet gas temperature and a higher bed outlet temperature. A thermocouple, or other temperature monitoring device, is placed at the inlet to the catalyst bed to measure the temperature of the preheated waste gas.
stream. A thermocouple at the outlet to the catalyst bed can be connected to a controller that maintains the desired catalyst bed temperature by altering the rate of auxiliary fuel consumption in the oxidizer’s burner. A variety of operating parameters that may be used to indicate good operation include: outlet VOC concentration, inlet temperature (prior to catalyst bed), outlet temperature (after catalyst bed), pressure differential across oxidizer sections (preheat, catalyst bed, heat exchanger), auxiliary fuel input, and outlet CO concentration. Periodic tests of samples of the catalyst also may be used to confirm performance of the catalyst.

B.7.2 Indicators of Catalytic Oxidizer Performance

The primary indicators of catalytic oxidizer performance are the outlet VOC or volatile HAP concentration, catalyst bed inlet temperature, and catalyst activity. Other indicators of catalytic oxidizer performance include outlet CO concentration, temperature rise across the catalyst bed, exhaust gas flow rate, catalyst bed outlet temperature, fan current, outlet O₂ or CO₂ concentration, and pressure differential across the catalyst bed. Each of these indicators is described below. Table B-7 lists these indicators and illustrates potential monitoring options for catalytic oxidizers that are used for VOC or volatile HAP control.

Outlet VOC concentration. The most direct single indicator of the performance of a catalytic oxidizer is the VOC or volatile HAP concentration at the outlet of the unit.

Catalyst bed inlet temperature. The temperature at the inlet to the catalyst bed is a key catalytic oxidizer operating parameter. The inlet gas stream must be heated to the minimum temperature at which catalytic oxidation will occur on the bed. Above this minimum temperature, as temperature increases, control efficiency also increases.

Catalyst activity. When the catalyst becomes contaminated or masked, the control efficiency of the unit decreases. Catalyst deactivation will result in increased VOC emissions. The catalyst should be tested periodically to determine its activity.

Outlet CO concentration. The CO concentration at the outlet of a catalytic oxidizer provides a good indication of combustion efficiency. The presence of CO indicates incomplete combustion. An increase in CO levels indicates a decrease in combustion efficiency.

Temperature rise across catalyst bed. The temperature rise across the catalyst bed provides an indication of the degree of combustion that is occurring in the unit. The greater the level of combustion, the greater the rise in temperature. Because the temperature rise is dependent on the degree of combustion occurring across the catalyst, the temperature rise is dependent upon the inlet VOC loading to the catalyst. In other words, if the VOC loading to the oxidizer is reduced, the temperature rise across the catalyst will decrease. Consequently, a decrease in temperature rise across the catalyst is not necessarily an indication of reduced performance, but may simply be an indication of reduced VOC loading to the oxidizer.
Exhaust gas flow rate. Catalytic oxidizer control efficiency is primarily a function of catalyst bed inlet temperature and space velocity (similar to residence time), and space velocity is a function of exhaust gas flow rate. Consequently, as flow rate increases, space velocity increases and control efficiency may decrease. For processes with fairly constant flow rates, exhaust gas flow rate is not as good an indicator of performance as is bed inlet temperature because temperature has a much greater effect on control efficiency than small variations in flow rates.

Catalyst bed outlet temperature. For a particular type of catalyst, there is a maximum operating temperature, above which the catalyst begins to sinter. Monitoring the bed outlet temperature can ensure that the temperature within the bed does not exceed its working limit. In addition, the bed outlet temperature is an indicator that minimum oxidation temperatures are occurring in the unit.

Fan current. Changes in fan current generally correspond to changes in exhaust gas flow rate. Consequently, fan current can be a surrogate for exhaust gas flow rate. An increase in fan current would signify an increase in flow rate and space velocity.

Outlet O₂ or CO₂ concentration. Outlet O₂ or CO₂ concentration by itself does not provide an indication of thermal oxidizer performance. However, monitoring the O₂ or CO₂ level provides an indication of the excess air rate and may be used to normalize the measured VOC concentration to a standard O₂ or CO₂ level. For emission limits that specify VOC concentrations corrected to a specified percent O₂, monitoring both the VOC and O₂ concentrations would be required to determine compliance.

Pressure differential across catalyst bed. For inlet gas streams that contain significant levels of PM, bed fouling or plugging can be a problem. An increase in pressure differential across the bed is an indicator that plugging is occurring. Pressure differential across the catalyst bed should be maintained within an optimal pressure differential range for the system. Changes in pressure differential are likely to be gradual over time.

B.7.3 Illustrations

The following illustration presents examples of compliance assurance monitoring for catalytic oxidizers:

7a: Monitoring catalyst bed inlet temperature and catalyst bed outlet temperature.
7b: Monitoring catalyst bed inlet temperature and catalyst activity check.
7c: Monitoring catalyst bed inlet temperature, catalyst bed outlet temperature, and outlet CO concentration.

B.7.4 Bibliography
<table>
<thead>
<tr>
<th>Parameters</th>
<th>Performance indication</th>
<th>Approach No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Illustration No.</td>
<td>7a</td>
<td></td>
<td></td>
<td></td>
<td>7b</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Example CAM Submittals</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Comment</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Primary Indicators of Performance</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Outlet VOC concentration</td>
<td>Direct measure of outlet concentration. Most direct single indicator of oxidizer performance.</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalyst bed inlet temperature</td>
<td>Indicator that bed inlet is of sufficient temperature to initiate oxidation. Above the minimum oxidation temperature, control efficiency increases with increasing bed inlet temperature.</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Catalyst bed activity</td>
<td>Indicates contamination, masking, or deactivation of the catalyst; the control efficiency of the unit decreases as catalyst activity decreases.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td><strong>Other Performance Indicators</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Outlet CO concentration</td>
<td>Indicator of combustion efficiency. Presence of CO indicates incomplete combustion.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Temperature rise across bed</td>
<td>Indicates level of combustion occurring in unit. The greater the degree of combustion, the greater the temperature rise. NOTE: Degree of combustion and resulting temperature rise is dependent upon VOC loading to control device. As VOC loading decreases, temperature rise also will decrease, even when combustion efficiency is being maintained. Therefore, may not be an appropriate indicator for situations where VOC loading to oxidizer varies greatly.</td>
<td></td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exhaust gas flow rate</td>
<td>Determines space velocity within catalyst bed. Increase in flow rate generally indicates an increase in space velocity and may result in a decrease in control level.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Catalyst bed outlet temperature</td>
<td>Indicates level of combustion occurring in unit. Indicator used to assure temperature does not exceed design limits of bed. If bed outlet temperature exceeds working limit, the catalyst bed can be destroyed.</td>
<td></td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### TABLE B-7. (Continued)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Performance indication</th>
<th>Approach No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure differential across bed</td>
<td>Indicator of bed fouling or plugging. Increase in pressure differential indicates that bed is becoming fouled or plugged. Changes in pressure differential are likely to be gradual.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
</tbody>
</table>

**Comments:**
- Approach No. 1 is specified by several NSPS and by 40 CFR 63, subparts U (Polymers and Resins I), DD (Offsite Waste and Recovery), JJ (Wood Furniture), HH (Oil and Natural Gas), and OOO (Polymers and Resins III).
- Approach No. 2 is required by 40 CFR 60, subparts III ( ) and NNN (Wool Fiberglass).
- Approach No. 3 is specified as an alternative monitoring approach by 40 CFR 63, subpart G (HON), DD (Offsite Waste and Recovery), HH (Oil and Natural Gas), MMM (Pesticides) and OOO (Polymers and Resins III).
- Approach No. 4 is required by 40 CFR 63, subpart G (HON), CC (Petroleum Refiners), EE (Magnetic Tape) GG (Aerospace), MMM (Pesticides), and JJJ (Polymers and Resins IV).
- Approach No. 5 corresponds to 40 CFR 63, subpart JJ (Wood Furniture) for fluidized catalyst bed.

*Both KK & O use inlet T only.* Do not include/recommend these.
CAM ILLUSTRATION
No. 7a. CATALYTIC OXIDIZER FOR VOC CONTROL

1. APPLICABILITY

1.1 Control Technology: Catalytic incinerator [019]; also applicable to catalytic afterburners with or without heat exchangers [019, 020]

1.2 Pollutants
   Primary: Volatile organic compounds (VOCs)
   Other: High molecular weight organic compounds

1.3 Process/Emissions Unit: Coating, spraying, printing, polymer manufacturing, distillation units, wastewater treatment units, air oxidation units, petroleum refining, miscellaneous SOCMI units

2. MONITORING APPROACH DESCRIPTION

2.1 Parameters to be Monitored: Catalyst bed inlet and outlet temperatures.

2.2 Rationale for Monitoring Approach
   • Catalyst bed inlet temperature: Indicates whether the gas flowing into catalyst bed is of sufficient temperature to initiate oxidation.
   • Catalyst bed outlet temperature: Indication that combustion is occurring on the catalyst bed, allows for calculation of temperature differential across bed, and that temperature does not exceed design limits of the catalyst.

2.3 Monitoring Location
   • Catalyst bed inlet temperature: Preheat chamber outlet or catalyst bed inlet.
   • Catalyst bed outlet temperature: Catalyst bed outlet.

2.4 Analytical Devices Required: Thermocouples, RTDs, or alternative methods/instrumentation as appropriate for specific gas stream.

2.5 Data Acquisition and Measurement System Operation
   • Frequency of measurement: Hourly if manually read, or recorded continuously on strip chart or data acquisition system; continuously if CEMS.
   • Reporting units: Degrees Fahrenheit or Celsius (°F, °C).
   • Recording process: Operators log data manually, or recorded automatically on strip chart or data acquisition system.

2.6 Data Requirements
   • Baseline catalyst bed inlet and outlet temperatures concurrent with emission test; or
   • Historical plant records on catalyst bed inlet and outlet temperature measurements.

2.7 Specific QA/QC Procedures
   • Calibrate, maintain, and operate instrumentation using procedures that take into account manufacturer’s specifications.

2.8 References: 1, 2, 3, 4, 16, 17.
3. COMMENTS

3.1 Data Collection Frequency: For large emission units, collection of four or more data points each hour is required. (See Section 3.3.1.2.)
1. APPLICABILITY

1.1 Control Technology: Catalytic incinerator [019]; also applicable to catalytic afterburners with or without heat exchangers [019, 020]

1.2 Pollutants
   Primary: Volatile organic compounds (VOCs)
   Other: High molecular weight organic compounds

1.3 Process/Emissions Unit: Printing and publishing

2. MONITORING APPROACH DESCRIPTION

2.1 Parameters to be Monitored: Catalyst bed inlet temperature and catalyst activity.

2.2 Rationale for Monitoring Approach
   • Catalyst bed inlet temperature: Indicates whether the gas flowing into catalyst bed is of sufficient temperature to initiate oxidation.
   • Catalyst activity: Determines conversion efficiency of catalyst; indicates that catalyst is not poisoned or masked beyond operational range.

2.3 Monitoring Location
   • Catalyst bed inlet temperature: Preheat chamber outlet or catalyst bed inlet.
   • Catalyst activity: Sample of catalyst.

2.4 Analytical Devices Required
   • Temperature: Thermocouples, RTDs, or alternative methods/instrumentation as appropriate for specific gas stream.
   • Catalyst activity: Qualified laboratory (e.g., catalyst manufacturer) for determining activity of catalyst sample.

2.5 Data Acquisition and Measurement System Operation
   • Temperature:
     – Frequency of measurement: Hourly or recorded continuously on strip chart or data acquisition system.
     – Reporting units: Degrees Fahrenheit or Celsius (°F, °C).
     – Recording process: Operators log data manually, or recorded automatically on strip chart or data acquisition system.
   • Catalyst activity: Annual analyses of catalyst sample.

2.6 Data Requirements
   • Temperature:
     – Baseline catalyst bed inlet and outlet temperatures concurrent with emission test; or
     – Historical plant records on catalyst bed inlet and outlet temperature measurements.
   • Catalyst activity: Laboratory results of conversion efficiency.

2.7 Specific QA/QC Procedures
• Calibrate, maintain, and operate instrumentation using procedures that take into account manufacturer’s specifications.

2.8 References: 1, 2, 3, 4, 16, 17.

3. COMMENTS

3.1 Data Collection Frequency: For large emission units, a measurement frequency of once per hour would not be adequate; collection of four or more data points each hour is required. (See Section 3.3.1.2.)

3.2 This illustration is applicable for catalytic systems controlling process streams that exhibit a highly variable range of VOC concentration, thereby making the use of temperature differential as a routine monitoring parameter impractical.
1. APPLICABILITY

1.1 Control Technology: Catalytic incinerator [019]; also applicable to catalytic afterburners with or without heat exchangers [019, 020]

1.2 Pollutants
   Primary: Volatile organic compounds (VOCs)
   Other: High molecular weight organic compounds

1.3 Process/Emissions Unit: Coating, spraying, printing, polymer manufacturing, distillation units, wastewater treatment units, air oxidation units, petroleum refining, miscellaneous SOCMI units

2. MONITORING APPROACH DESCRIPTION

2.1 Parameters to be Monitored: Catalyst bed inlet and outlet temperatures and outlet CO concentration.

2.2 Rationale for Monitoring Approach
   • Catalyst bed inlet temperature: Indicates whether the gas flowing into catalyst bed is of sufficient temperature to initiate oxidation.
   • Catalyst bed outlet temperature: Indication that combustion is occurring on the catalyst bed, allows for calculation of temperature differential across bed, and that temperature does not exceed design limits of the catalyst.
   • Outlet CO concentration: CO is a product of incomplete combustion and is an indicator of combustion efficiency.

2.3 Monitoring Location
   • Catalyst bed inlet temperature: Preheat chamber outlet or catalyst bed inlet.
   • Catalyst bed outlet temperature: Catalyst bed outlet.
   • Outlet CO concentration: Outlet to oxidizer.

2.4 Analytical Devices Required
   – Catalyst bed inlet temperature: Thermocouples, RTDs, or alternative methods/instrumentation as appropriate for specific gas stream.
   – Catalyst bed outlet temperature: Thermocouples, RTDs, or alternative methods/instrumentation as appropriate for specific gas stream.
   – Outlet CO concentration: Nondispersive infrared (NDIR) analyzer calibrated to manufacturer’s specifications, or other methods or instrumentation.

2.5 Data Acquisition and Measurement System Operation
   • Frequency of measurement
     – Catalyst bed inlet temperature: Hourly, or recorded continuously on strip chart or data acquisition system.
     – Catalyst bed outlet temperature: Hourly, or recorded continuously on strip chart or data acquisition system.
     – Outlet CO concentration: Continuously.
• Reporting units
  – Catalyst bed inlet temperature: Degrees Fahrenheit or Celsius (°F, °C).
  – Catalyst bed outlet temperature: Degrees Fahrenheit or Celsius (°F, °C).
  – Outlet CO concentration: Parts per million by volume (ppmv), dry basis.
• Recording process: Operators log data manually, or recorded automatically on strip chart or data acquisition system.

2.6 Data Requirements
• Baseline catalyst bed inlet and outlet temperatures and outlet CO concentration concurrent with emission test; or
• Historical plant records on catalyst bed inlet and outlet temperature and outlet CO concentration measurements.

2.7 Specific QA/QC Procedures
• Calibrate, maintain, and operate instrumentation using procedures that take into account manufacturer’s specifications.

2.8 References: 1, 2, 3, 4, 16, 17.

3. COMMENTS

3.1 Data Collection Frequency: For large emission units, a measurement frequency of once per hour would not be adequate; collection of four or more data points each hour is required. (See Section 3.3.1.2.)