Catalytic oxidation controls VOC emissions

The best way to reduce volatile organic compounds (VOCs) is to not generate them in the first place. Recycling, source reduction, alternative materials, and improved processing equipment and procedures often can reduce or eliminate VOCs. If this is not possible, they must be removed from the exhaust by either oxidation, condensation, scrubbing or adsorption.

Oxidation, or incineration, is used most often because, among other things, it generates no solid or liquid waste and so creates no waste-disposal concerns. Chemical Process Industries' (CPI) exhausts are usually dilute mixtures of combustible gases in air with too low a heating value to burn completely. To avoid the organic compounds that form during partial combustion, which could worsen the VOC load, gases entering the incinerator are heated to a high enough temperature so the VOCs oxidize to water and carbon dioxide. If not enough oxygen is available, supplemental air is added.

VOC oxidizers are either thermal units that use heat alone or catalytic units that pass VOCs over a catalyst at an elevated temperature. The latter speed oxidation and are able to operate at temperatures well below those of thermal systems.

Thermal systems
The simplest thermal system is a direct-flame incinerator that has a combustion chamber lined with heat-resistant ceramic and a nozzle burner. Incinerator temperature depends on the VOCs present, how much is to be destroyed and residence time in the reactor. Temperature typically lies between 1350°F and 2000°F for residence times of a second or less. Field data show that 98% of non-halogenated VOCs are oxidized at 1600°F in 0.75 seconds.

Fuel use, the major operating expense in a thermal unit, is reduced by transferring heat from the hot exit gases to those entering the oxidizer. Recuperative incinerators recycle as much as 70% of the heat in the exit gas back to the combustion chamber. Incoming gases are kept below 1200°F so they do not combust in the exchanger. The unit can include a second exchanger to extract heat to make steam for use in the process or elsewhere in the facility.

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combustion chamber. The exit gas heats one bed until its temperature stabilizes. The flow is then reversed so incoming gas is heated by this bed. The exit gas heats the other bed until it equilibrates, and the flow is once again reversed.

**Catalytic systems**

Catalytic systems for VOC abatement are usually fixed-bed units that heat process off-gases to reaction temperature before they contact the catalyst. They often include primary and secondary heat exchangers (Figure 1). Residence times are on the order of 0.05 to 0.1 second or roughly a tenth of those in thermal incinerators because oxidation occurs more rapidly. Catalytic systems operate at 300°F to 1000°F cooler than thermal systems. Figure 2 shows catalyst operating temperatures needed for a range of solvents and other organic chemicals with standard-activity VOC catalysts. New high-activity catalysts often enable operation at an even lower temperature.

The lower temperature and residence time as compared to thermal oxidizers mean that catalytic units have:

- a smaller reactor with far less thermal insulation;
- heat exchangers made from low-grade stainless steel, rather than from expensive, high-temperature alloy steels;
- less thermal stress, which decreases leakage and lowers maintenance, especially in units started and stopped frequently. Repair or replacement of refractory and expensive shell-and-tube heat-exchanger components is decreased.
- lower ignition temperatures reduce fuel costs (Figure 1). Thermal systems often cost more than twice as much to run, even with the factor of 60% heat recovery.

The catalyst can be either a precious metal like platinum, palladium or rhodium or a base metal like copper, manganese or cobalt. Platinum is most frequently used because it functions well at low temperatures yet has good high-temperature stability and resists contaminants.

**Designing an incinerator**

VOC oxidizers are tailored to each application based on such detailed information as:

- process exhaust-gas flow rate, temperature, pressure and composition. The latter includes VOCs present, oxygen, moisture and particulate content.
- federal and state regulations governing VOC oxidation and other gases. For example, the high temperature in thermal facilities may generate excess nitrogen oxides.
- the gas stream’s lower explosion limit and heat of combustion; and
- the end user’s safety and equipment specifications.

In thermal units, reactor temperature is defined by the VOCs present, how much of the VOCs must be eliminated and residence time. Heat-exchanger size balances exchanger cost and fuel reduction. Heat exchangers also are sized to keep incoming gas temperature below the combustion point in the exchanger but high enough to prevent any acid vapors present from condensing out.

Catalytic units go through many of the same design calculations as thermal units. Reactor temperature, which is the sum of inlet temperature and the temperature rise as the VOCs combust, must remain below 1475°F to prevent catalyst damage.

**Choosing the right technology**

Thermal and catalytic units destroy nearly all VOCs. Until now, approximately 70% of all VOC oxidizers have been thermal units because they have been used in large facilities that needed the steam and heat generated. Thermal units are used, for example, in maleic anhydride plants where large amounts of carbon monoxide and butane give the off gases a high heating value. As chemical facilities that have a lesser need for steam and heat or exhaust streams with lower heat contents install VOC-abatement equipment to comply with legislation, catalytic systems will play a greater role.

Given the many factors involved, energy and economic analyses are the only way to choose which unit to use. The choice between the two types of units depends on considerations like:
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- waste-stream heating value. Low heating values due to low VOC concentration make catalytic systems more attractive because thermal systems require more fuel to reach operating temperature. Catalytic systems are often not used when VOC concentration is greater than 25% of the lower explosive limit.

- waste-gas components that might affect catalyst performance. This issue has been solved to a great extent by new catalyst formulations that overcome many contaminant problems. Catalyst systems can use a guard bed to protect the catalyst.

- the type of fuel available. Natural gas and #2 fuel oil work well in catalytic systems. Other fuels should be evaluated on a case-by-case basis.

- incinerator space and weight limitations that favor the smaller and lighter catalytic systems, especially in retrofits. Existing thermal oxidizers can frequently be converted to catalytic operation to increase conversion or reduce fuel use.

  Thermal oxidation is often selected when a waste stream has enough VOCs to sustain complete oxidation with little or no auxiliary fuel, when steam generation is of value and when effluent contaminants would hinder catalyst operation.

  Catalytic oxidation is commonly chosen to reduce fuel consumption when smaller, lighter systems are needed and when potential NOx and CO emissions from a thermal unit could exceed locally regulated levels. Catalytic units are often best for variable or batch processes because they are easily started and shut down. Catalytic systems are highly economical. They have become more flexible due to the development of new catalyst formulations that have higher activity and/or resist contaminants. In addition, improved regeneration methods have extended the life of catalysts.

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