VOC and Air Toxics Control by Oxidation and Other Methods

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State and federal regulations require control of a wide range of organic vapors. Control applications exist in food processing, coatings, general manufacturing, plastics/rubber, packaging/printing, pharmaceuticals, chemicals, refining, electronics, pulp/paper/engineered wood, and other industries. This article covers the major issues involved in design and specification of organic vapor control systems.

Controls for volatile organic compounds (also referred to variously at VOCs, air toxics, and organic vapors) are generally required to provide >95 percent removal. In addition to old limits such as 100 tpy of VOCs per facility, some compounds are subject to more stringent limits of 10 tpy depending on the severity of air pollution in a non-attainment area and the emitted compound. Specific regulations aside, states have "nuisance odor" regulations that also come into play. Non-production emissions are also regulated, such as those from tank storage, valve stem leaks, pump shaft seals, etc.

Sources of VOC Emissions

There are many processes that generate and vent gases containing VOCs. Table 1 lists a range of sources and typical emission controls.

Controls

Major VOC controls are thermal oxidation, adsorption via activated carbon (and / or zeolites), condensation, and biofilters. The following data is required to choose the right type:

Table 1

Typical VOC Sources and Controls

Application	VOC issue	Typical control
Food processing	Odor control	RTOs
Coating and finishing	Solvent; adhesives	RTOs
Ethanol/biodiesel, biofuels, and bread baking	Ethanol vapor	RTOs
Plastics/rubber/asphalt	Odor and organics	Direct fired, RTOs
Packaging/printing	Solvent based inks	Catalytic recuperative, RTOs
Pharmaceuticals	Solvents from batch processes	RTOs, catalytic recuperative
Web printing	Solvents	RTOs, catalytic recuperative
Refining and chemicals	Organic vapors from production, tanks and transfer	Flares, RTOs and direct fired oxidizers
Electronics	Solvent vapors	RTOs
Pulp/paper/lumber and engineered wood products	NCGs/reduced sulfur compounds from pulping; blue haze from dry kilns	Direct fired, RTOs

• Vent flow rate

• Concentration of the VOCs

• Dust / solid particulate

• Process cycle (continuous or batch)

• Potential for use of waste heat

• Regulations

• Chemical properties (especially sulfur and chlorine which form acid gases)

The majority of industrial VOC controls are oxidation-based, hence they are emphasized in this article. Other controls, such as condensers, are used for small flow / high concentration (e.g., 50 percent by volume VOC gasoline vapor from loading racks). Adsorbers are used for small volume applications at low concentration (e.g., lab vents) and for applications where recovered solvents may be returned to the process, and biofilters have been popular in the food processing industry.

TMTS has recently completed refinery-wide Best Available Control Technology (BACT) analysis comparing multiple control options for a wide range of vents from tanks to barge loading racks. While the usual flare / oxidizer / RTO options frequently came out on top, in some cases reconfiguring the storage tank (e.g., adding an external dome to an internal floating roof tank) had a better economic outcome.

Use of atmospheric air vent condensers on asphalt / heavy oil tanks also had merit.

Figure 1 shows, in general, where different types of control equipment work best based on VOC concentration. *Choosing the wrong oxidizer means higher fuel use, higher emissions, and potential for overtemp shutdowns.*

Table 2 shows approximate equipment cost for four VOC control systems. This does not include installation, permitting, testing, utilities, etc.

Thermal Destruction of VOCs

Combustion safety is a major aspect of design for VOC treatment systems. A major consideration is whether to design and operate above or below 25 percent LEL (lower explosion limit). Systems running below that value are covered by basic controls per National Fire Protection Association (NFPA) codes. Higher concentrations require more robust and sophisticated controls and safety precautions, such as seal pots and flame arrestors and VOC monitors. The UEL is the upper explosion limit, and mixtures between LEL and UEL will burn when ignited. Table 3 summarizes LEL and UELs for typical VOCs. These values are at standard conditions with a VOC mixed in air at room temperature. A hot VOC / air mixture or one enriched with oxygen has an extended range between LEL and UEL.

Explosions can occur when VOC concentration changes suddenly and a combustible mixture enters

Figure 1

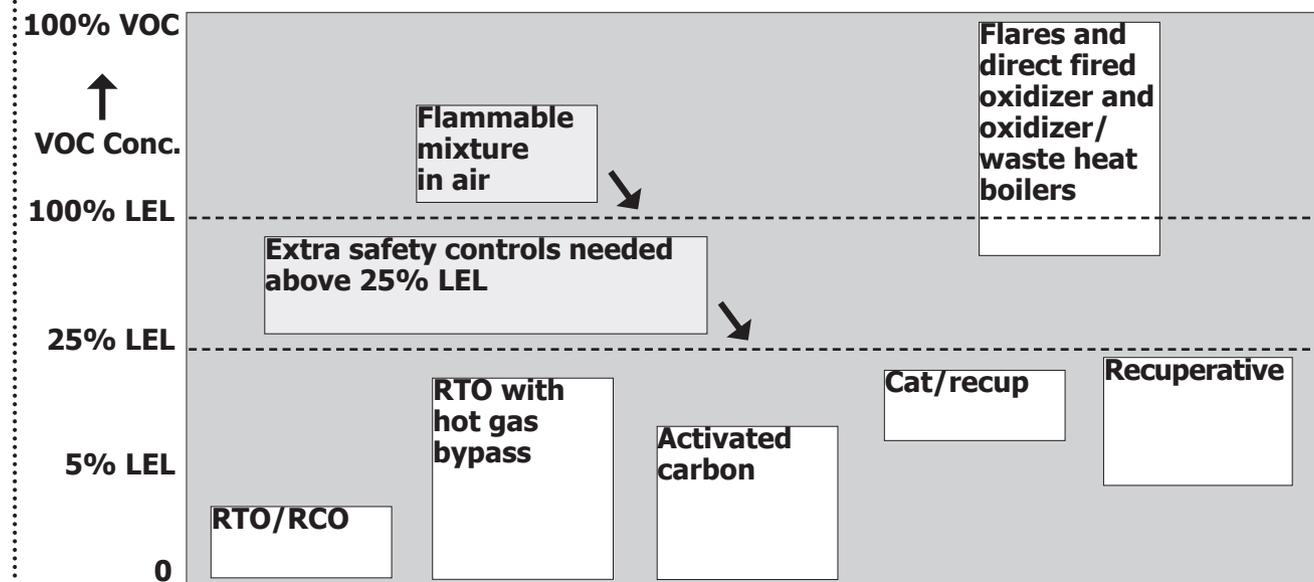### Flow, VOC Concentration, and Type of Control Equipment

Table 2

Approximate Capital Cost for 50,000 cfm Control System with 5-15% LEL Loading

Type	Approximate cost	Comment
RTO	$900,000	With hot gas bypass
Recuperative	$1,500,000	Metallic heat exchanger heat recuperation
Catalytic	$1,500,000	Catalytic plus heat exchanger
Carbon/with solvent reclaim	$1,400,000	With steam regenerator system, condenser, distillation column

the oxidizer. The mixture can flash back through ductwork and cause equipment damage and injury. Good design of the process and controls includes consideration of probable failure modes, in particular, loss of electrical power. The system should be fail-safe, and should not be able to re-start until VOC concentrations are again in the design range. NFPA and other codes offer guidance on this subject, and equipment vendors, such as those selling flame arrestors (See Figure 2) are an additional resource. Starting oxidizers on fresh air with a slow transition to fume is a good design principle to prevent a slug of high-VOC-concentration gas that may have accumulated in the system from entering the combustor.

Thermal systems combust the VOCs in the vent stream using thermal energy in the VOCs plus that in the auxiliary fuel. It is critical that the choice of oxidizer be made to match the VOC fuel value to prevent overheating/overtemp shutdown, as well as excessive use of auxiliary fuel for too low a concentration fume. Table 4 lists temperature rise vs. LEL values for selected VOCs. A rule of thumb is that 1 percent of LEL will produce a 25°F temperature rise across the catalyst (or any oxidizer), or 2,500°F for 100 percent of LEL.

Flares

Flares are used primarily to dispose of combustible gases during a process upset condition, but for some applications, flares are the best way to treat ongoing and routine rich emissions. In some cases, where rich gas is routinely generated in volume and the facility has heat requirements that exceed the fume heat release, heat may be recovered from routine emissions by burning combustible waste gases in boilers or heaters.

Flares are used for waste gases that are above the UEL, and boost fuel can be added in marginal cases to provide a stable, burnable mixture. Air or steam may be injected to promote mixing with air and reduce cracking, soot formation, and smoking. Figure 3 shows an elevated enclosed flare, which has the bonus of not requiring stack testing, as EPA considers it to have 98 percent organic destruction efficiency.

Direct Thermal Oxidizers

Oxidizers use the VOC, boosted by auxiliary fuel as required, to raise the gas stream to the temperature required for good destruction. Most VOCs will be removed to desirable levels at exit gas temperatures of >1,500°F.

Theoretical flame temperatures of about 2,200°F and above are necessary to sustain combustion *in* a flame. This is attainable with mixtures of air and VOC, which are >120 Btu/cubic foot when fed to high-intensity burners run at low excess oxygen levels. Auxiliary fuel is required for mixtures below this level, with much of the destruction occurring *outside* the flame using a 1- to
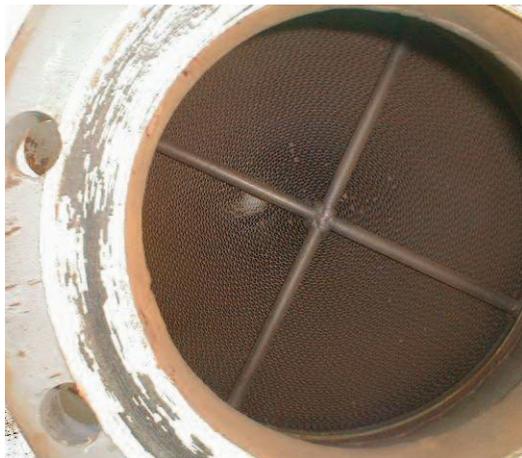
Table 3

Upper and Lower Explosion Limits of VOCS in Air[1]

VOC Compound	LEL%	UEL%
Acetone	2.6	12.8
Benzene	1.4	6.8
Cyclohexane	1.3	8.4
Ethyl alcohol	3.3	19.0
Ethyl ether	1.9	48.0
Gasoline (varies)	1.3	6.0
Isopropyl alcohol	2.0	11.8
Methyl alcohol	6.7	36.5
Methyl chloride	8.2	18.7
Toluene	1.3	6.8
Vinyl chloride	4.0	21.7
Xylene	1.0	6.0

Figure 2

Wound Crimped Metal Flame Arrestor

Table 4

Temperature Rise, °F, vs. % of LEL[2]

VOC/Fume Constituent	25% LEL	100% LEL
Methane	589	2,355
Propane	630	2,520
n-Heptane	680	2,772
Ethanol	618	2,465
Ethyl acetate	680	2,720
Methyl ethyl ketone	639	2,555
Methyl isobutyl ketone	720	2,880
Toluene	662	2,646
M-Xylene	706	2,825
Carbon monoxide	517	2,070

2-second residence time, augmented by good mixing of air and fume. When odor is the prime problem (sewage treatment plants, coffee roasters, etc.), oxidizer temperatures of 1,200-1,400°F are normal. Direct thermal oxidizers are of particular use for dirty streams (See Figure 4) that contain dust, which would foul RTOs and foul and erode recuperative heat exchangers.

Regenerative Thermal Systems (RTOs)

Regenerative thermal oxidizers (Figure 5) offer higher fuel efficiencies than either the catalytic or direct thermal oxidizers, but they are much larger and more expensive to purchase. The VOC-air mixture passes through a ceramic bed (heated in a previous cycle) and is raised to a temperature usually exceeding 1,200°F. It then passes into an oxidization chamber and is mixed with the products of combustion from a small auxiliary fuel burner, raising the mixture to about 1,500°F. The hot effluent from this chamber passes through a second ceramic bed on its way to the stack, preheating the ceramic material to a high temperature. When the ceramic material has been heated by exhaust gases, pairs of valves in the VOC inlet and regenerator chamber exhaust gas lines reverse position, starting another cycle. For odor control, when using an RTO, a three-chamber type or one with a "puff chamber" is a good idea to prevent a half second, or so, emission of untreated fume when the switched-bed valves change over. Regenerative units typically are designed for 95 percent heat recovery. At extra cost, a hot gas bypass can be added to stretch the normal 3-5 percent of LEL limit to 20-25 percent of LEL. The incoming fume stream should be free of particulate and liquid. If "cold face buildup" may occur (such as with spray paint/coating fumes, which produce a varnish-like fouling), a bakeout cycle should be included in the spec. If organic chlorine or sulfur are in the fume, a stainless steel shell will be required to combat dew-point corrosion. A catalyst layer can be added to the top of the switched beds to cut fuel use and combustion chamber temperature for very weak fumes.

Catalytic Recuperative Oxidizers

The catalyst is similar to those used in automobiles. It increases the rate of the reaction and allows it to occur at lower temperatures and, therefore, uses less auxiliary fuel. Catalytic oxidizers are used for low (25 percent LEL) concentrations of VOCs. Care must be exercised in catalytic oxidizer applications to prevent overheating, poisoning, and fouling. It is a good idea

Figure 3

Elevated Enclosed Flare and Detail of Shield

Photos courtesy John Zink

for this type, and also other oxidizers, to field check the high temperature limit thermocouple to prove out that shutdown function.

Exhaust and Makeup Air Design

The design of ductwork for high-volume/low-concentration VOC streams is critical to proper control of emissions, worker health, and plant safety. For tank farm vents, such elements as a vertical slip-fit duct (which allows air/fume in but prevents liquid entry due to overfilling), along with conservation vents, trapped overflow piping, and controls to shut down the vent system if overfilling of tanks occurs, must be part of the design.

Proper design of hoods/pickup points for the VOC vapor is required to minimize fume flow and maximize capture for manufacturing operations. Makeup air must be supplied properly in terms of volume, velocity, and point of delivery. For PTE[3] (permanent total enclosures, such as those used for flexographic printing), good design provides a slight negative pressure (typically 0.01-0.1" w.c.; EPA's minimum is 0.007" w.c. corresponding to 200 fpm average velocity though natural draft openings) to prevent fugitive emissions. One benefit of PTE design is that no "capture test" is required, and capture is assumed to be 100 percent. Poor design with "short-circuiting" of makeup and exhaust air can cause high VOC concentrations in stagnant areas and low concentrations in areas with high air velocity. The principles of good HVAC design[1,4,5] must be employed to do a proper job.

Summary

Economical and safe control of VOCs, while burning a minimum of auxiliary fuel, entails having good data on fume flow and concentration at the start of the project. The designer must be aware of constituents, such as chlorine and sulfur that may create acid gases, and dust levels, which may cause fouling as well as poisoning of catalysts. When that data is in hand, the right VOC control system can be chosen and proper design of ductwork and hoods can be executed to complete the design.

References

1. Industrial Ventilation, 19th Ed., 1986, ACGIH, and later editions.

2. Santoleri, J. J., Energy Recovery from Low Heating Value Industrial Waste. ASME Industrial Power Conference, May, 1975.

3. U.S. EPA PTE, Document EPA/452/B-02-001, http://www.epa.gov/ttn/catc/dir1/cs2ch3.pdf.

4. ASHRAE Fundamentals Handbook, ASHRAE Publications, Atlanta, GA.

5. McGowan, Thomas F., D. Coughlin, B. Axon, T. Wechsler, and J. Santoleri, VOC. Emission Controls for the CPI, *Chemical Engineering* magazine, February, 2007.

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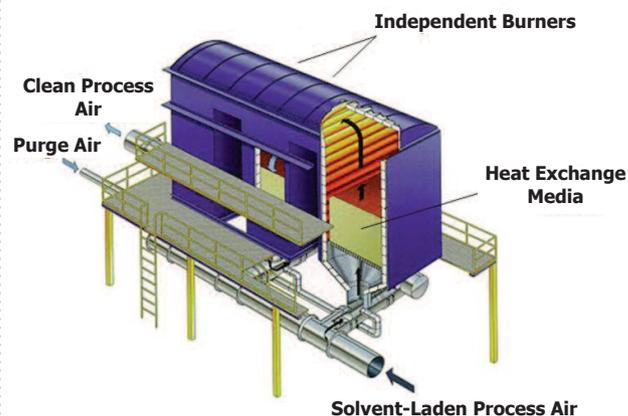
Figure 4

Direct Fired Oxidizer with Upstream Cyclone for Dirty Fume Application

Figure 5

Three Bed RTO with Bed Purge for Off-Cycle Bed

Courtesy Durr Clean Technology Systems