

VOC Oxidizers: Where to begin?

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If you want to solve a VOC (volatile organic compound) air pollution problem, how do you begin? You want a solution that is best suited for your specific application; in the initial cost but also for the long-term operation efficiencies and flexibility for future modifications. How would an engineer know that a thermal oxidizer (TO) is the best solution over other options such as carbon systems, concentrators, flares, or bio systems? Should the TO be a Regenerative (RTO), Recuperative, or direct fired (DFTO) or TO? When are other types of controls used to capture/destroy VOCs? What other characteristics place added constraints on the selection? This article identifies the different types of thermal oxidizers and other VOC control devices. It also identifies with what type of application each control method is best used. Additionally, more equipment may be necessary for complete control of some compounds present in specific applications. Those characteristics in the gas stream to be controlled are identified.

When determining the oxidizer that best suits an application, plant personnel need to first consider the flow rate of the gas. Thus, one of the first steps is to consider the normal flow rate but also what is the maximum flow rate in any upset condition. The maximum flow rate sets the size and allows the plant to determine how best to manage the process. Perhaps, better control is needed at the process level to maintain a fairly constant flow rate or heating value. A system that requires little turndown operates near its optimum more often.

The Recipe for thermal oxidizers:

The 3T's of thermal oxidation are Time, Temperature and Turbulence. To destruct the VOC's adequately in a thermal process, each of these factors interrelate in the calculations. The VOC's must reside for enough Time at the right Temperature and mix with proper Turbulence for efficient combustion and destruction. When operating at higher percentages of the maximum flow, the turbulence is optimized with a well-designed thermal oxidizer. The higher flow rates encourage higher pressure drops, better gas or combustion air penetration, and thus better mixing (or turbulence). Not only is the flow rate for the oxidizer important, but the types of compounds entering the thermal oxidizer are just as important. Let's say that a flow rate is 1000 scfm of a gas. That seems to be a fairly small flow rate and should be a fairly small thermal oxidizer, right? However, we have made some assumptions about the composition. We believed that the 1000 scfm was mostly air and may have some organic contaminants. If it were 100% methane or say naphthalene or benzene, we suddenly have a much different scenario. Our thermal oxidizer is now required to handle (combust) 1000 scfm of, say, methane (if 100% the calculation used is 913 Btu/ft³):

1000 scfm
x 60 min/hr

$$\begin{array}{r} \times 913 \text{ Btu/ft}^3 \\ \hline 54,780,000 \text{ Btu/hr} \end{array}$$

This means just burning the gas from the process will release almost 55MM Btu/hr. This requires a fair sized burner and oxidizer chamber when compared to that required for 1000 scfm of air:

$$\begin{array}{r} 1000 \text{ scfm} \\ \times 60 \text{ min/hr} \\ \times 0.0765 \text{ lb/hr} \\ \hline 4590 \text{ lb/hr air} \end{array}$$

This amount of air would require:

$$\begin{array}{r} 4590 \text{ lb/hr} \\ \times 0.25 \\ \times (1400^\circ\text{F} - 60^\circ\text{F}) \\ \hline 1,560,600 \text{ Btu/hr of auxiliary fuel to heat the air} \end{array}$$

Therefore, we see that considering only the flow rate, can mislead us into a wrong sized thermal oxidizer. The volume of a 1000 scfm system may end up being the same size or bigger than that for a 25,000 scfm flow of “air.” In addition, if the 1000 cfm was nearly all inert or oxygen-poor, such as steam or nitrogen, then it would be critical to add enough air (O₂), plus some excess to the mixture to oxidize the VOCs, plus the fuel required to raise the entire mixture to the appropriate temperature.

Note: A potential bonus of the VOC stream used in this example is that the gas produces more heat than it requires to combust, which makes it exothermic. In this type of application, it might be handy to recover the extra heat in order to reduce plant operating costs by using this “free” energy source. Hot exhaust gas released from an exothermic process gas may be used to make steam or preheat oil or preheat the process gas. Additional system considerations including ducting and equipment are engineered on a custom basis.

Let us review the composition of the gas to be treated too. This is critical to the selection of thermal oxidizer. A gas that is nearly 100% air with little contaminants steers us into one type of thermal oxidizer. If the VOCs in an air stream are relatively high in percentages, this drives us into a different thermal oxidizer. Before we enter the selection process, let’s review the types of thermal oxidizers. Then identify which are better used for VOC levels of varying degrees.

RTO or Regenerative Thermal Oxidizer:

A regenerative thermal oxidizer has a high efficiency (highest form) heat recovery. The heat recovery process occurs by passing the hot exhaust gas through ceramic packing,

often a “honeycomb” structured type. This ceramic is heated up as the hot gas exits the regenerative thermal oxidizer. The ceramic packing is on multiple (2 or more) entries and exits. Periodically, the exit path is reversed and switched by large valves. The inlet gas is switched to enter the ceramic bed that was serving as the exhaust path. This process heats up the inlet gas since the “hot” bed is now being used for preheat. After this switch, the discharge gas is the “hot” exhaust gas and this gas serves to heat up the exit ceramic bed. Soon this bed becomes the “hot” bed after it has been heated by the “hot” oxidizer exhaust as it exits towards the stack. After a time the preheated bed has its temperature reduced a bit and so the path is switched again by the valves to repeat the process. The preheating bed becomes the exit bed which is then heated back up to the exhaust temperature. Some Regenerative Thermal Oxidizers use 3 beds (or an odd number of beds) that rotate their use. This is to make sure that the DRE (Destruction Rate Efficiency) is sufficient to meet higher requirements by bleeding the untreated gas in the idle bed through the combustion chamber, instead of letting it go out the stack during valve changeover. This momentary reduction in oxidation, with a short burst of raw fume making it to the stack reduces DRE by about 1%. The "odd chamber" adds to the cost of the RTO system but is necessary to meet the higher DEs. Many applications require 95% DRE per regulations. 2 chamber RTOs can achieve as high as 98%, and those with odd number of chambers, 99%. An alternate to the odd chamber approach is a puff chamber, which does much the same thing, cycling raw gas that would normally go out the stack back to the RTO combustion chamber. Optionally, this type TO can be a similar “rotary” type.

Recup or Recuperative thermal oxidizer:

If the VOC concentration is higher than the low levels that an RTO normally serves, the type of thermal oxidizer recommended is a recuperative thermal oxidizer. The heat recovery is normally provided by a gas to gas heat exchanger that preheats the inlet gas that is being treated. This uses a metallic heat exchanger to recover the heat as it exits the thermal oxidizer. Recuperative thermal oxidizers may recover heat up to 70% effectively and even provide higher efficiencies if desired. Higher efficiencies may increase the initial cost more than what the additional fuel savings are worth but higher heat recovery levels may be achieved, but be cautious not to lead to corrosion due to dewpoint condensation of acid gases. These units are usually permitted for 95% DRE, but can reach 99% plus depending on the VOC being destroyed. Some compounds require relatively high oxidizer operating temperatures. The recuperative thermal oxidizer has a limited operating temperature based on the temperature that the metallic heat exchanger can withstand during normal operation. Excursions in temperature could present a problem since metallic heat exchangers have operating temperature limitations. The limits may vary by manufacturer. However, with careful engineering, the operating temperature may be optimized if necessary by the heat exchanger design and metal selection. A basic metallic heat exchanger could be good for a 1400°F, 1500°F, or maybe 1600°F oxidizer operating temperature while tubular design, co-current flow, and metallurgy may be used for higher oxidizer temperature requirements. Generally, the recuperative thermal oxidizer may achieve slightly higher DREs than the RTO.

However, the major reason to use a recuperative thermal oxidizer is that the VOC concentration in the gas stream being treated is somewhat higher and provides more heat than what the RTO needs with its heat recovery of 95%. For higher heat content process gas, an RTO may be equipped with a bypass to prevent overheating of the oxidizer. Without a bypass or cooling method, this could mean overrunning the setpoint and a runaway operating temperature in an RTO. Recuperative thermal oxidizers have a better tolerance for VOC content since the heat recovery is less than that of an RTO. Thus, when the VOC content is increased by the customer process, it does not override the operating temperature because the heat exchanger efficiency is lower in anticipation of higher levels of VOC concentrations (unless the VOC concentration exceeds that for which the heat exchanger has been designed). In general, the recuperative oxidizer is less efficient but is well used for applications in which the VOC content provides a certain level of heat release from the VOC oxidation, but when the high heat recovery efficiency of the RTO is too much. In some applications, the treated process gas has a VOC content that varies from high to low. The recuperative thermal oxidizer may be the best selection for these applications since the VOC content may overheat the RTO but can be accommodated by the recuperative thermal oxidizer. The recuperative system uses auxiliary fuel when the VOC content is low but when VOC increase, the auxiliary burner is turned down so the operating setpoint is maintained without overheating or requiring a bypass. A heat exchanger bypass may be necessary if the VOC spikes do reach high levels that increase the setpoint beyond the limits of the equipment. The recuperative systems, as well as other oxidizers, have their limits, and if exceeded, the units will shut down on over temperature. Other cost effective methods of reducing the temperature without large increases in initial cost may be introduced if the application needs. These are in addition to those regularly used like the bypass and may be discussed outside this article by contacting the author.

Recuperative thermal oxidizers are also effectively used to recover the heat in methods other than simply preheating the incoming gas stream. Metallic heat exchangers may be added to heat other gases like air for ovens or for heating the plant. Additionally, heat exchangers may be added to heat liquids like hot oil or asphalt or water. These are additional heat recovery methods that meet a plant preference other than simply recovering the heat by preheating the incoming gas stream which mainly reduces the auxiliary fuel consumption / burner size. While recuperative thermal oxidizers are more widely used for applications with particulate present and are more accepting of particulate in the gas stream than RTOs, plugging can still be a concern. Soot blowers or sonic horns may be used to loosen particulate from the internal surfaces if particulate is a known concern. If particulate is too great, it may be best to reduce the particulate levels with a device upstream or use a direct fired thermal oxidizer.

Direct Fired Thermal Oxidizer:

A direct fired thermal oxidizer has no internal heat recovery. These are effective for exothermic gas streams. That is, if the VOC content in the process gas is high enough to contribute sufficient heat to serve as the “fuel” that heats the oxidizer. Liquid streams are also readily oxidized in direct fired thermal oxidizers if they have significant heating

value. Often the (lower) heating value of the process gas is calculated from its composition and the resulting auxiliary heat required for the oxidizer operation at its setpoint temperature calculated. If the heating value of the gas is sufficient to not require auxiliary fuel, the oxidizer is said to be self-sustaining. This means that no auxiliary fuel is normally required outside of fuel enough to serve as the “pilot.” These direct fired thermal oxidizers may have more than enough heat being released from the process gas combustibles. In this case, overriding the operating temperature is not that critical since there are no components downstream that have restrictive temperature limits. In extreme cases, the refractory or insulation selected will have temperature restrictions that come into play but the insulation may be selected to accommodate the application. Direct fired thermal oxidizers may be so exothermic that the oxidizer may need a quench method to keep the firing temperature to a reasonable level. Quench air or quench water may be used. Both must be injected with care into the direct fired thermal oxidizer so as not to disturb the burner / flame stability nor promote CO formation.

Direct fired thermal oxidizers may be operated at the highest operating temperatures needed. If a particularly high DRE is required, a direct fired thermal oxidizer may be required whether heat recovery is added on or not. The thermal oxidizer may need up to 99.99% DE (or 99.9999% for TSCA organics such as PCBs) so this direct fired system may be required. Many times, the heat release from the process gas provides sufficient heat to reach these higher operating temperatures without a penalty in fuel consumption. When the heat release of the process gas provides sufficient heat to meet the operating temperature much of the time, the direct fired thermal oxidizer provides a “free” source of heat. In such cases, a waste heat recovery boiler may be added on the back end to produce steam to the plant’s specifications. Other methods of heat recovery may be provided based on customer needs. Again, asphalt or oil preheat, water heating, gas preheat, etc. may be added depending on plant needs. Direct fired thermal oxidizers are also best for “dirty” applications where particulate may be an issue. Sometimes, carbon particulate is an issue that mandates a clear path and longer residence time provided by the direct thermal oxidizer. In all these cases, custom designed thermal oxidizers best accommodate the application to address specific concerns. Direct fired thermal oxidizers may accommodate the applications that have known process gas spikes to high levels of VOCs at times. Varying VOC levels when at the peak could overheat both a regenerative and recuperative thermal oxidizer. Sometimes, if these spikes are the exception rather than the rule, a bypass may be the answer, but if the application generally has richer VOC levels that provide a good heat source, the direct fired thermal oxidizer is best. In some cases, the heating content is so rich that a flare is better suited for these occurrences (depending on DRE required). Flares usually “burn” a rich stream which is well above the LEL (lower explosion limit) that is capable of burning with only the assistance of a constant pilot. . Flares are another option but are not a main consideration for this article.

Direct fired thermal oxidizers increase plant thermal efficiency when used for preheating gases, combustion air, or for steam or hot oil production. Direct fired thermal oxidizers are often used for gas streams or liquid streams that include halogens (Cl, F, etc.) or S or other acid producing components. The DFTO design can accommodate the acid presence in the products of combustion best by mitigating the concerns most effectively of all the

options. "Hot wall" design is used, with shells at 400°F or more to prevent dewpoint condensation and acid gas attack. If a downstream scrubber is required, the products of combustion are quenched and enter into the packed tower for acid removal. When using waste heat boilers with high sulfur waste streams, a coalescing mist eliminator may be needed after a wet scrubber to remove submicron SO₃/H₂SO₄. Careful considerations must be taken for both acids and particulate presence. An experienced thermal oxidizer system provider accounts for all of the concerns of the system by properly selecting each component, whether it be the thermal oxidizer type, material, inlet design, burner type, valves, refractory, boiler, heat exchanger, insulation, quench design or material, scrubber, fans, and stack. Careful consideration prior to building the system will make it serve the proper purpose optimally while lasting a life that keeps the user satisfied.

Other Options: Activated Carbon or Catalysts:

After a discussion of the major types of thermal oxidizers, it is wise to consider other less used designs as viable options for particular applications. A catalytic oxidizer may be used on particular applications that also have lower VOC concentrations. To reduce the operating cost, the catalyst is added to a thermal oxidizer that lowers the operating temperature required to destroy the VOC components. Sometimes, a catalyst is added to these types of oxidizers to combine some attributes of both, like recovering heat to reduce auxiliary fuel consumption via both preheat and catalyst use. The most common type is a catalytic recuperative type, which helps protect the metallic heat exchanger by allowing it to operate at no more than 1200-1300°F and often lower. Consideration must again be given to VOC concentration, spikes, particulate, elements and compounds that may foul or poison the catalyst.

Carbon beds are another method of VOC control. Carbon is used to adsorb VOCs as the VOC laden gas passes through the carbon. These beds "catch" and hold the VOCs up to its saturation point after which the VOCs will pass through uncollected. Once at the carbon adsorption threshold, the carbon bed must be replaced to continue to be effective. Thus, carbon beds are generally good for low VOC concentrations that do not "exhaust" the carbon in the bed too quickly so as to require replacement too often. If concentrations are too high, the beds need replaced frequently which could make the system of carbon less economical than other control systems due to constant carbon replenishment (and used carbon bed disposition). In addition, higher VOC concentrations have caused many activated carbon bed fires.

Carbon beds (or zeolites) may be used for higher VOC concentrations if the VOCs are "desorbed" on site. Carbon adsorbers may be in the form of a wheel that adsorb on part of the carbon "wheel" and, during each slow rotation, is desorbed of the captured VOCs. The carbon may then again be used to collect or adsorb the VOCs with each rotation. The desorbed gas may be recovered if it is desirable (and economical) or may be destroyed in a thermal oxidizer. These systems are effective because they concentrate the VOCs by taking them out of a low concentration gas stream and concentrating them in a low flow gas stream. The concentration for some of these systems reaches 100:1, decreasing the size and cost of a thermal oxidizer.

Another form of activated carbon system uses a fluid carbon bed which provides additional carbon pores available to adsorb the VOCs. The VOCs are then passed into a desorber chamber. (Carbon is generally desorbed by heating by a few hundred degrees). The desorbed VOCs are then in a concentrated stream. This type of fluid bed system concentrates the VOCs up to 500:1 which makes the resulting recovery further concentrated. For each carbon system, the compound needing control is very important. Carbon does not adsorb small compounds like methanol well while elevated temperatures reduce the amount of VOC the carbon can adsorb. Therefore, like all of the applications, the optimum control system must be selected wisely.

TYPICAL BUT NOT EXCLUSIVE APPLICATION TYPES:

Briefly, the best options for particular applications may be generalized as follows but are best reviewed and recommended by an expert.

| Application | RTO | Recup- erative | Direct | Carbon Concentr |
|---|------------|---------------------------|---------------|----------------------------|
| Paint booths or ovens: | x | | | x |
| Dynamometers: | | x | | |
| Printing operations: | x | | | |
| Chemical process: | | | x | |
| Refinery Process: | | | x | |
| Asphalt Process: | | x | | |
| Metal recycling furnace afterburner: | | x | x | |
| Ethanol process: | x | x | | |
| Carbon Black: | | x | x | |
| Pharmaceuticals: | | x | x | |
| Acrylonitrile: | | | x | |
| Gasifier off gas: | | | x | |
| Tobacco: | | x | | |
| Recycling center: | x | | | x |
| Marine production: | x | | | x |
| Rendering: | | x | | |
| Wood Processing or Paper plants: | x | x | | |
| Spray Dryer: | | x | | |
| Silicon/silanes: | | | x | |

| | | | | |
|-----------------------------|----|--|---|--|
| Syn gas production: | | | X | |
| Biomass gas: | X* | | X | |
| Ore Kilns: | | | X | |
| Thermal Desorber: | | | X | |
| Anaerobic wastewater treat: | X | | | |

*For Biomass dryer offgas

KEYS TO THERMAL OXIDIZER DESIGN:

The keys to identify each application are mainly:

- Flow rate: Min-Normal- Max (large enough for economy of scale for RTOs or carbon concentrators?)
- VOCs or composition: % of each VOC or combustible (high concentration produces plenty of heat so direct TO may be best.)
- Oxygen concentration: % O2 (impacts burner selection and operation.)
- Inert concentration: Inclusion of lots of H2O or CO2 impacts design and burner selection
- Temperature: Slightly over ambient temperature could mean carbon cannot adsorb while much higher temperatures mean less auxiliary fuel required and easier to destroy but accommodations needed for high gas temperature.
- Particulate presence: High Particulate must be dealt with by TO design or auxiliary equipment addition.
- Acid production/presence: Acid presence impacts TO design and addition of auxiliary equipment.
- Auxiliary fuel available: Type of fuel to be fired impacts burner and TO design.
- N compound presence: Nitrogen compounds impact TO design because N compounds may produce high levels of NOx.

Other application parameters impact the selection and design of TOs, e.g., client's level of DRE, need for steam, or client preference to minimize auxiliary fuel consumption impacts design. All of these parameters enter into the type of thermal oxidizer selected.

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