METHANE DESTRUCTION FOR EPA AND ASTM FUGITIVE EMISSIONS

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Introduction

Thermal Oxidizer in the gas industry is primary used for the destruction of fugitive emissions for EPA Toxic Release Inventories Gases (TRI), Volatile Organic Compounds (VOC), Hazardous Air Pollutants (HAP), benzene, toluene, ethylbenzene, xylenes. (BTEX) and methane (Natural Gas). These gases are regulated by the EPA, TCEQ and AQMD for compliance with regard to gases that would otherwise be sent to a flare.

Background

Thermal Oxidization (T.O.) has long been the standard method of destroying waste gas streams such as VOC's in large quantities' Traditionally T.O. devices have been installed in very passive environments which can tolerate extreme external temperatures such as, an open field, atop of structural towers in non-hazardous environment. Natural gas combustion has been the preferred method of generating the heat necessary to allow oxidation to take place in these large systems. Excess air, internal to the waste gas stream or mechanically injected by a separate supply device, provides the Oxygen for Oxidation. With the advent of new regulations and tightening of existing allowable limits regulation such as Title VI of US EPA, and specifically the TRI regulations, smaller and smaller quantities of VOC's emissions are being tolerated.

The waste gas stream, for this discussion relates to those compounds (natural or manmade) which are known as VOC, TRI, HAP, BTEX and Methane (natural gas) that require oxidization by US EPA or other Jurisdictional air quality authorities such as South Coast AQMD (California) and TCEQ (Texas).

Destruction of these VOC, TRI, HAP, BTEX and Methane (natural gas) gasses need to comply with governmental regulations for combustion air requirement(s) of 20% additional air and a combustion chamber(s) temperature(s) of no less than 1400 ºF (760 ºC) that also allows adequate residence time at said temperature to achieve 99.9% destruction of waste gases. Typical reporting requirements demonstrating compliance is for emissions from the combusted waste gas stream measured at the combustion tube exhaust. The temperature being reported shall have an accuracy of $\leqq\pm0.75\%$ of the temperature being measured.

Thermal Oxidizers require the following design parameters to be in full compliance with EPA and ASTM standards:

- Combustion Air to be greater than the stoichiometric combustion point of the waste gas stream
- Maintain 1400 ºF (760 ºC) in the combustion section(s)
- Turbulent mixing/nozzle-stabilized of the waste gas with combustion air
- Residence time of the turbulently mixed waste gas and air in the combustion section(s)
- Control of the T.O. with regard to excess combustion air and temperature in the combustion chamber at all times
- Blocking valve so that gases cannot enter prior to combustion chambers reaching the required 1400 ºF (760 ºC)

EPA: "...*Thermal oxidizers or thermal incinerators are combustion systems that control VOC, CO, and volatile HAP emissions by combusting them to carbon dioxide (CO2) and water. The design of an incineration system is dependent on the pollutant concentration in the waste gas stream, type of pollutant, presence of other gases, level of <u>oxygen, stability of processes vented to the system</u>, and <u>degree of control required</u>. <u>Important design factors include temperature (a temperature high enough to ignite the organic constituents in the waste gas stream), residence time (sufficient time for the combustion reaction to occur), and turbulence or mixing of combustion air with the waste gas. Time, temperature, degree of mixing, and sufficient oxygen concentration governs the completeness of the combustion reaction.</u>...*"

EPA: "…*The heart of the thermal oxidizer is a <u>nozzle-stabilized flame</u> maintained by a combination of auxiliary fuel, waste gas compounds, and supplemental air added when necessary. Upon passing through the flame, the waste gas is heated from its inlet temperature (e.g., 37.8°C (100°F)) to its ignition temperature. The ignition temperature varies for different compounds and is usually determined empirically. It is the temperature at which the combustion reaction rate (and consequently the energy production rate) exceeds the rate of heat losses, thereby raising the temperature of the gases to some higher value. Thus, any organic/air mixture will ignite if its temperature is raised to a sufficiently high level…*"

Theory of Operation

The ASTM standard for Thermal Oxidizers specifically for the VOC, TRI, HAP, BTEX and Methane (natural gas) gases consist of Hydrogen and Carbon molecules which by themselves or in combination with other elements form highly toxic substances or are environmentally egregious in their natural state such as Natural Gas, which is mostly Methane (CH_4). When Natural gas reacts with air in the process of combustion heat and light is released. In that process air, containing 20% Oxygen and 80% Nitrogen is mixed with Natural Gas (Fuel) in a ratio of 10 Cubic feet of air and 1 cubic foot of fuel. Theoretically, there is enough Oxygen (O_2) in 10 Cubic foot of air to completely unite with the Hydrogen and Carbon that contained in 1 Cubic foot of Natural Gas (CH_4). If all of the Oxygen (O_2) is completely united with all of the Carbon and Hydrogen, then the reaction is as follows:

$$Air = O_2 + 4N_2 \text{ and Natural Gas} = CH_4 \text{ (1)}$$

$$2O_2 + 8N_2 + CH_4 \rightarrow CO_2 + 2H_2O + 8N_2 \text{ (2)}$$
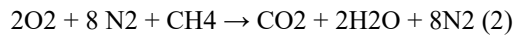
In the process Products of Combustion (P.O.C) are elevated to 3600 ºF. This perfect mixture is said to be a Stoichiometric mixture.
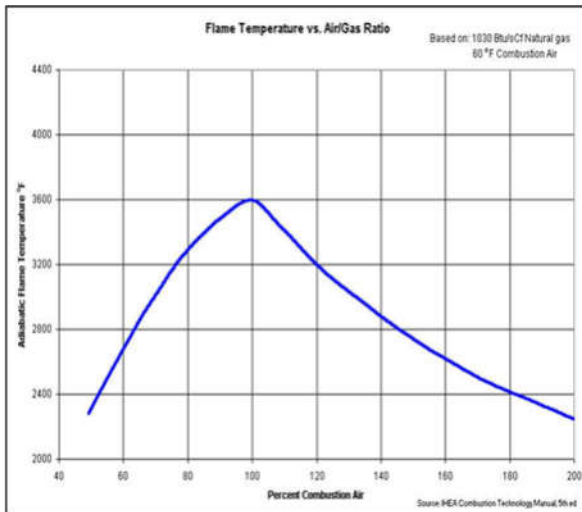

If perfect mixing of the fuel and air does take place it will result in forming Carbon dioxide (CO_2) and Water Vapor (H_2O) while releasing heat. Because the N2 introduce with the air is inert, it may pass through the T.O. unchanged chemically but elevated in temperature.

If complete mixing does not occur, then Carbon Monoxide (CO) is formed in various amounts as follows:

$$2O_2 + 8N_2 + CH_4 \rightarrow CO + CO_2 + 2H_2O + 8N_2 + O \text{ (3)}$$
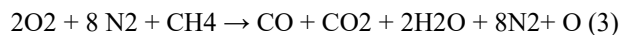
In order to ensure that more than enough Oxygen is available a minimum of 15% additional air molecules needs to be present during the process of combustion or 11.5 Cubic Feet of air per 1 Cubic foot of Natural Gas or:

2.3 O2 + 9.2 N2 + CH4 → CO2 + 2H2O + 9.2N2 +0.3 O2 = 15% excess air with (Products of combustion at 3200 ºF). (4)

FLUE GAS ANALYSIS CHART
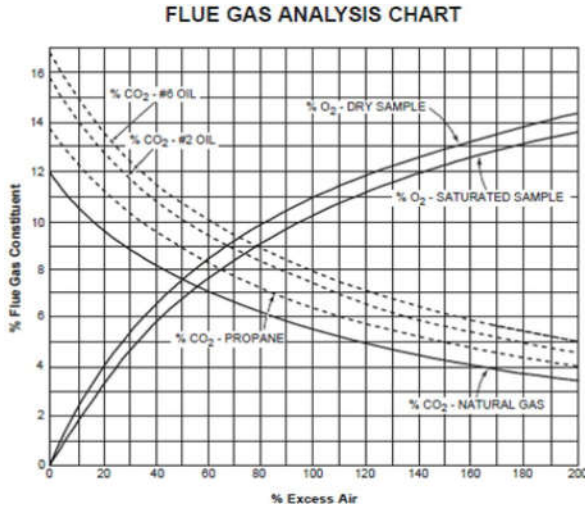
The higher the excess air is, the lower the exit gas temperature of Products of Combustion (POC) will be. This is true for all gases listed in standard Tables of Combustion Constants. If a large amount of air is present in a Fuel/Air mixture, lowering the (Hydrocarbons/Air) ratio to (< 0.4:10) such that the amount of natural gas in the mixture is less than 4% of the total, it is said to be too lean for auto ignition or below the Lower Explosion Limit (LEL). This means that such mixtures at ambient temperatures, when exposed to an Ignition source, will not react. On the other hand, if the mixture is too rich with fuel i.e., > 15% (1.5cf. fuel: 10 cf. air) it will not ignite because it is said to have exceeded the Upper Explosion Limit (UEL).

Complete conversion of hydrocarbons to H2O
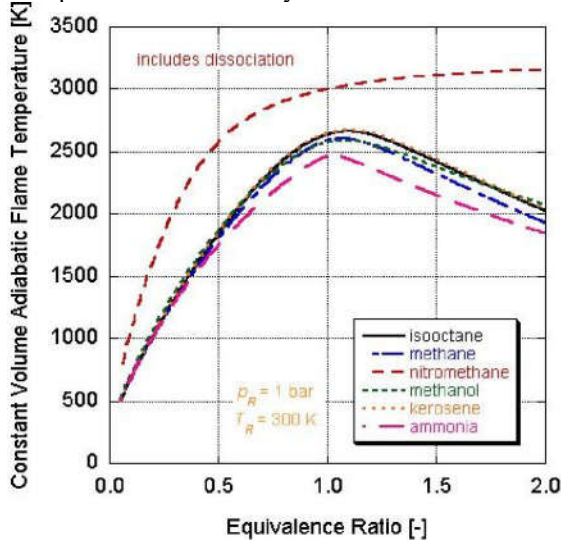
and CO2 through Thermal Oxidation can only take place if a sufficient amount of Oxygen (normally from Air) is available in the presents a of heat source for a sufficient amount of time for the reaction to take place.

The normal state of operation of many T.O. systems is that of a waste gas stream is in the LEL range with an insufficient quantity of hydrocarbons to allow for self-sustained combustion. Without an external heat source to heat the contaminated waste stream, typically a Natural gas flame to provide the heat source as stated earlier.

Destruction of VOC, TRI, HAP, BTEX and Methane (natural gas)
Excess O2 and temperature are indicators as to quality of destruction.

Flammable Range

Natural Gas Concentration In Air
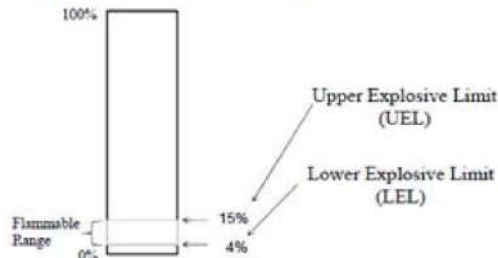
Therefore, depending on the waste gas to be destroyed the T.O. exit gas temperature is maintained between 1100 ºF and 1800 °F and contains sufficient excess air to measure a minimum of 3% O2 in the exit flue gas sample or 15% excess air in a chamber sized to provide for retention times of no less than 0.3 seconds on the low end to 2 seconds on gases containing Dioxins and Furans.

Thermal Oxidizer design compliant t to EPA, SCAQMD, TECQ & ASTM
The Oxidization Chamber is preheated to 1500 ºF by an electrical heating element (or can use gas fired), the waste gas is introduced in a vertical flow that must rise through the oxidation chamber and cross the heating elements. At the same time air is admitted at the unit's base and is mixed with the waste gas stream. Both the waste gas and the air are elevated to >1400 °F as they exit the oxidation chamber. Oxidation begins to occur at the point where heated fuel and air mixing begins.
A secondary retention time in utilized to allow the hydrocarbons in the waste gas to react with the oxygen in the air to complete the combustion process which converts Hydrogen to H2O (Water Vapor) and Carbon to Carbon Dioxide CO2. The residence time requirements need to be met and is called out by the EPA and ASTM to insure 99.9% destruction or the T.O. is not compliant.

In practice the actual constituents being delivered to the. T.O. unit are not known as they are often a mixture of several different sources and can vary from LEL to UEL within the waste gas stream or have no Hydrocarbons at all as in the case of a Nitrogen Purge. Because the waste gas stream may be an unknown analysis at any given time, its flow is limited such that, irrespective of the waste streams constituents, the T.O. will deliver a sufficient amount of combustion air to maintain a minimum of 11.5:1 ratio of air to waste gas.

Methodology
Destruction of waste gases send to the T.O. will take place after the mixing with the required combustion air composition of waste gas being delivered to the T.O. unit is unknown as it is often a mixture of several different waste streams which can have variable LEL to UEL characteristics or even have no hydrocarbons at all such as when the waste gas is from a nitrogen purge. Because the waste gas stream may be an unknown at any given time, its flow is limited such that, irrespective of the waste streams constituents, the T.O. will deliver sufficient air to maintain a minimum of 11.5:1 ratio of air to waste gas stream. Therefore, the T.O. can ensure that the unit will always have sufficient oxygen to oxidize the hydrocarbons in the waste gas stream at desired efficiency.

The required efficiency is accomplished by the introducing a fixed amount of air and limiting the waste gas stream to a prescribed design value on a worst-case basis. Additionally, the waste gas flow is controlled by a flow limiting orifice and static supply pressure based on the expected gas composition. And the heat in the T.O. thermolysis cell is supplied by an electric heating element(s) specifically design for this.

Combustion Air may be supplied by simple induction from the bottom of the cell or by a power blower /compressor depending on the application's combustion air requirement and the destruction capacity
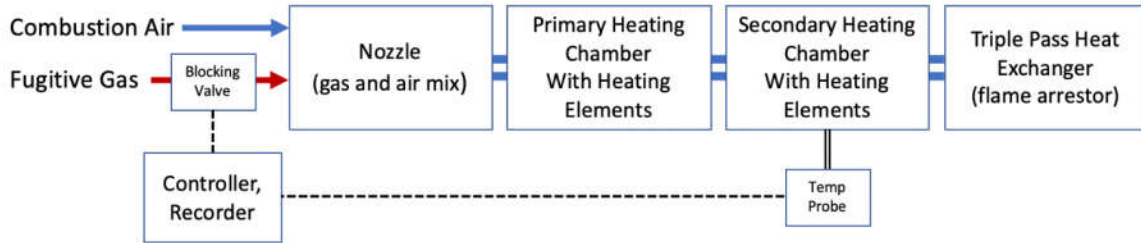
needed to meet governmental or business requirements. Oxidized products of combustion (POC), inert waste gas and associated heat is exhausted to atmosphere out the top of the TO (typically though a flame arrestor).

T.O. designs will need to have a nominal residence time of the reacting waste gas in the combustion chamber.

Residence time is determined by using the combustion chamber volume and then dividing it by the volumetric flow rate of the gas.

Typically, most thermal systems are designed to provide no more than 1 s of residence time of the waste gas with typical temperatures of 649 °C (1200 °F) to 1093 °C (2000 °F).

Once the unit is designed and built, the residence time is not easily changed; hence, the required reaction temperature becomes a function of the particular gaseous species and the desired level of control. Table 1 illustrates the variability in (theoretical) reactor temperatures that is required to destroy 99.99 % of the inlet mass of various noxious compounds with excess air for a 1- s reactor residence time.

Combustion Air → Fugitive Gas → [Blocking Valve] → [Nozzle (gas and air mix)] = [Primary Heating Chamber With Heating Elements] = [Secondary Heating Chamber With Heating Elements] = [Triple Pass Heat Exchanger (flame arrestor)]

[Controller, Recorder] -------- [Temp Probe]

Calculation of Combustion Air

Determining the amount of combustion air to ensuring excess air to a T.O. is shown in the tables below for methane and propane. The thermodynamic heating value (calorific) load value will vary based on the constituent(s) as the amount of oxygen required to combust a methane/propane (C3H8) mixture is greater than that of a methane (CH4) alone; so, you will need to supply enough combustion air to meet the excess air (oxygen) requirement to comply with the regulatory requirements that typically state and amount above the stochiometric combustion point of the waste gas stream. Calculated values for the actual combustion at the stochiometric point can real to a lean combustion and you will be out of compliance because the amount of supplied will not be enough because most all systems are not 100 % efficient; thus, incomplete combustion will occur and result in undesirable by products from incomplete combustion. Products such as carbon (soot) and/carbon monoxide can be emitted to T.O. exhaust. Another term typically used here is excess air when dealing with combustion systems and is why you will find this noted in EPA and ASTM standards because running at the stoke your metric combustion point is not feasible due to all systems not being 100% efficient, therefore excess air (oxygen) is required to properly combust and ensure destruction of waste gases.

Btu/CF	Gas	LPM	CFM	Btu/M	Btu's/hr.	CF/H	Max Air CFH
1012	Methane	1	0.035315	35.7385	2,144.31	2.12	32.16
Liter Per CF		2	0.070629	71.477	4,288.62	4.24	64.33
28.3168	1	3	0.105944	107.2155	6,432.93	6.36	96.49
		4	0.141259	142.954	8,577.24	8.48	128.66
		5	0.176574	178.6925	10,721.55	10.59	160.82
		6	0.211888	214.431	12,865.86	12.71	192.99
		7	0.247203	250.1695	15,010.17	14.83	225.15
		8	0.282518	285.908	17,154.48	16.95	257.32
		9	0.317833	321.6465	19,298.79	19.07	289.48
		10	0.353147	357.385	21,443.10	21.19	321.65
		11	0.388462	393.1235	23,587.41	23.31	353.81
		12	0.423777	428.862	25,731.72	25.43	385.98
		13	0.459091	464.6005	27,876.03	27.55	418.14
		14	0.494406	500.339	30,020.34	29.66	450.31
		15	0.529721	536.0775	32,164.65	31.78	482.47
		16	0.565036	571.816	34,308.96	33.90	514.63
		17	0.60035	607.5545	36,453.27	36.02	546.80
		18	0.635665	643.293	38,597.58	38.14	578.96
		19	0.67098	679.0315	40,741.89	40.26	611.13
		20	0.706294	714.77	42,886.20	42.38	643.29

Btu/CF	Gas	LPM	CFM	Btu/M	Btu's/hr.	CF/H	Max Air CFH
2561	Propane	1	0.035315	90.44101	5,426.46	2.12	81.40
Liter Per CF		2	0.070629	180.882	10,852.92	4.24	162.79
28.3168	1	3	0.105944	271.323	16,279.38	6.36	244.19
		4	0.141259	361.764	21,705.84	8.48	325.59
		5	0.176574	452.2051	27,132.30	10.59	406.98
		6	0.211888	542.6461	32,558.76	12.71	488.38
		7	0.247203	633.0871	37,985.22	14.83	569.78
		8	0.282518	723.5281	43,411.68	16.95	651.18
		9	0.317833	813.9691	48,838.15	19.07	732.57
		10	0.353147	904.4101	54,264.61	21.19	813.97
		11	0.388462	994.8511	59,691.07	23.31	895.37
		12	0.423777	1085.292	65,117.53	25.43	976.76
		13	0.459091	1175.733	70,543.99	27.55	1058.16
		14	0.494406	1266.174	75,970.45	29.66	1139.56
		15	0.529721	1356.615	81,396.91	31.78	1220.95
		16	0.565036	1447.056	86,823.37	33.90	1302.35
		17	0.60035	1537.497	92,249.83	36.02	1383.75
		18	0.635665	1627.938	97,676.29	38.14	1465.14
		19	0.67098	1718.379	103,102.75	40.26	1546.54
		20	0.706294	1808.82	108,529.21	42.38	1627.94

Application Example – Measurement Shelter

Fugitive emissions can be generated by pressure containing equipment such as analyzers and meters, instrument - analyzer shelters, tanks, gas line (blowdowns, and other control or switching devises that have a vent that can be plumed into a T.O. for destruction of these fugitive emissions.

Instrument shelter example: where several instruments are contained within a shelter or building, you have bypass gas or vent gas that contains fugitive emissions. Rather than venting these emissions to the atmosphere these bypass or vent lines are connected to a single thermal oxidizer for destruction. Typically, these venting and bypassing analyzers and meters are sensitive the back pressure and therefore a localized T.O. is an optimal choice rather than trying to plumb these gases into a flare header that will produce back pressure from the sweep-gas and other processes that are venting.
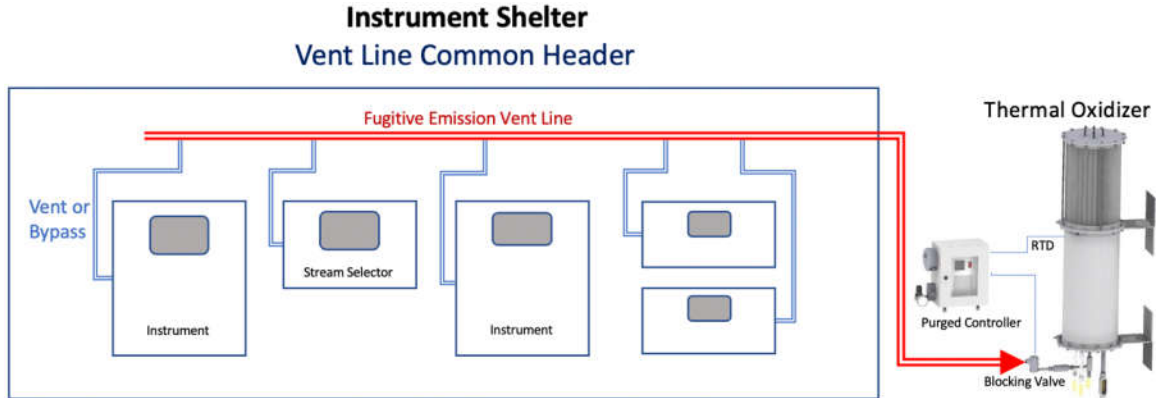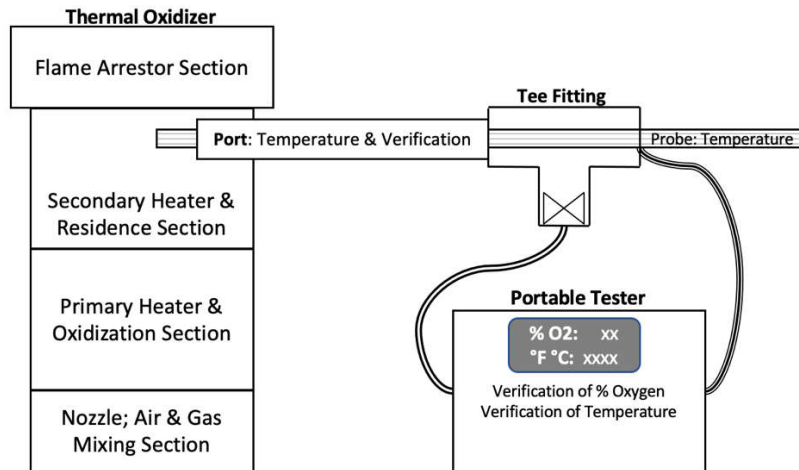

Verification Testing Required

The determination of destruction efficiency is primarily determined by use of temperature sensing to ensure a 1400 ºF (760 ºC) at the exhaust point is maintained and is reportable. The temperature is a direct measurement of the combustion chambers efficiency as mandated in US EPA documents and stipulated in the ASTM standard to achieve a 99.9 % hydrocarbon destruction efficiency for fugitive emissions passing through the T.O.. Should the temperature of the exhaust gas to dip below the minimum 1400 ºF (760 ºC), the T.O. will activate a blocking valve, so that un-combusted gases will not pass through the chamber and therefore maintaining the required efficiency requirement. Large T.O. combustion chamber temperature excursions will also be detected and mitigated as needed in the control system to maintain the 99.9 % destruction efficiency.

Periodic verification of parameters such as combustion exhaust residual oxygen can be performed via the T.O. exhaust to verify a minimum 3 % oxygen concentration is present as required by the users own environmental requirements or consent decree(s) requirement and on a schedule deemed appropriate by the user

Analysis verification is usually taken from a port located at the exhaust portion of the combustion section for both the residual oxygen percentage of that needs to be $\geq$ 3 % and exhaust temperature of $\geq$1400 ºF (760 ºC). Portable testers are used for verification of precent oxygen present via a verification port sampling a slipstream.

Thermal Oxidizer

Flame Arrestor Section

Port: Temperature & Verification

Secondary Heater & Residence Section

Primary Heater & Oxidization Section

Nozzle; Air & Gas Mixing Section

Tee Fitting

Probe: Temperature

Portable Tester

% O2: xx
°F °C: xxxx

Verification of % Oxygen
Verification of Temperature

Conclusion

Thermal Oxidizers are a key component for methane destruction and maintaining compliance with regulatory bodies. They are very easily deployed and maintained while providing a reduction in methane and harmful fugitive emissions such as VOC, TRI, HAP and BTEX.

Work Cited:

1. Combustions Systems Inc – CSI Emission Rx: http://www.combustionsystemsinc.com (Thermal Oxidizer use and graphics, charts, formulas)
2. ASTM: https://www.astm.org (Standard for Thermal Oxidizers)
3. EPA: https://www.epa.gov (Thermal Oxidizer destruction requirements)
4. South Coast AQMD: http://www.aqmd.gov (Thermal Oxidizer destruction requirements)
5. TCEQ: https://www.tceq.texas.gov (Thermal Oxidizer destruction requirements)
6. US PATENT OFFICE: https://www.uspto.gov (Thermal Oxidizer operation, methodology)

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