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Enhancement of organic vapor incineration by using ozone

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Abstract

Incineration of dilute mixtures of volatile organic compounds (VOCs) in air was studied in an externally heated quartz tube reactor. A dilute stream of ozone (O_3) in air was injected into the flowing VOC-in-air stream at various molar ratios of O_3 to VOCs. A number of trials were made to determine the degree of enhancement of the destruction of several VOCs—heptane, isopropanol, chlorobenzene, and trichloroethylene. Temperatures studied for heptane destruction ranged from 637°C to 687°C and residence times varied from 0.26 to 0.84 seconds. It was shown that O_3 definitely increased the rate of destruction of n-heptane, but apparently had no effect on the other organics tested. At the residence times and temperatures studied, both organic intermediates and CO persisted. The results for n-heptane using O_3 were compared with results previously reported for n-heptane using hydrogen peroxide.

Introduction

Incineration of waste gases and liquids has long been used as an accepted means of destroying volatile organic compounds (VOCs). The main advantage of incineration is the positive destruction of toxic or otherwise hazardous materials. Disadvantages include cost and possible air pollutant emissions including products of incomplete combustion (PICs), such as VOC intermediates or CO, as well as NO_x. The use of lower than flame temperatures for the thermal oxidation of VOCs is quite common and has been practiced extensively. Chemical enhancement of such oxidation might be an effective way to further reduce emissions of toxic air pollutants and reduce NO_x formation as well.

In a recent paper [1], the authors reported results showing the enhancement effects of hydrogen peroxide. Ozone is another possible enhancer. Ozone has long been used as an oxidizer in water and wastewater applications. Also, ozone

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is a reactive gas which actively oxidizes VOCs in ambient air during photochemical smog episodes. It was postulated that ozone might behave similarly to H_2O_2 and increase the destruction of VOCs at intermediate temperatures in a laboratory scale vapor incinerator. The potential benefits are more rapid destruction (smaller equipment), more complete destruction (less pollutant emissions), and/or lower temperatures (fuel savings and/or lower NO_x emissions).

Background

It has long been known that in flame combustion, there are free radicals present which are essential to hydrocarbon oxidation via a chain-branching mechanism [2]. For example, the oxidation of heptane is initiated by the attack of $H^\bullet$, O, and/or $OH^\bullet$ radicals on heptane to form the heptyl radical.

$$C_7H_{16}+HO^\bullet \rightarrow C_7H_{15}^\bullet + H_2O \qquad (1)$$

$$C_7H_{16}+O \rightarrow C_7H_{15}^\bullet + HO^\bullet \qquad (2)$$

$$C_7H_{16}+H^\bullet \rightarrow C_7H_{15}^\bullet + H_2 \qquad (3)$$

The heptyl radical could then decompose to form alkenes and successively smaller carbon chain alkyl radicals,

$$C_7H_{15}^\bullet \rightarrow C_5H_{11}^\bullet + C_2H_4 \qquad (4)$$

and/or decompose to yield a hydrogen atom and an alkene,

$$C_7H_{15}^\bullet \rightarrow C_7H_{14} + H^\bullet \qquad (5)$$

The alkyl radicals are highly unstable; for this reason the decomposition reactions are more likely than the recombination or disproportionation reactions with O_2 and $O^\bullet$.

It can be assumed that the decomposition to smaller radicals will continue until $C_2H_5^\bullet$ and $CH_3^\bullet$ are obtained. The mechanism of oxidation of the ethyl and methyl radicals has been well explained [3] and includes addition and H-atom abstraction by H-atoms, O-atoms, and $HO^\bullet$ radicals resulting in branching and propagation reactions leading to the formation of H_2O and CO.

The mechanism of oxidation of H_2 and CO is very well documented [4], and includes chain propagation and branching reactions involving the $H^\bullet$, O, and $OH^\bullet$ radicals; the formation and consumption of $HO_2^\bullet$ radicals that produce $HO^\bullet$ radicals, H_2, O_2 and H_2O; and finally oxidation of CO by the reaction

$$CO+HO^\bullet \rightarrow CO_2 + H^\bullet \qquad (6)$$

Effect of enhancers, H_2O_2 and O_3 on reaction mechanism

Hydrogen peroxide thermally dissociates preferably to hydroxyl radicals

$$H_2O_2 \rightarrow 2\,HO^\bullet \qquad (7)$$

The additional $HO^{\bullet}$ radicals produced by reaction (7) in a reaction mixture containing heptane will enhance the important initiation reaction (1), to produce the very active heptyl radical and the relatively stable water molecule.

The final oxidation of carbon monoxide to CO_2 by the $HO^{\bullet}$ radical will also be enhanced by the additional available $HO^{\bullet}$ radicals supplied by the peroxide.

The dissociation of ozone by thermal decomposition:

$$O_3 \rightarrow O_2 + O \tag{8}$$

results in the generation of oxygen atoms, enhancing the initiation reaction (2) producing as before the heptyl radical and one hydroxyl radical.

Previous studies have shown that oxygen atoms also attack H_2O molecules to yield more reactive $HO^{\bullet}$ radicals [5].

$$H_2O + O \rightarrow 2\ HO^{\bullet} \tag{9}$$

An advantage of H_2O_2 over O_3 as a kinetic enhancer may be explained by noting that reaction (1) results in the formation of one radical and one stable molecule, which is more favorable than reaction (2) which produces two radicals. However, reaction (9) is more effective with $O(^1D)$ atoms that are formed by photo decomposition of ozone, for this reason an ultraviolet/ozone system may work better than one with thermally generated oxygen radicals. Palazzolo et al. [6] reported a destruction and removal efficiency (DRE) of 75% vs. 64% for chlorinated compounds when such a system was tested.

Global modeling

As described in our previous paper, the model of a first order reaction occurring in an idealized plug flow reactor (PFR) was used to analyze our results. While the Reynolds number in our reactor was low (<600) and clearly indicated flow in the laminar region, the large length to diameter ratio (>390) allowed the use of a PFR model. Mathematically, if the gas temperature is constant (both radially and longitudinally), then the fraction of organic compounds remaining at the exit of the PFR is given by:

$$\frac{C}{C_o} = e^{-kt} \tag{10}$$

where C denotes the exit concentration of VOC, C_o the inlet concentration of VOC, t the residence time of gases in the PFR ($t = L/v$, where v is average gas velocity, and L the length of reactor), and k a global, first order reaction rate constant. The rate constant is usually represented by an Arrhenius model, i.e.:

$$k = k_o e^{-E/RT} \tag{11}$$

where k_o is the pre-exponential factor, E the activation energy, R the ideal gas law constant (energy units), and T the absolute temperature.

In our previous paper, results were reported for H_2O_2 enhancement of VOC destruction and a global kinetic model was presented. In this paper, our primary purpose is to report the experimental results for ozone injection. Because ozone proved to be less versatile than H_2O_2 (in fact, O_3 had no effect on some compounds), our modeling efforts were restricted to statistical curve fitting. No mechanistic models are being proposed at this time.

For the unenhanced (no added H_2O_2 or O_3) thermal destruction, a global first-order model is:

$$-\frac{d[C]}{dt}=k[C] \tag{12}$$

As in our previous work with H_2O_2, when O_3 was added to the hot gases an initial, very fast partial destruction of n-heptane (a “jump”) was noticed followed by a return to a more “normal” rate of destruction. It was observed that ozone seemed to affect both the initial amount of destruction and the rate constant for subsequent destruction. Testing various models, a statistically significant relationship was found for both effects. Our final proposed model is given by eq. (13). It is emphasized that this is a global model and *not* a mechanistic model.

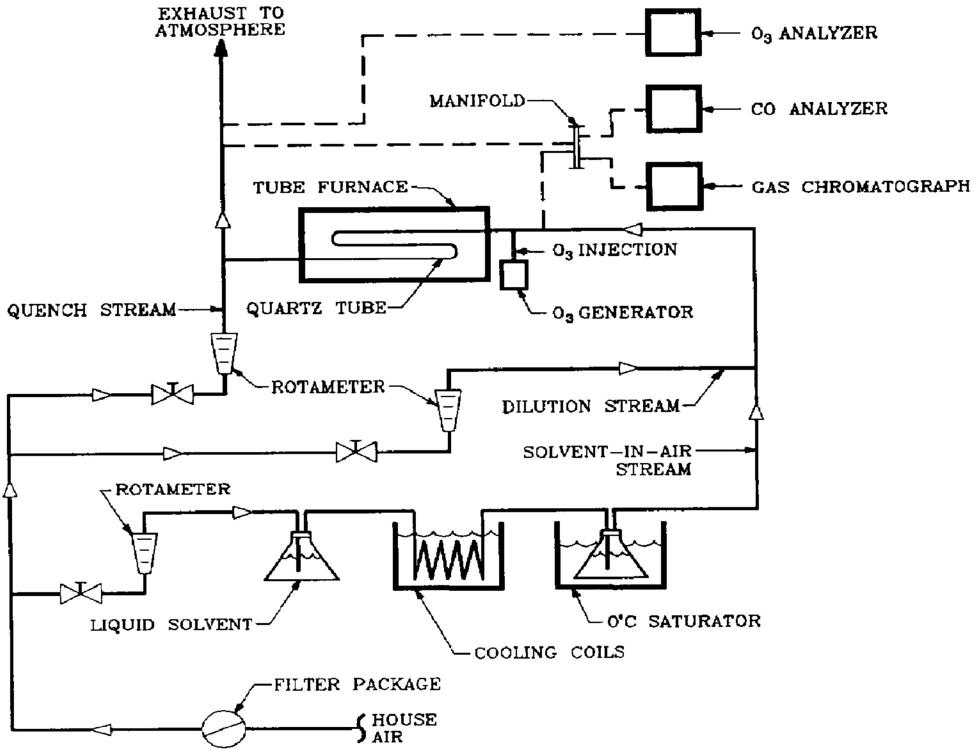

Fig. 1. Schematic diagram of experimental equipment.

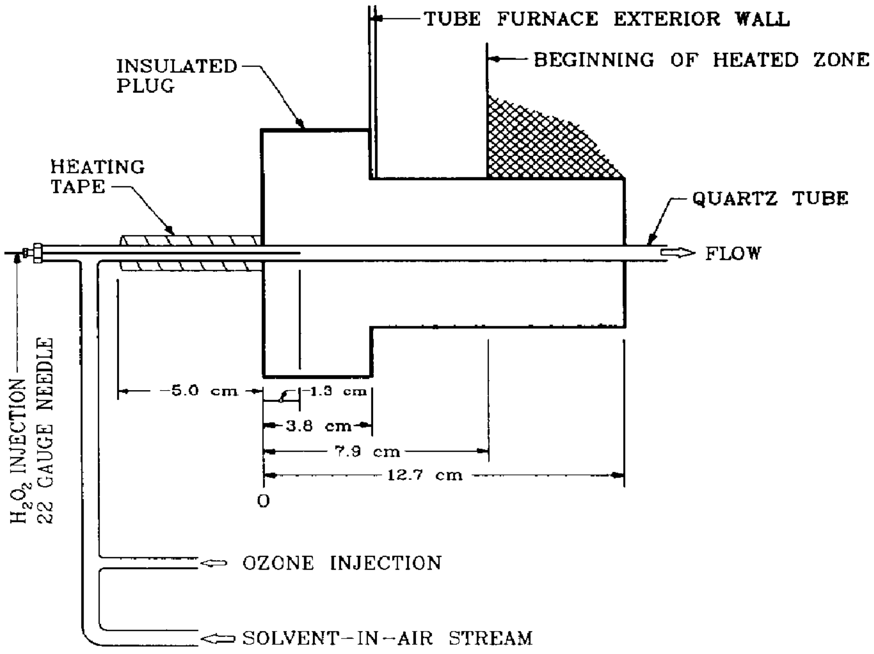

Fig. 2. Reactor inlet zone.

$$C=C_o(1-Z_1)[O_3]^{z_2})\exp(-k(1+Z_3[O_3])t) \tag{13}$$

where $[O_3]$ denotes the inlet ozone concentration (ppm), k the global first order rate constant for thermal (unenhanced) destruction (s^{-1}), t the residence time (sec), while Z_1, Z_2, and Z_3 are statistically fitted parameters. For ease of plotting, the fractional destruction (D) is simply $1-C/C_o$.

Experimental equipment and methods

The experimental equipment and methods were described in detail recently [1], however, a brief summary is presented here as well. The experimental system consisted of several components. The reactor was a 200 cm long, 6 mm OD, 4 mm ID, quartz tube, externally heated in a Lindberg tube furnace, similar to a system used by other investigators in the past [7,8]. A network of calibrated rotameters provided precise and reasonably accurate air flow controls. A dual saturator system allowed for producing saturated VOC-in-air concentrations [9] which could be diluted to a desired inlet concentration (about 1000 ppm). A Fisher (Antek) GC (with a FID) and Thermo Electron Model 48 CO analyzer were used to measure the VOC and CO concentrations respectively. In addition to external temperature control, internal gas temperature at two positions were measured with thermocouples, inserted axially. A schematic diagram of the experimental equipment is presented in Fig. 1.

The ozone-in-air stream was generated by a Model 03V5-0 OREC ozone generator and injected into the VOC-in-air stream just upstream of the heated

TABLE 1

Fractional destruction of n-heptane with and without ozone addition

Reactor temp. (°C)	Residence time (s)	Ozone concentration (ppm)			
		0.0	0.5	1.5	3.0
637	0.28	0.05	0.17	0.25	0.28
637	0.36	0.06	0.21	0.23	0.26
637	0.45	0.08	0.22	0.26	0.28
637	0.53	0.08	0.25	0.25	0.32
637	0.69	0.10	0.33	0.38	0.42
637	0.84	0.07	0.29	0.36	0.40
650	0.27	0.08	0.20	0.34	0.35
650	0.36	0.10	0.26	0.36	0.36
650	0.44	0.11	0.27	0.32	0.39
650	0.52	0.12	0.35	0.40	0.42
650	0.68	0.14	0.37	0.45	0.49
650	0.83	0.15	0.37	0.46	0.52
662	0.27	0.11	0.27	0.37	0.38
662	0.35	0.12	0.31	0.39	0.41
662	0.44	0.14	0.25	0.39	0.47
662	0.52	0.18	0.38	0.42	0.49
662	0.67	0.21	0.44	0.52	0.55
662	0.82	0.21	0.46	0.50	0.58
675	0.26	0.18	0.36	0.43	0.51
675	0.35	0.24	0.37	0.48	0.55
675	0.43	0.31	0.52	0.53	0.59
675	0.51	0.31	0.53	0.61	0.68
675	0.66	0.44	0.60	0.73	0.76
675	0.80	0.63	0.82	0.83	0.84
687	0.26	0.34	0.57	0.64	0.68
687	0.34	0.42	0.65	0.72	0.78
687	0.43	0.48	0.66	0.73	0.80
687	0.50	0.57	0.76	0.80	0.85
687	0.65	0.82	0.92	0.93	0.95
687	0.79	0.78	0.95	0.97	0.98

zone of the reactor (see Fig. 2). The gas stream then continued through the externally heated, quartz tubular flow reactor. The inlet O_3 concentration was determined by diluting it and measuring the mixture using a Thermo Electron O_3 Analyzer (Model 49).

In each set of constant temperature experiments, gas residence time in the tubular reactor was controlled by adjusting gas flow rate. Tests at several different residence times were made. On exiting the reactor, the gases were immediately quenched and diluted with a measured flow rate of air. Inlet and

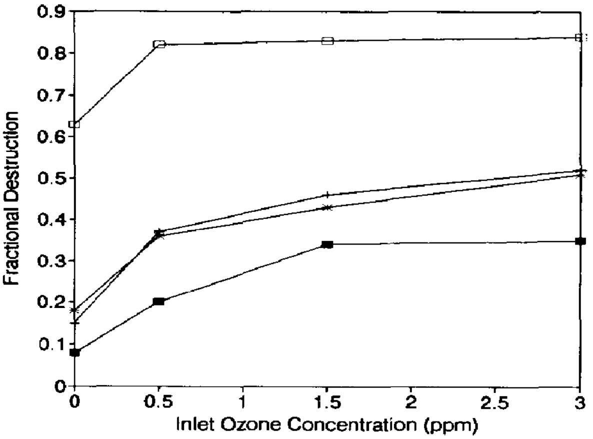

Fig. 3. Fractional destruction on n-heptane. Conditions: (■) 650 °C, 0.27 s; (+) 650 °C, 0.83 s; (∗) 675 °C, 0.26 s; and (□) 675 °C, 0.80 s.

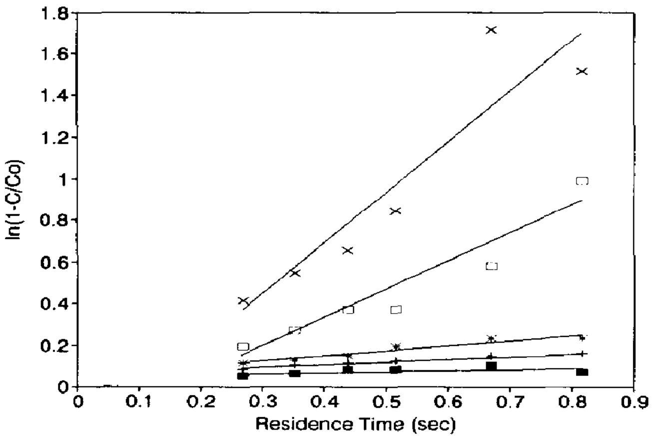

Fig. 4. Evaluation of thermal (unenhanced) rate constant for n-heptane destruction. Conditions: (■) 637 °C, (+) 650 °C, (∗) 662 °C, (□) 675 °C, and (×) 687 °C.

outlet concentrations of the parent VOC were measured by GC. Outlet CO concentrations were also measured and are reported in this paper. In all cases, no O_3 was observed exiting the reactor, in keeping with the rapid decomposition of ozone at these temperatures.

Results

The results for O_3 are interesting in that O_3 had a marked effect on n-heptane but no effect on isopropanol or on either of the chlorinated organics. The results for n-heptane are displayed in Table 1. For ease of plotting the results, the fractional destruction $(1-C/C_o)$ was used, where C represents the concen-

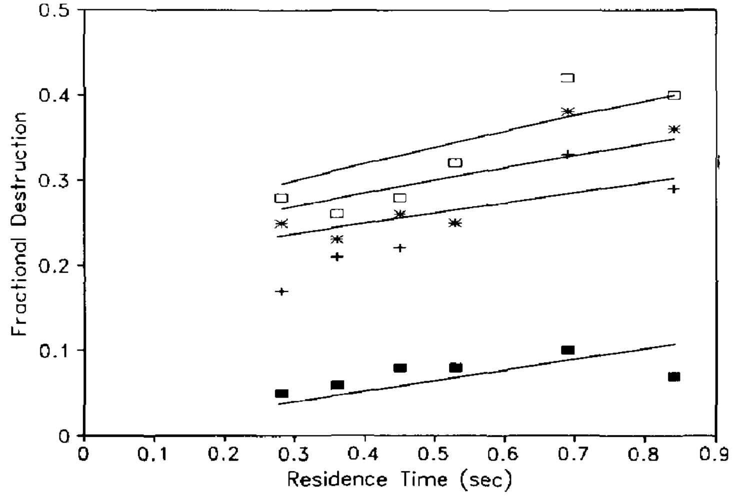

Fig. 5. Fractional destruction of n-heptane at 637 °C. Inlet [O_3]: (■) 0.0, (+) 0.5, (∗) 1.5, and (☐) 3.0 ppm. (Symbols are experimental data; lines are best fit model.)

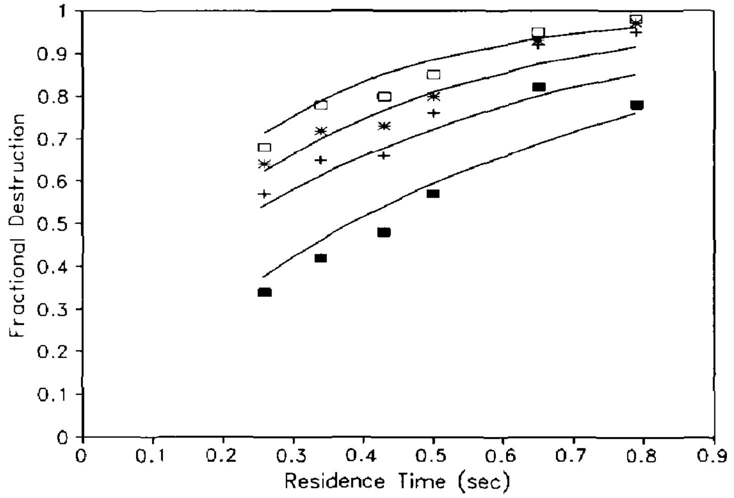

Fig. 6. Fractional destruction of n-heptane at 687 °C. Inlet [O_3]: (■) 0.0, (+) 0.5, (∗) 1.5, and (☐) 3.0 ppm. (Symbols are experimental data; lines are best fit model.)

tration of n-heptane. For temperatures between 637 and 687 °C, the fractional destruction of n-heptane increased with increasing amounts of O_3, from no effect (when injecting no ozone) to over a 500% increase (observed when 3.0 ppm O_3 was used at 637 °C and 0.28 seconds residence time). The effect is greater at shorter residence times as shown in Fig. 3. This large effect of O_3 limited the upper temperature to which we could operate and achieve measurable fractional destructions with our equipment. Temperatures below 637 °C were not tested because of the low (essentially zero) destruction observed without ozone injection.

TABLE 2

Best fit parameters for modeling n-heptane destruction[a]

Reactor temp. (°C)	k (s^{-1})	Z_1	Z_2	Z_3
637	0.136	0.214	0.090	0.371
650	0.231	0.214	0.090	0.371
662	0.339	0.214	0.090	0.371
675	0.912	0.214	0.090	0.371
687	1.806	0.214	0.090	0.371

[a] Model is: Destruction $= 1-C/C_o$ where $C = C_o(1-Z_1[O_3]^{z_2})\exp(-k(1+Z_3[O_3])t)$.

TABLE 3

Fractional destruction of various VOCs with and without O_3 and H_2O_2 addition

Reactor temp. (°C)	Residence time (s)	O_3 Effects		H_2O_2 Effects	
		$[O_3]$ at inlet (ppm)	Fractional destruction	$[H_2O_2]$ at inlet (ppm)	Fractional destruction
			Isopropanol		
662	0.94	0	0.59	0	0.60
662	0.94	5	0.59	400	0.62
662	0.94	10	0.57	800	0.65
662	0.94	20	0.57	1900	0.71
662	0.94	40	0.58	2400	0.76
675	0.28	0	0.38	0	0.40
675	0.28	5	0.37	400	0.43
675	0.28	–	–	800	0.48
675	0.28	–	–	1900	0.63
675	0.28	–	–	2400	0.68
			Chlorobenzene		
725	0.50	0.0	0.28	0.0	0.32
725	0.50	120	0.31	805	0.38
725	0.50	150	0.31	3363	0.44
725	0.50	200	0.31	9238	0.53
			Trichloroethylene		
600	0.25	0.0	0.28	–	–
600	0.25	1.0	0.32	–	–
600	0.25	2.2	0.32	–	–
600	0.25	8.7	0.33	–	–
600	0.49	–	–	0	0.27
600	0.49	–	–	800	0.32
600	0.49	–	–	1860	0.36
600	0.49	–	–	3200	0.39

TABLE 4

Carbon monoxide production (ppm) for n-heptane with and without ozone addition

Reactor temp. (°C)	Residence time (s)	Ozone concentration (ppm)			
		0.0	0.5	1.5	3.0
637	0.28	26	63	127	195
637	0.36	24	77	128	168
637	0.45	23	89	138	156
637	0.53	30	138	154	188
637	0.69	32	145	279	336
637	0.84	32	183	253	325
650	0.27	26	68	127	141
650	0.36	27	72	148	171
650	0.44	26	84	160	218
650	0.52	25	127	209	232
650	0.68	26	148	304	354
650	0.83	26	160	301	410
662	0.27	37	88	162	198
662	0.35	32	116	204	250
662	0.44	34	152	210	270
662	0.52	44	160	224	300
662	0.67	68	232	391	498
662	0.82	73	282	415	578
675	0.26	42	140	190	271
675	0.35	54	125	239	325
675	0.43	65	241	342	354
675	0.51	73	240	363	464
675	0.66	222	560	718	898
675	0.80	371	1023	1194	1382
687	0.26	86	205	457	580
687	0.34	106	294	515	767
687	0.43	164	435	563	738
687	0.50	354	1023	742	1080
687	0.65	709	1595	1935	2408
687	0.79	908	1891	–[a]	–[a]

[a] These values are off the CO analyzer scale.

Global first order rate constants were calculated per eq. (10) for thermal destruction at each temperature using the computer program SAS (version 6.06.01, 1989 [10]). Plots of the rate data using eq. (10) are shown in Fig. 4. Next, values for the parameters Z_1, Z_2, and Z_3 in eq. (13) were determined by a non-linear least squares fitting of all the ozone enhanced data. This statistical fitting produced reasonably good results as shown in Figs. 5 and 6. The values of the parameters are given in Table 2.

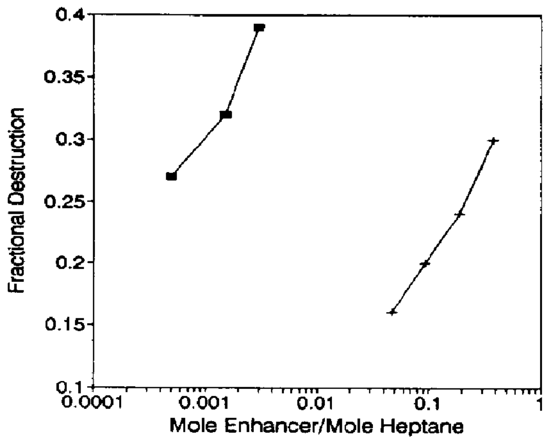

Fig. 7. Comparison of ozone (■) and hydrogen peroxide (+) for effectiveness of n-heptane destruction ($T=650°C$, $t=0.44$ s).

Tests on the other VOCs showed no effect at various levels of ozone as shown in Table 3. As was the case with our previous tests using H_2O_2, CO was generated and persisted during the destruction of the VOC. The CO results are shown in Table 4. It is noted that if O_3 or H_2O_2 permits lower temperature incineration of VOCs, the process may be limited ultimately by CO. On the other hand, if O_3 or H_2O_2 is injected at the tail end of the process to scavenge low concentrations of organics, CO production may not be a problem.

A comparison of the effectiveness of H_2O_2 and O_3 is shown in Figure 7. As can be seen, O_3 is much more effective (on n-heptane) per mole than H_2O_2. However, O_3 appears to be less versatile than H_2O_2 because it worked on only one type of VOC tested. This is likely because the ozone attack is via an O biradical, whereas the H_2O_2 attack begins with an $HO^{\bullet}$ radical.

The surface effects of the reactor were not examined in this study; however, radicals may be energized or de-energized by collisions against the reactor walls. In general, as the surface to volume (S/V) ratio of the reactor increases, the wall effects on the total reaction become of greater importance. Conversely, importance of wall reactions drops as S/V is reduced. Ritter et al. [11] observed in quartz tube experiments that higher conversion was found for 4 mm diameter tubes than in 10.5 or 16 mm tubes.

This research has potential usefulness to commercial hazardous waste incinerator (or even solid waste incinerator) operators. For an existing incinerator that is not meeting standards for destruction of toxics, the introduction of H_2O_2 or O_3 into the post flame gases may be an economical way to achieve a better destruction efficiency, and might even allow operation at a lower temperature (thus reducing NO_x formation).

Conclusions

The introduction of O_3 into a hot air stream with premixed n-heptane vapors clearly enhances n-heptane oxidation. This enhancement does not occur for three other VOCs tested. Carbon monoxide is produced as one of the products of incomplete combustion and persisted at the temperatures of our experiments. It is possible that O_3 injection may prove to be a commercially economical way to provide destruction of certain hazardous organics, but more study is needed to quantify all the benefits and costs. Such study should include consideration of other alternatives such as carbon adsorption or fixed bed catalytic oxidation systems.

Acknowledgements

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