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Project Summary

Destruction of Chlorinated Hydrocarbons by Catalytic Oxidation

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This report gives results of a study to determine the effectiveness of catalytic oxidation for destroying vapor-phase chlorinated hydrocarbons. The study was conducted on two pilot-scale catalytic incinerators: one employed a metal oxide catalyst in a fluidized-bed configuration; and the other, a fixed-bed proprietary catalyst, supplemented with ultraviolet (UV) light and ozone injection. Both systems were tested under a variety of temperatures and space velocities. The test vapor streams consisted of low concentrations (3 to 200 ppmv) of mixtures of organic compounds, and included three streams which represented emissions from air strippers used to treat contaminated groundwater at U.S. Air Force bases. Study results showed that the fluidized-bed catalytic incinerator was capable of achieving total organic destruction efficiencies of greater than 98%. The UV/ozone catalytic system failed to achieve high destruction efficiencies: with ozone injection, total destruction was 75%; and without ozone, the maximum destruction efficiency was 64%.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

A test program has been completed for the EPA and the Air Force to investigate, on an experimental scale, the effectiveness of catalytic oxidation as a means of destroying specific volatile organic compounds (VOCs) and hazardous/toxic air pollutants (HAPs). Two pilot-scale catalytic oxidation units and a test mixture vapor generation system were used for the testing. Objectives of the study were broad and two-fold: (1) to generate additional publicly available data on the performance of commercial catalytic oxidizers, with particular emphasis on chlorinated hydrocarbons; and (2) to investigate the performance of commercially available catalytic oxidation systems that may be suitable for the treatment of gas streams from air strippers used in groundwater cleanup. Three of the four VOC/HAP mixtures tested were representative of actual off-gases from such air strippers.

Test System

Parametric testing of two skid-mounted catalytic oxidation systems was performed to assess the effects of operating and design parameters on destruction efficiency. The oxidation systems tested were a 500 scfm* fluidized-bed catalytic incinerator leased from ARI International and a 20 scfm ultraviolet (UV)/catalytic oxidizer leased from Ultrox International. A test compound vapor generation system, which included a pump, a glass mixing chamber, and motor-driven syringes, was used to produce spiked air streams with the desired concentration of organic vapors. Figures 1 and 2 are diagrams of the fluidized-bed and UV catalytic systems, respectively.

Experimental Design

Before the tests, major vendors of catalytic oxidation systems were contacted to: (1) investigate the availability of catalysts

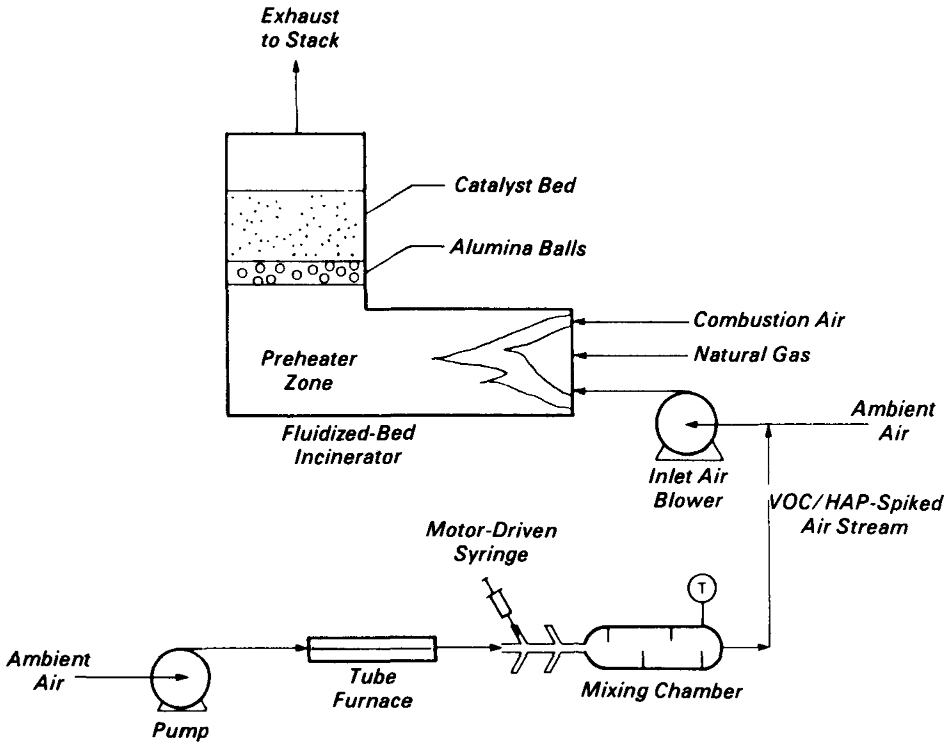

Figure 1. *Fluidized-bed catalytic test system.*

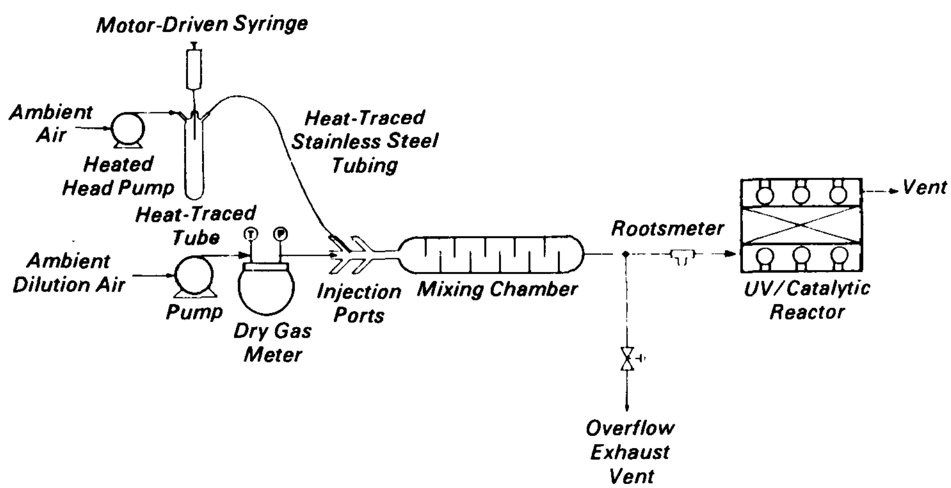

Figure 2. *UV/catalytic test system.*

and catalytic systems suitable for destroying chlorinated hydrocarbons, and (2) identify vendors with existing laboratory- or pilot-scale units that could be tested under this program. This effort identified only the two systems tested.

Major operating parameters that were varied during the fluidized-bed incinerator testing included VOC/HAP mixture, catalyst inlet temperature, space velocity, and inlet concentration. Testing was generally conducted to characterize destruction across the gas-fired preheater and th catalyst bed as a "system." Howeve heater and catalyst destruction efficier cies were also determined separately a most test conditions.

Operating parameters that were varie during the UV/catalytic oxidizer testing ir cluded space velocity, inlet concentratior UV intensity, humidity, and ozone additior

Components and target concentration for the test mixtures are shown in Tabl 1. All four mixtures shown in Table 1 wer tested with the fluidized-bed system, bu only one mixture was tested with the U\ catalytic oxidizer. The ranges of operatin conditions tested for the two catalyti systems are summarized in Table 2. A shown in Table 2, the fluidized-bed syster was tested at two space velocities for ca alyst inlet temperatures ranging from 65 to 950 °F. Two inlet concentrations fc Mixture 4 were also tested. The UV/cat lytic oxidizer was tested at three spac velocities, two humidities, and with/witl out ozone addition. Two inlet concentra tions for Mixture 1 were also tested.

Fluidized-Bed Incinerator Results

Results for the fluidized-bed incinerat showed average system destruction eff ciencies for total VOCs in the 97 to 99 range for all four test mixtures. Cataly inlet temperature showed a strong effec on destruction efficiency, while mixtur composition, air-to-gas (fuel) ratio, spac velocity, and inlet concentration a showed marginal or statistically insign icant effects.

The effect of catalyst inlet temperatur on mixture system destruction efficiencie is shown in Figure 3 for a space velocit of 10,500 hr^{-1}. Comparison of destru tion efficiencies for the different mixture shows that the highest efficiencies we observed for Mixture 2 and the lowest, fc Mixture 4. The low destruction efficienc of Mixture 4 is attributed to the presenc of tetrachloroethylene, which showed th lowest destruction efficiency of the 1 compounds tested.

The effect of catalyst inlet temperatu on component destruction efficiency wa similar for all test compounds excej trichloroethylene and benzene in Mixtu 2. These compounds (in particular be zene) showed a very sharp increase destruction between 650 and 800 °F. Or possible explanation for the observed e

*Readers more familiar with the metric system m use the conversion factors at the back of t Summary.

ıble 1. *Mixture Compositions and Target Concentrations for Catalytic Oxidation Tests*

Mixture Designation	Concentration Level	Mixture Compounds	Target Inlet Concentration ppmv[a]
1	Baseline	Trichloroethylene	6.3
		1,2 dichloroethylene	8.5
			14.8
1	Low	Trichloroethylene	1.9
		1,2 dichloroethylene	1.0
			2.9
2	Baseline	Trichloroethylene	2.7
		Benzene	1.5
		Ethylbenzene	5.6
		Pentane	11.5
		Cyclohexane	14.1
			35.4
3	Baseline	Vinyl Chloride	7.5
		Trichloroethylene	1.8
			9.3
4	Baseline	1,2 dichloroethane	10
		Trichloroethylene	10
		1,1,2-trichloroethane	10
		Tetrachloroethylene	10
			40
4	High	1,2 dichloroethane	50
		Trichloroethylene	50
		1,1,2-trichloroethane	50
		Tetrachloroethylene	50
			200

ɔpmv = parts per million by volume as compound.

'able 2. *Summary of Operating Conditions Tested*

Catalytic System	Test Parameter	Conditions Or Values Tested
Fluidized-Bed Incinerator	VOC/HAP Mixture	Mixtures 1, 2, 3, 4
	Space Velocity	7,000 and 10,500, hr^{-1}
	Operating Temperature (Catalyst Inlet)	650 to 950°F
	Inlet Concentration	Baseline and High[a]
UV/Oxidizer	VOC/HAP Mixture	Mixture 1
	Space Velocity	200 to 3000 hr^{-1} (1 to 15 scfm)
	Inlet Concentration	Baseline and Low[a]
	Humidity	Ambient 150% Ambient
	Ozone	Without Ozone With Ozone
	UV Intensity	UV Lamps On UV Lamps Off

[a]Mixtures and concentrations are summarized in Table 1.

fect is the low concentration of benzene and trichloroethylene in Mixture 2 relative to the other three compounds.

Destruction efficiency across the gas-fired preheater generally ranged from 15 to 55% for Mixtures 1, 3, and 4, which contained only chlorinated hydrocarbons. Heater destruction efficiencies for Mixture 2 were slightly higher (40 to 60%).

Other results from the fluidized-bed incinerator testing included:

- Low concentrations of several chlorinated products of incomplete oxidation were identified by mass spectrometry.
- Incinerator outlet CO concentrations were less than 100 ppmv for most test conditions.
- No statistically significant effect was found for space velocity on destruction efficiency (although an apparent trend is seen when comparing mean values).
- Inlet concentration had no effect on Mixture 4 destruction efficiency over the range tested.
- Method 18 and the Tenax-GC sampling method destruction efficiencies showed good agreement for all species and mixtures, except benzene in Mixture 2.
- Maximum theoretical HCl emissions from Mixtures 1, 2, and 3 were estimated to range from 0.06 to 0.3 lb/hr (6.3 to 28 ppmv) for a 1,000 scfm inlet gas stream.

UV/Oxidizer Results

Test results for the UV/catalytic system without ozone showed total VOC destruction efficiencies ranging from 16 to 67%. The single most important parameter affecting destruction efficiency was space velocity, and the highest efficiencies were observed at a space velocity of 200 hr^{-1} (or a residence time of 18 seconds).

With ozone addition, complete oxidation of the test mixture components was achieved, but high concentrations of several unidentified reaction products were observed. Two of these products were identified by mass spectrometry as methyl formate and methyl acetate.

Conclusions

The fluidized-bed incinerator testing verified that overall destruction efficiencies of total VOCs in the 97 to 98% range are achievable with catalytic incineration for chlorinated hydrocarbon mixtures. Results from this testing also indicate that catalytic incineration may be a viable option for the control of VOC/HAP emissions from groundwater air strippers.

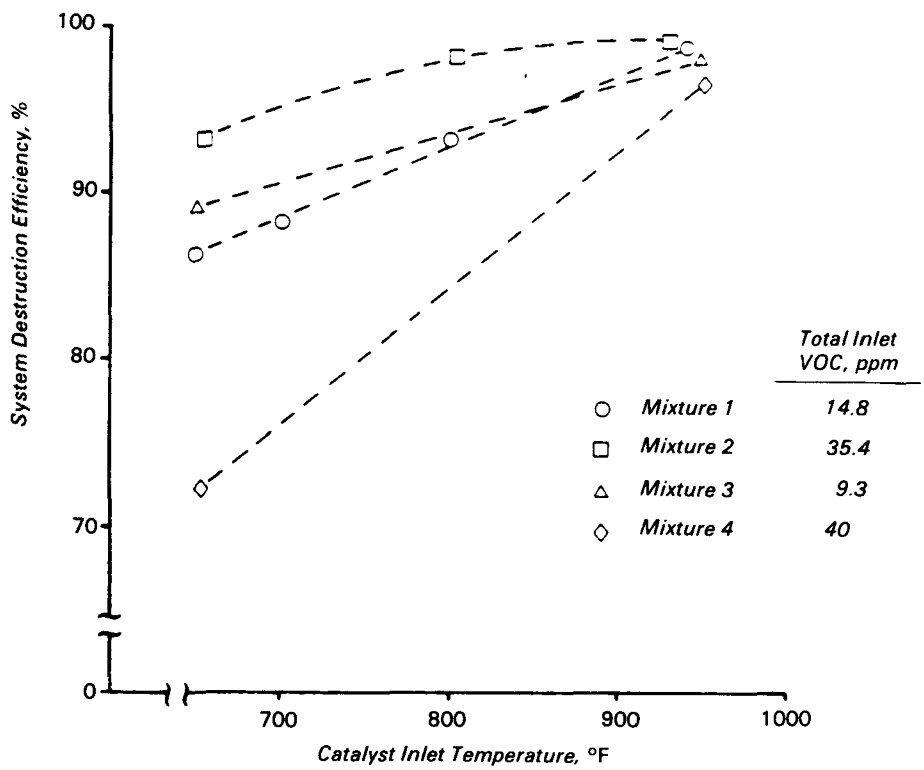

Figure 3. *Fluidized-bed catalytic system destruction efficiencies (total organics) for four test mixtures.*

The UV/catalytic oxidizer testing show ed that unreasonably long gas residenc times are required to achieve acceptabl destruction without ozone addition an that high concentrations of reaction prc ducts are observed with ozone addition fc this system. At this time, the UV/catalyti oxidizer would not be considered appropr ate for controlling VOC/HAP emissions.

Conversion Factors

Readers more familiar with the metri system may use the following factors t convert the nonmetric units used in thi Summary.

Nonmetric	Times	Yields Metri
cfm	1.70	m^3/hr
°F	5/9(°F-32)	°C
lb	0.454	kg

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***Bruce A. Tichenor** is the EPA Project Officer (see below).*
The complete report, entitled "Destruction of Chlorinated Hydrocarbons by Catalytic Oxidation," (Order No. PB 87-101 234/AS; Cost: $16.95, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
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