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Project Summary

Experimental Investigation of PIC Formation in CFC Incineration

Garth R. Hassel

The purpose of this study was the collection of combustion emission characterization data from chlorofluorocarbon (CFC) incineration. A bench scale test program to provide emission characterization data from CFC incineration, with emphasis on products of incomplete combustion (PIC) formation, was developed and performed. Tests involved separately metering CFC-11 and -12 into a propane gas primary flame. Propane also fueled an afterburner. Simultaneous combustion gas samples were taken upstream and downstream of the afterburner. The gas samples were analyzed for the CFCs to determine the destruction efficiencies (DEs) of the CFCs and for the major PICs from each CFC. Sampling was performed one time to screen for polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polycyclic aromatic hydrocarbons (PAHs) while incinerating CFC-12. Toluene and xylene were the two most frequently occurring PICs in this study. Most of the PICs identified were non-halogenated. PIC concentrations were independent of the concentration of CFC in the fuel. Flammability limits were 39 volume percent CFC-11 and 58 volume percent CFC-12 in propane. DEs of at least 99.999% can be repeatedly attained for both CFC-11 and -12 even from a relatively low temperature flame. The use of an afterburner is not necessary to attain high DEs of CFC-11 and -12. DEs of greater than 99.999% still allow for high generation of PCDD/PCDF. Extensive PCDD/PCDF formation when burning CFC-12 was apparently independent of entrained particulate matter. The wide variety of PICs, ranging from aliphatic to aromatic species, observed in the study is a strong indication that CFC destruction during thermal incineration occurs through complex reaction pathways.

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

Chlorofluorocarbons (CFCs) are implicated in the depletion of stratospheric ozone, and are also contributors to global warming. As a result of the Montreal Protocol and other pending international and national agreements that will curtail the production of the traditional CFCs and halons, it may be necessary to thermally destroy considerable quantities of these materials in order to reduce their current inventory. Thermal incineration is the only technology available at commercial scale for CFC destruction. Incineration may be an appropriate technology in helping to reduce the global inventories, if no significant health or environmental risks result from the combustion emissions of the CFCs.

The environmental concerns resulting from CFC incineration include possible formation of potentially toxic products of incomplete combustion (PICs), and acid and halogen gas emissions. PIC formation, in general, involves poorly understood phenomena associated with waste incineration, which is further complicated for CFC incineration processes since no data on PIC formation are available.

The purpose of this study was the collection of combustion emission characterization data from CFC incineration. The objectives were to evaluate thermal incineration as one of the appropriate technologies for the safe disposal of CFCs, and to improve the CFC incineration technology by identifying the incinerator designs and operating conditions which minimize the formation of hazardous PICs. To achieve the goals of this project, information was obtained on the relationship between PIC emissions and combustion conditions using supplemental fuels which are employed in CFC incineration. Since no significant test burn data are available, a test program to provide emission characterization data from CFC incineration, with emphasis placed on PIC formation, was developed and performed. The goal of the study was to provide information on which incinerator designs and operating conditions are needed to maximize CFC destruction efficiency and minimize PIC formation. Users of data and findings in this report should note that test results and conclusions are based on experimental, not validated, procedures. A QA program implemented on this project is reported in Appendix E of the Final Report.

Experimental

The turbulent flame reactor (TFR) used as the primary combustor for this study was a swirling air/liquid spray or gas injector burner firing into a 12 in.* ID by 24 in. long enclosure. Following the TFR was an afterburner (AB) consisting of a 12 in. ID refractory lined chamber with three fuel/air injectors near its base. At the exit of the AB was a 4 in. ID 304 stainless steel duct that wound about 30 ft** before reaching a scrubber.

Tests involved separate metering of CFC-11 and -12 into a propane gas flame. Flammability limits (maximum volume % in the fuel) were determined for both CFCs. The test matrix is presented in Table 1. The baseline condition (medium concentration of CFC-12 in the fuel) was repeated twice, yielding triplicate data at baseline conditions.

Combustion gas samples were taken upstream and downstream of the afterburner simultaneously using EPA Method 18, "Measurement of Gaseous Organic Compound Emissions by Gas Chromatography." The gas samples were analyzed for the CFCs to determine the destruction efficiencies of the CFCs. An attempt was also made at quantifying many of the major PICs from each CFC. A system blank was taken to evaluate the background organic species produced by the propane fuel. Sampling was performed one time at the baseline condition with the objective of screening for PCDD/PCDF and PAH while incinerating CFCs. Sampling was performed according to California Air Resources Board Method 428, "Determination of Polychlorinated Dibenzo-p-dioxin (PCDD), Polychlorinated Dibenzofuran (PCDF), and Polychlorinated Biphenyl Emissions from Stationary Sources." The sample was taken downstream of the afterburner.

Table 1. *Target Volumetric Concentration of CFC in TFR Fuel*

CFC-	*2%*	*10%*	*20%*
12	*X*	*XXX**	*X*
11	*X*		*X*

* *Baseline condition, tested in triplicate plus one-time sampling for dioxin.*

Temperatures were measured by thermocouples protruding to the centerline of the furnace. Pretest temperatures were also taken using a suction pyrometer. The flue gas was continuously monitored downstream of the AB for combustion products. The continuous monitoring system (CMS) included oxygen (O_2), carbon dioxide (CO_2), carbon monoxide (CO), nitrogen oxides (NO_x) as nitric oxide (NO), and total unburned hydrocarbons (THCs).

The TFR was fired at 73,000 Btu/hr* at a stoichiometric ratio of 1.1 (2% O_2). Combustion air for the primary flame was preheated to 375°F.** The target AB conditioners were 1800°F and 7% excess O_2. Attaining 1800°F at 7% O_2 required that AB be fired at 91,000 Btu/hr, with the O_2 being supplied by compressed O_2 instead of air.

Results

Flammability limits were determined by slowly increasing the flow of CFC into the steady stream of propane fuel leading to the TFR until the flame was extinguished. The flammability limit for CFC-11 (39% by volume, 67% by weight) was lower than that of CFC-12 (58% by volume, 79% by weight), which could be expected because of the greater molecular weight of CFC-11. Because the flammability limits were higher than anticipated, these tests could not be completed under conditions identical to those of the destruction efficiency (DE) tests. The firing rate (fuel flow) had to be approximately halved compared to the DE tests.

Figure 1 shows the average system temperatures and AB residence times. Table 2 summarizes the DEs and the PICs. PIC concentrations were generally low. Some PICs most likely reflect interaction of the CFC with the propane fuel, such as hexafluoropropene, trichlorotrifluoroethane, and chloroform. Toluene and xylene were the two most frequently occurring PICs in this study. Because they are non-halogenated, condensed-ring structures, their presence is indicative of pyrolysis of the fuel alone. Most of the PICs identified were non-halogenated. Overall, PICs formed at least as frequently in the secondary flame as in the primary flame.

The PCDD/PCDF levels were surprisingly high. Fluorinated dioxins and furans were not detected; however, calibration standards for these species were not available. Table 3 lists the PCDD/PCDF emissions. The lack of contamination and particulate matter in the system implies that a significant PCDD/PCDF formation mechanism exists that is not catalyzed by entrained particulate matter. The PCDD/PCDF probably formed either in the primary flame and survived the afterburner via cold pathways along the walls and near the burner jets or in the long section of 4 in. stainless steel flue duct, which was about 20 ft in length from the AB exit to the point of semivolatile organics sampling. The detection limits for the volatile organics (tedlar bag) analyses alone were high enough (63 ng/L) that sufficient concentrations of organic precursors could have been present to yield the concentrations of PCDD/PCDF detected (24 ng/L).

Conclusions

Flammability limits were 39 volume % CFC-11 and 58 volume % CFC-12 in propane.

Destruction efficiencies of at least 99.999% are attainable for both CFC-11 and -12 even from a relatively low temperature flame. The use of an afterburner is not necessary to attain high DEs of CFC-11 and -12. The results are repeatable.

* 1 in. = 2.54 cm
** 1 ft = 0.3048 m

* 1 Btu/hr = 0.293 W
** °C = 5/9 (°F - 32)

DEs of greater than 99.999% still allow for high generation of PCDD/PCDF. Extensive PCDD/PCDF formation when burning CFC-12 was apparently independent of entrained particulate matter. PCDF concentration was 6.6 times the PCDD concentration.

Most PICs are non-halogenated species. PIC concentrations were independent of the concentration of CFC in the fuel. PAHs were not detected. The wide variety of PICs, ranging from aliphatic to aromatic species, observed in the study is a strong indication that CFC destruction during thermal incineration occurs through complex reaction pathways.

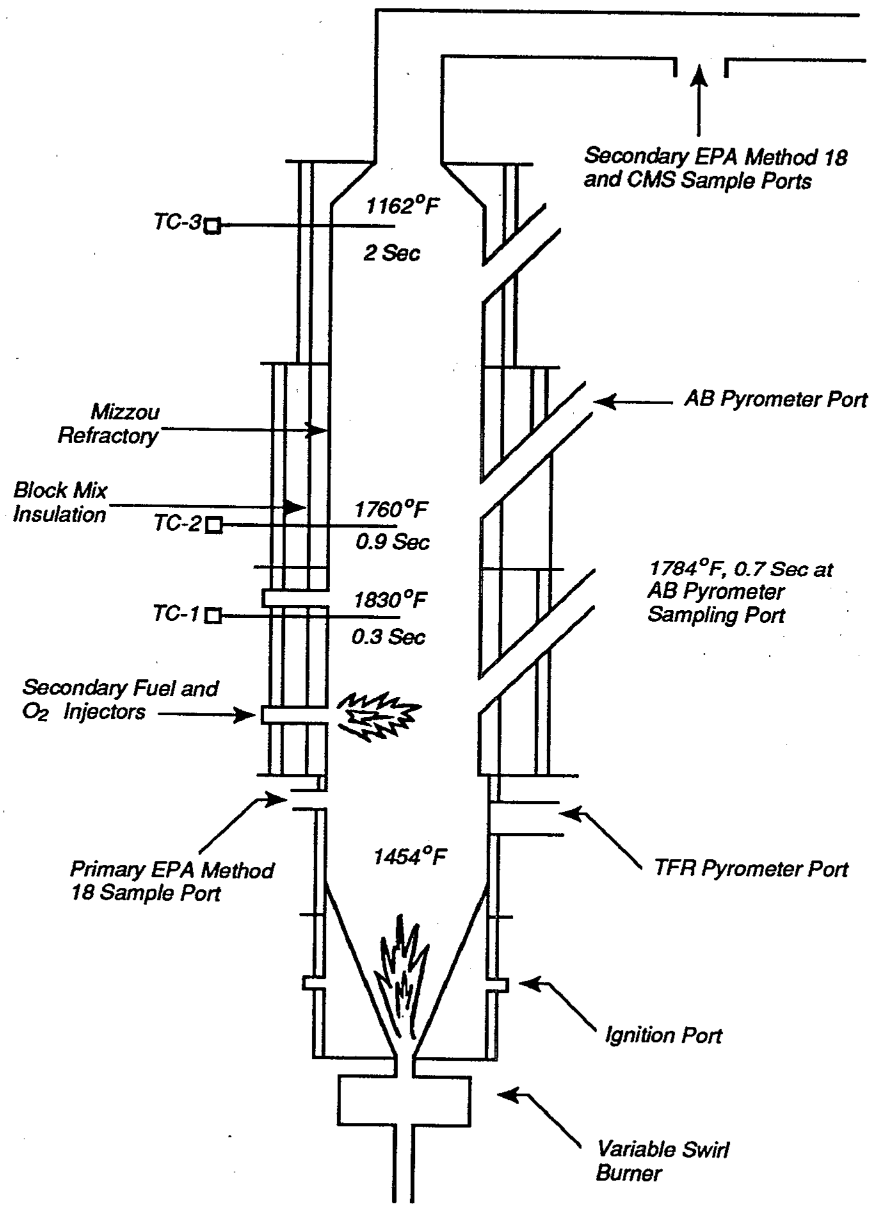

Figure 1. System diagram indicating average operating temperatures and cumulative AB residence times.

Table 2. *Destruction Efficiencies and Tentatively Identified Products of Incomplete Combustion*

	CFC-12		
Vol. % CFC in Fuel	8.3	8.3	8.3
Primary Flame			
CFC, ng/L	<63	<63	<63
DE, %	>99.9996	>99.9996	>99.9996
TICs,[1] ng/L	ND[2]	CFC-11, 81	ND
Secondary Flame			
CFC, ng/L	<63	<63	<63
Overall DE, %	>99.9994	>99.9994	>99.9994
TICs, ng/L	unknown, 69 toluene, 31 xylene, 19	hexafluoropropene, 781 unknown HC, 1000	hexafluoropropene, 2400 Unknown compound, 494 carbon disulfide/ trichlorotrifluoroethane, 438

	CFC-12	
Vol. % CFC in Fuel	14	1.3
Primary Flame		
CFC, ng/L	93	<63
DE, %	99.9997	>99.997
TICs[1] ng/L	CFC-11, 81 unknown HCs, 44, 256, 25 unknown compound, 225 toluene, 488 bicyclo[4,2,0]octa-1,2,5-triene, 644	chloroform, 213 pentane, 225 toluene, 50 xylene, 50
Secondary Flame		
CFC, ng/L	<63	<63
Overall DE, %	>99.9997	>99.996
TICs, ng/L	CFC-11, 250 methyl propene, 550 pentane, 581 trichlorotrifluoroethane, 325 toluene, 219 ethyl benzene, 113 xylene, 369	chloroform, 213

	System Blank	CFC-11	
Vol. % CFC in Fuel	0	1.3	13
Primary Flame			
CFC, ng/L	<63	181	<63
DE, %	NA[3]	99.993	>99.9998
TICs,[1] ng/L	ND[2]	unknown HCs, 550, 806, 5600 methyl propene, 713 trichlorotrifluoroethane, 413 cyclohexane, 556 ethylbenzene, 144 xylene, 450	ND
Secondary Flame			
CFC, ng/l	<63	<63	<63
Overall DE, %	NA	>99.997	>99.9997
TICs, ng/L	ND	unknown HCs, 44, 81 toluene, 19 xylene, 31	ND

[1] tentatively identified compounds
[2] not detected
[3] not applicable

Table 3. *PCDD/PCDF Results for 8.3% by Volume CFC-12 in Propane*

	Flue Gas Concentration µg/dscm	Generation Rate µg/g of CFC
Total PCDD	3.13	0.28
Total PCDF	20.70	1.82
PCDD/PCDF	23.80	2.09

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Garth R. Hassel is with Energy and Environmental Research Corporation, Irvine, CA 92718.
C.W. Lee is the EPA Project Officer, (see below).
The complete report, entitled "Experimental Investigation of PIC Formation in CFC Incineration," (Order No. PB92-126952/AS; Cost: $26.00, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650
The EPA Project Officer can be contacted at:
Air and Energy Engineering Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park NC 27711

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