United States
Environmental Protection
Agency

Air and Energy Engineering
Research Laboratory
Research Triangle Park, NC 27711

Research and Development

EPA/600/SR-93/103 August 1993

EPA

Project Summary

Characterization of the Organic Emissions from the Thermal Destruction of CFCs

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As a result of the Montreal Protocol, an international accord implemented to reduce the production and use of stratospheric ozone depleting substances, considerable quantities of chlorofluorocarbons (CFCs) and halons may be accumulated and ultimately require disposal or destruction. Incineration is a potential destruction technology; however, little is known of the combustion emission characteristics from CFC incineration. A study has been performed that characterizes the organic emissions resulting from the pilot-scale incineration of trichlorofluoromethane (CFC-11) and dichlorodifluoromethane (CFC-12) under varied feed rates. A 293 kW (1 million Btu/h) incinerator was made available to the EPA for these tests. The emissions characterizations focused on determining the destruction efficiencies (DEs) and major products of incomplete combustion (PICs) for each CFC evaluated. Sampling was performed to screen for volatile and semivolatile organic emission products including chlorinated aliphatics, chlorobenzenes, chlorophenols, polychlorinated dibenzodioxins and furans (PCDDs and PCDFs), and polyaromatic hydrocarbons (PAHs). Results indicate that five nines (99.999%) DE can be achieved at a CFC-11 feed rate as high as 69% by mass. The formation of volatile and semivolatile organic PICs was minimal. "Less than" concentrations are presented for target analytes not detected. Total PCDD/PCDF emission concentrations did not exceed 140 ng/Nm³. The injection of water into the combustion zone may improve the thermal destruction process.

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

Halogenated hydrocarbons such as chlorofluorocarbons (CFCs) have been implicated in stratospheric ozone depletion. International accords are in place to phase out the production and/or use of these ozone-depleting substances (ODSs) before the end of the century. Although some of these ODSs will be recycled, it will probably be necessary to destroy substantial quantities of some CFCs to reduce current inventories. A United Nations Environment Programme (UNEP) technical advisory committee was formed in 1991 to evaluate the most appropriate ODS destruction technologies. Incineration was identified as a potentially viable CFC destruction technology. However, the combustion emissions from CFC incineration have not been well characterized. Characterizing products of incomplete combustion (PICs) and determining destruction efficiencies (DEs) are required to fully evaluate the viability of incineration as a CFC destruction technology.

Relatively little information is available regarding CFC incineration, particularly in the area of PIC characterizations. Data have been collected indicating that various CFCs have been destroyed effectively by full-scale incineration. However, information regarding PICs is virtually nonexistent. EPA's Air and Energy Engineering

Research Laboratory (AEERL) initiated a program to evaluate the viability of CFC incineration, including characterization of PICs. As part of this program, a bench-scale study was performed that characterized the emissions from trichlorofluoromethane (CFC-11) and dichlorodifluoromethane (CFC-12) incineration. An emission sample was collected to screen for polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). The screen revealed that substantial quantities (23.8 μg/Nm³ total PCDD/PCDF) of PCDD/PCDF material were present in the incinerator emissions. Full-scale CFC incineration emissions data were needed to substantiate or refute this finding.

Through an agreement with EPA, a pilot-scale incinerator was made available to evaluate the incineration of CFC-11 and CFC-12 under conditions representative of full-scale incineration facilities. Under this agreement, T-Thermal, Inc., provided the equipment and labor support to prepare and operate the facility for the CFC incineration tests. Acurex Environmental Corporation directed these tests including coordination of sampling and analytical efforts.

Objectives

The primary objective of this study was to characterize organic emissions resulting from CFC incineration using a representative incineration facility. Particular emphasis was placed on characterizing PICs. A secondary objective was to confirm or refute the presence of PCDDs/PCDFs in the incineration emissions at concentrations similar to those observed during the previous AEERL-sponsored CFC incineration study. Should similar PCDD/PCDF emission concentrations be observed, the screening of incinerator emissions for volatile and semivolatile organic PICs may provide insight into potential PCDD/PCDF formation precursors or intermediates.

Experimental

The incineration tests were performed at T-Thermal, Inc.'s Conshohocken, PA, test facility. The test materials (CFC-11 and CFC-12) were incinerated at varied feed conditions. Four tests were performed. Table 1 presents the target CFC feeds for each test. Note the inclusion of a combustion blank (no CFC incineration) as a test condition.

Emissions samples were collected for volatile and semivolatile organics and subsequently analyzed to determine DEs and screen for PICs. Emissions were sampled downstream of all pollution control devices. Scrubber liquor samples were collected to also screen for semivolatile organic PICs. T-Thermal collected and provided the data pertaining to test facility operation including, waste and air flows, critical temperatures, continuous emission monitoring (CEM) data, and CFC feed rates.

Table 1. Target CFC Feed Conditions

Test	Test Conditions
1	*No. 2 fuel only*
2	*3% (by mass) CFC-12/balance No. 2 fuel oil*
3	*3% (by mass) CFC-11/balance No. 2 fuel oil*
4	*50% (by mass) CFC-11/balance No. 2 fuel oil*

The T-Thermal pilot-scale test facility is a down-fired, turbulent flame incinerator nominally rated at 293 kW (1 million Btu/h). A diagram of the test facility is presented in Figure 1. The incinerator consists of a T-Thermal LV-1.3 high intensity vortex burner mounted tangentially near the top of the vertical, refractory-lined incineration chamber. The No. 2 fuel oil and the CFC waste stream are introduced through the side mounted burner, while cooling water is introduced through the axially mounted top injector. The cooling water is injected into the flame region to maintain a consistent incineration temperature of 1,093°C (2,000°F).

Hot gases leaving the incinerator pass through a water-washed downcomer and bubble up through a pH-controlled water bath. The saturated gas leaves the quench tank at approximately 88°C (190°F) and enters a liquid separating tower prior to passing to the venturi scrubber for particulate removal. An alkaline solution (potassium hydroxide) is added to the quench tank to neutralize acid gases resulting from CFC destruction. Gases leaving the venturi scrubber pass through another liquid disentrainment tower prior to exhausting to a packed column scrubber. The pH-controlled packed column scrubber neutralizes any remaining acid gases. No induced draft fan is used on the incineration/pollution control system. Instead, the gases are directed through the system under positive pressure. All sampling and monitoring locations were at the exit of the packed tower.

Results

The incinerator operational data are summarized in Table 2. The data contained in this table were provided by T-Thermal. The summary data presented are based on the average of the measurements taken over each test period. The CFC feed rates are presented as a percentage of the sum of fuel and waste mass flows. The CFC feed rates obtained were in accordance with those established in the original test matrix. However, the obtained CFC feed rate for the high CFC feed rate test condition (68.9%) was actually significantly greater than the targeted level (50%). The 50% feed rate was expected to represent the maximum feed rate likely to be employed.

Five nines (99.999%) DE was achieved for the CFC-12 low feed rate (2.3%) and the CFC-11 high feed rate (68.9%). Only three nines DE was achieved for the CFC-11 low feed rate (2.9%). The DE for this test condition may have been affected by a CFC-11 sampling contaminant. CFC-11 was presented in CFC-12 and No. 2 oil baseline test samples as well as field blanks.

The addition of water to the combustion chamber to control burner temperature may also enhance the thermal destruction of CFCs. The addition of water would result in an increase in hydroxyl (OH) radicals. The OH radicals provide a bimolecular destruction mechanism in addition to unimolecular bond rupture decomposition.

Very few volatile PICs were present in the baseline, low feed rate CFC-12, and low feed rate CFC-11 test conditions. Many of the PICs present were at or near practical quantifiable levels. The CFC-11 high feed rate test condition did reveal several PICs in substantial concentrations. Chloroform was present at a relatively high concentration (1,500-1,600 μg/Nm³). Carbon tetrachloride was also evidenced but at a much lower concentration (170 μg/Nm³). Unexpectedly, the most prevalent PICs were brominated. Bromodichloromethane, dibromochloromethane, and tribromomethane (bromoform) were the three most prevalent PICs present. The presence of these PICs is surprising because no source of bromine was identified in the fuel and/or waste feed.

PCDDs and/or PCDFs were detected in all samples collected. However, the masses of PCDD/PCDF material present in most of the test samples were at or near levels present in field blanks. The data are more than sufficient to provide a quantitative comparison with PCDD/PCDF emission concentrations observed during the previous AEERL bench-scale study. Total PCDD/PCDF emissions measured in this study were a factor of 100 less than those observed earlier. It is difficult to determine if PCDD/PCDF concentration is a function of CFC feed rate. Figure 2 graphically depicts total PCDD/PCDF

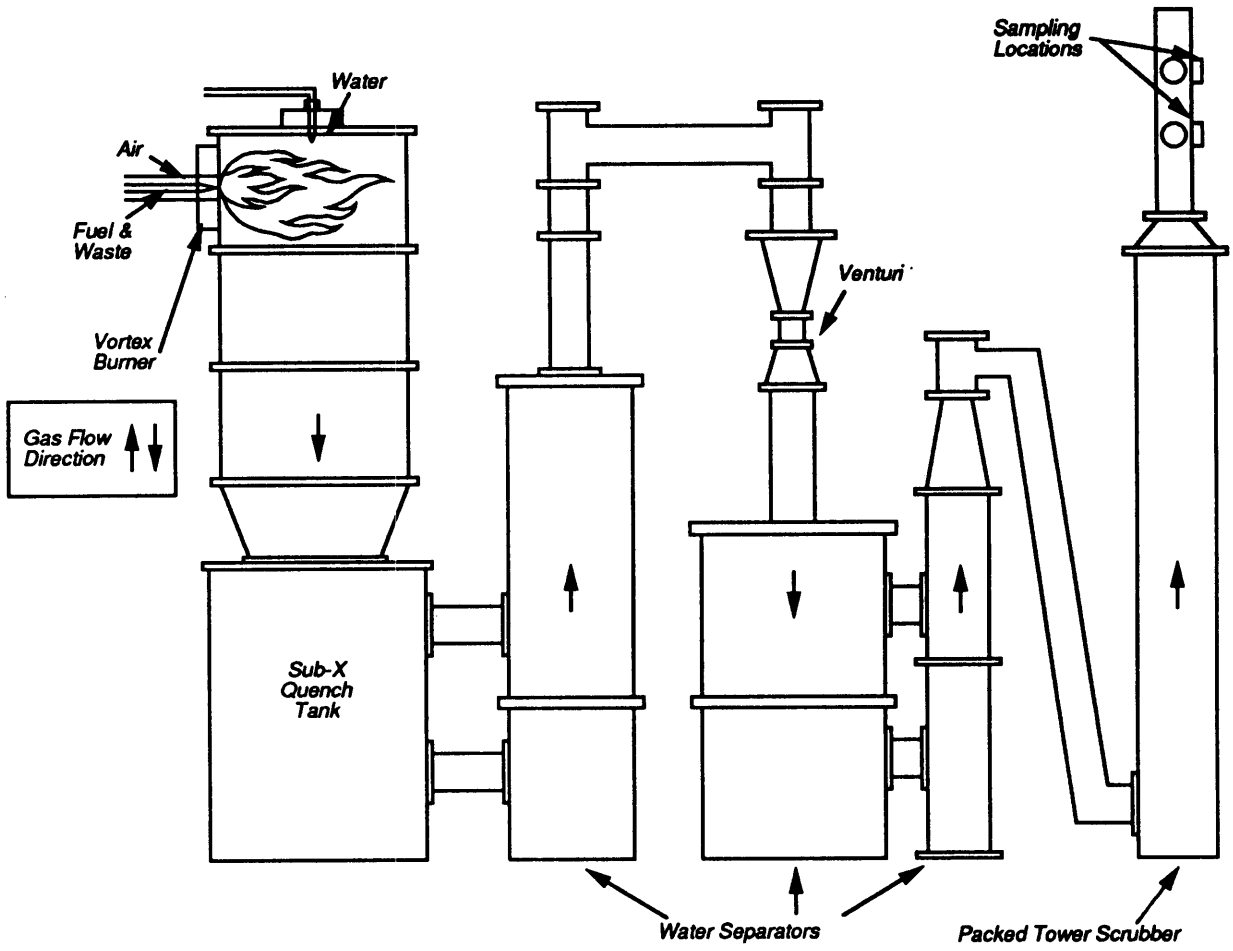

Figure 1. *T-Thermal incineration facility.*

Table 2. *T-Thermal Incinerator Operational Data*

	Test 1	Test 2	Test 3	Test 4
Primary Combustion Air Flow-kg/h (lb/h)	285.7 (629.3)	293.7 (647.0)	300.5 (661.8)	295.3 (650.5)
Secondary Combustion Air Flow-kg/h (lb/h)	100.9 (222.3)	106.4 (234.3)	106.9 (235.5)	110.8 (244.0)
Purge Air Flow-kg/h (lb/h)	8.6 (19.0)	9.2 (20.3)	9.8 (21.5)	9.1 (20.0)
Cooling Water Flow-kg/h (lb/h)	NA	14.7 (32.4)	9.1 (20.1)	8.7 (19.2)
No. 2 Fuel Oil Flow-kg/h (lb/h)	16.2 (35.6)	19.1 (42.0)	18.5 (40.8)	18.8 (41.4)
CFC-12 Flow-kg/h (lb/h)	0.0	0.5 (1.0)	0.0	0.0
CFC-11 Flow-kg/h (lb/h)	0.0	0.0	0.5 (1.2)	41.6 (91.7)
Total Fuel/CFC Flow-kg/h (lb/h)	16.2 (35.6)	19.5 (43.0)	19.1 (42.0)	60.4 (133.1)
% CFC of Total Flow	0.0	2.3	2.9	68.9
% Excess Air	25.1	6.2	12.0	-6.1
Firing Rate, kW (MMBtu/h)	198 (0.676)	234 (0.797)	227 (0.776)	246 (0.839)
Incinerator Temperature-°C (°F)	1,070 (1,958)	1,092 (1,998)	1,092 (1,998)	1,121 (2,049)
Oxygen (% dry)	15.9	8.9	9.0	7.3
Carbon Dioxide (% dry)	7.0	10.7	9.3	10.6
Carbon Monoxide (ppmv dry)	0	8	10	15
Nitrogen Oxides (ppmv dry)	65	43	149	50

NA = Not available.

emissions for each test. It appears that the high CFC-11 feed rate condition resulted in slightly increased PCDD/PCDF emissions. PCDD/PCDF analysis of scrubber water samples yielded inconclusive data. The inconsistent results observed were likely attributable to a sampling or analytical contaminant.

Method 23 and scrubber water samples were screened for semivolatile organic PICs considered to be PCDD/PCDF precursors. Essentially all of the target analytes were not detected. Based on instrumentation detection levels, "less than" emission concentration levels are presented. No semivolatile organic target analytes were detected in the scrubber water samples.

Summary and Conclusions

This study effectively characterizes the organic emissions resulting from the pilot-scale incineration of CFCs. CFC-12 and CFC-11 were thermally destroyed at feed rates representative of full-scale thermal destruction facilities (2.3 and 2.9%, respectively). A high CFC-11 feed rate condition (68.9%) was also evaluated. Greater than five nines DE (99.999%) was observed for the CFC-12 and high CFC-11 test conditions. Only three nines DE (99.9%) was observed for the low CFC-11 feed rate test condition.

The presence of volatile and semivolatile organic PICs was screened for. The PIC screens included target analytes such as chlorinated aliphatics, chlorobenzenes, chlorophenols, PAHs, and PCDDs/PCDFs. Essentially no target PICs were found in the low CFC feed rate test conditions. For the high CFC-11 feed rate test condition, PIC screens indicated that several volatile organic target PICs as well as several non-target volatile organic PICs were indeed present. Chloroform, bromodichloromethane, dibromochloromethane, and bromoform were emitted in substantial concentrations (1,500-2,300 μg/Nm³). Carbon tetrachloride was also emitted, but at a lower concentration (170 μg/Nm³). The presence of brominated PICs was particularly surprising, as no source of bromine was readily identifiable; the CFC-11 and fuel oil used during testing were analyzed specifically for trace bromine. Prior tests on the incineration test facility were suspected as a residual bromine source.

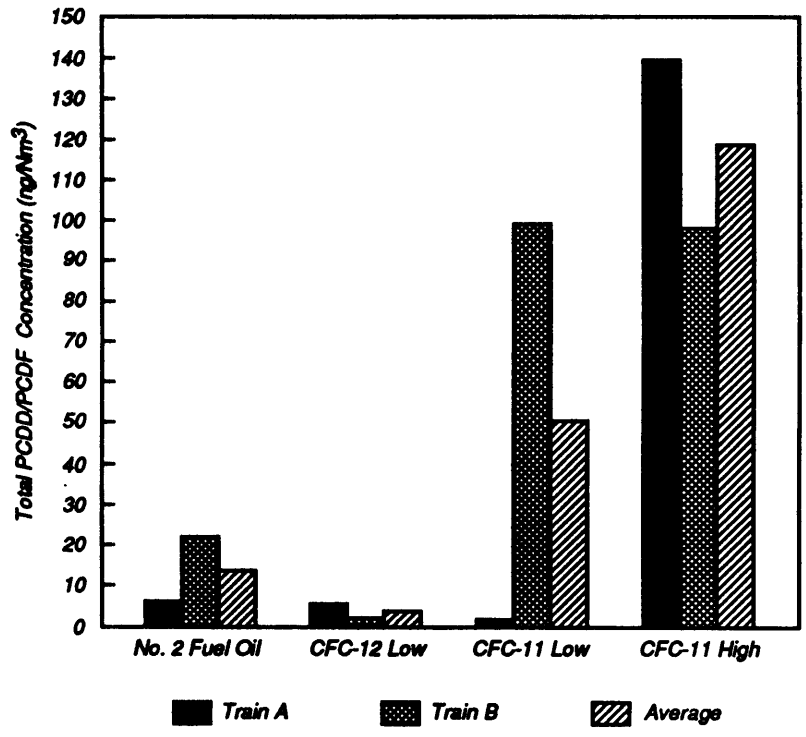

Figure 2. Total PCDD/PCDF emissions for each test condition.

Essentially all semivolatile organic PICs target analytes were not detected. This finding is significant in that chlorobenzenes and PAHs, PICs identified in a bench-scale CFC incineration study, were not detected. A bench-scale study found the formation of these PICs to be a function of the halogen/hydrogen ratio.

The PCDD/PCDF emission concentrations measured (2-140 ng/Nm³) were a factor of 100 less than those reported in another AEERL-sponsored CFC incineration study, indicating that the formation of PCDDs/PCDFs from the incineration of CFCs may not be as large a concern as was initially suspected. It does appear, however, that increased PCDD/PCDF emissions were realized at the high CFC-11 feed rate test condition. The mechanisms involved in PCDD/PCDF formation from CFC incineration are not fully understood.

The injection of water into the combustion zone to control incinerator temperature may have several added benefits. The injection of water may enhance CFC destruction efficiency. Water injection would lead to an increase in hydroxyl radical population, thereby providing a bimolecular destruction mechanism in addition to unimolecular thermal bond rupture. The injection of water may also minimize the formation of PICs. The injected water also provides an additional source of hydrogen. Hydrogen is involved in reactions that scavenge halogen free-radicals, potentially reducing PIC formation.

☆U.S. GOVERNMENT PRINTING OFFICE: 1993 - 750-071/80041

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The complete report, entitled "Characterization of the Organic Emissions from the Thermal Destruction of CFCs," (Order No. PB93-205 557/AS; Cost: $36.50 subject to change) will be available only from:
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