BOILER COFIRING OF CHLORINATED HYDROCARBONS

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ABSTRACT

Steady state and transient operating conditions were examined to determine the destruction and removal efficiencies (DRE) for the principal organic hazardous constituents (POHC) when cofiring liquid hazardous waste in a firetube package boiler. Results indicate that aromatic chloro-hydrocarbons are the most difficult to destroy. A DRE less than 99.99% was experienced for transient operating conditions in load, stoichiometry, and waste feed rate. Steady operation above 10% excess air ensures DRE's greater than 99.99%. Major products of incomplete combustion (PIC's) seen were methylene chloride and chloroform.

INTRODUCTION

Management of hazardous waste, which is generated in the U.S. at an annual rate of 265 million metric tons (0.58 million lb)[1-3], is a growing environmental concern. Stringent control over transportation and storage of these wastes, under the Resource Conservation and Recovery Act (RCRA) and subsequent land disposal restrictions under the Hazardous and Solid Waste Act (HSWA) of 1984, provide incentives for ultimate waste destruction techniques such as incineration.

Thermal destruction of hazardous waste is an attractive alternative to landfilling and is likely to grow in the future [2, 4–7]. Thermal destruction can be achieved by direct incineration or by cofiring hazardous waste in industrial boilers, furnaces, and kilns. Direct incineration of hazardous wastes is regulated by Part 264 of the RCRA, however, boiler cofiring, with subsequent energy recovery in some cases, is currently exempt from RCRA provisions. This exemption was based on the absence of a sufficient database on the practice, and because the byproduct of energy recovery is an attractive option. The incineration rules are designed to limit atmospheric emissions, and specifically mandate that principal organic hazardous constituents (POHCs) in waste must exhibit a destruction and removal efficiency (DRE) of \geq 99.99%. The DRE is defined as:

$$DRE = (M_{feed} - M_{stack})/M_{feed} \times 100$$

where

 $M_{\text{feed}} = \text{mass}$ flow rate of a POHC in the waste $M_{\text{stack}} = \text{stack}$ mass emission of a POHC POHCs are the compounds listed in Appendix VIII of the May 1980 RCRA amendments and have significant concentrations in the waste.

Cocombustion or cofiring of hazardous wastes with conventional fuels in industrial boilers is widely practiced in the U.S. as many wastes have significant heating values. The options of energy recovery,

conventional fuel saving, and on-site waste disposal are attractive. Many studies on the practice have examined the dependence of DRE on the boiler operation parameters and waste characteristics [8, 10]. Widely practiced waste cofiring has increased the availability of a database. With the growing concern over possible environmental impact, EPA is developing regulations to cover this practice; these regulations have been proposed in May 1987 (40 CRF Part 260 et al.). There still remains a need to characterize DRE during cofiring under nonstandard and transient conditions. Such conditions could be the result of facility startup, soot blowing, load change, hardware malfunction, overcharging, etc., and could lead to failure modes of operation where DRE is less than 99.99%. Some studies have been conducted under these conditions, yet the database needs to be expanded [11].

This paper is a result of a study sponsored by EPA's Combustion Research Branch in the Air and Energy Engineering Research Laboratory (AEERL) to examine the effects of boiler cofiring of hazardous waste on emissions, including those under nonstandard and/ or treatment boiler conditions.

EXPERIMENTAL FACILITY AND METHODS

The primary component of the test facility (see Fig. 1) was a North American Atlas brand, 0.8 MW (2.7 million Btu/hr), three-pass firetube package boiler capable of firing either fuel oil mixtures and/or natural gas. The boiler support systems were designed for independent control of combustion air, fuel(s), and air atomization. The boiler load was passed to a shell and tube heat exchanger, which subsequently transferred the load to an evaporative cooling tower loop.

Another major component of the test facility was the surrogate waste feed system. The waste mixture was contained in a steel drum, which was located on an electronic weigh scale for measurement of average waste consumption rates. From the drum the waste mixture was pumped into the boiler through a volume flowmeter and a manual flowmetering valve.

Stack concentrations of O_2 , CO_2 , CO_3 , and NO were measured by a Continuous Emissions Monitoring System (CEMS).

A variation of the Volatile Organic Sampling Train (VOST) procedure, called mini-VOST [12], was used to characterize the stack emissions of chlorinated hydrocarbons. Ten liter samples, in duplicate, were taken for the various data points. Tenax tubes, used to absorb chlorinated hydrocarbons, were analyzed within 24 hr of sampling.

APPROACH

The primary boiler fuel used was natural gas. Initially, boiler gaseous emissions were characterized under baseline (no POHC) cofiring steady state conditions. For POHC cofiring, the surrogate hazardous waste mixture used was 95% distillate fuel oil and 2% by weight each of carbon tetrachloride (CCl₄), monochlorobenzene (MCB), and perchloroethylene (PCE). Carbon tetrachloride, MCB, and PCE, listed in Appendix VIII of the May 1980 RCRA amendments, were chosen to be the POHCs used in this study. The composition and the amount of waste mixture cofired with natural gas were based on the range of heating values of the individual species and on the composition of hazardous waste mixtures encountered in previous field studies of boiler cofiring [13].

Under steady state cofiring conditions, the nominal boiler operating parameters of stoichiometric ratio and firing rate were chosen to be 1.10 and 0.64 MW (2.2 million Btu/hr), respectively. The percentage of boiler heat input contributed by the waste mixture determined the fuel heating value. The nominal value for this parameter was chosen to be 25%, corresponding to a fuel higher heating value (HHV) of 51.8 MJ/kg (22.3 kBtu/lb). Subsequently, parametric tests were carried out to study the effect of boiler stoichiometric ratio, firing rate, fuel heating value, and degree of waste mixture atomization on the DRE under steady state nonstandard boiler operation. Further tests were carried out to characterize the effects of transient boiler operating conditions on the DRE. The transient boiler conditions of load, stoichiometric ratio, and waste flow rate were chosen for testing, as these transient conditions do occur in commercial practice.

Products of incomplete combustion (PICs) could be just as, or even more, harmful as POHCs, hence PICs were also screened during the analysis of the mini-VOST samples.

RESULTS

DRE Versus Stoichiometric Ratio

The impact of stoichiometric ratio on DRE is depicted in Fig. 2. Operation at relatively low stoichiometric ratios could lower DREs due to oxygen deficiency. On the other end, operation at relatively high stoichiometric ratios at constant load could lower the temperature of the boiler and decrease the combustion gas residence time, resulting in the decrease of the destruction of POHC's and lower DREs. Based on these counter-balancing effects, a maximum in the



FIG. 1 EXPERIMENTAL FACILITY



FIG. 2 POHC DRE VERSUS STOICHIOMETRIC RATIO (SR)

DRE versus stoichiometric ratio (SR) curve would be expected. This trend is exhibited by the 80% firing rate and the 51.8 MJ/kg (22.3 kBtu/lb) higher heating value curve.

DRE Versus Firing Rate

An increase in the firing rate corresponds to a decrease in residence time of the combustion gases in the boiler. This could, potentially, lead to a decrease in the DRE for POHC's. The results for this effect are plotted in Fig. 3. The effect is visible for all tested combinations of stoichiometric ratio and higher heating values (HHV), except 1.1 and 51.8 MJ/kg (22.3 kBtu/hr), respectively. With 10% excess air and a higher heating value of 51.8 MJ/kg (22.3 kBtu/hr), perhaps the POHC destruction reaction kinetics are fast enough to mask the residence time effects.



FIG. 3 POHC DRE VERSUS FIRING RATE

DRE Versus Fuel Heating Value (HHV)

The effect of decreasing the fuel heating value (by increasing the amount of low heating value waste content in the fuel) at constant stoichiometric ratio and firing rate would be a decrease in the DRE via a decrease in the temperature of combustion gases. These trends are seen in Fig. 4. The DRE decrease, with a decrease in fuel heating value, is more dramatic for the case with a stoichiometric ratio of 1.0 perhaps due to additional effects of oxygen paucity.

DRE Versus Degree of Waste Mixture Atomization

The degree of atomization affects the combustion efficiency by decreasing/increasing the surface area of the fuel available for combustion. Poor atomization would lead to a decrease in surface area available for combustion and would be expected to lower the POHC DREs. Two different atomization states were established for the waste mixture by creating two different atomizing air flows to the atomizing nozzle. One of these states was "good" atomization and the other "poor," both of which were established visually. The



FIG. 4 POHC DRE VERSUS FUEL HEATING VALUE

atomization states were varied at nominal furnace conditions, and the results in Fig. 5 show the lowering of DRE with deterioration in atomization quality of the waste mixture.

Transient Ramping of Firing Rate

Maintaining the stoichiometric ratio at 1.1 and the waste flow rate constant under relatively good atomization conditions, the firing rate was ramped up from a baseline of 70% to about 90% and then ramped back down to 70%. The processes of ramping up and down were each completed at a constant rate in 15 min and during each ramping condition, mini-VOST samples were taken continuously over the entire period of the ramp. The test results are plotted in Fig. 6. On ramping up, the residence time of the combustion gases decreases and the total POHC DRE drops slightly; on ramping down the reverse happens and DRE increases slightly. The effect, if any, between the two baseline



FIG. 5 POHC DRE—GOOD ATOMIZATION VERSUS POOR ATOMIZATION

DREs at the beginning of ramping up and the end of ramping down is interesting and needs to be substantiated with more data.

The test results using a more rapid rate, 10 min rather than 15 min, are also plotted in Fig. 6. The difference in the two baselines (beginning and end of transient conditions) seems to be greater, suggesting that perhaps the effects of lower residence times during ramp up continued into the ramp down condition, with a greater degree during a relatively rapid transient phase. Thus, the time slope of the ramp up/ramp down condition seems to be related to DRE, but this needs to be substantiated by further study.

Transient Fluctuations in Stoichiometric Ratio

At nominal conditions of firing rate and waste heating value, the boiler stoichiometric ratio was varied between 1.1 and 1.0 in a periodic manner. This was done for two different wastes, corresponding to fuel mixture HHVs of 51.8 MJ/kg (22.3 kBtu/lb) and 48.8 MJ/kg (21.0 kBtu/lb). The test results are plot-



99,9999 POHC DRE (percent) 99.999 99.99 99.9 Baseline FR=80% Transien Baseline FR=80% Baseline FR=80% Baselin FR=80% SR SR=1.1 SR=1.0 SR=1.1 SR=1.0 Waste Waste Waste Waste Heat=50% Heat=50% Heat=25% Heat=25%

FIG. 7 DRE VERSUS TRANSIENT FLUCTUATIONS IN STOICHIOMETRIC RATIO

FIG. 6 POHC DRE VERSUS RAMPING OF FIRING RATE

ted in Fig. 7. Also plotted in Fig. 7, for comparison purposes, are the relevant baseline results. The decrease in DRE during transient conditions could be attributed to the sensitivity of DRE to stoichiometric ratio. Also, the stoichiometric ratio may have gone down even below 1.0 during transient conditions, thus giving a DRE even lower than that at steady state and a stoichiometric ratio of 1.0. No trend seemed apparent on changing the waste heating value from 51.8 MJ/kg (22.3 kBtu/lb) to 48.8 MJ/kg (21.0 kBtu/lb). It is worth noting that transient fluctuations in stoichiometric ratio could easily lower DRE values to below 99.99%, as indicated in Fig. 7.

Transient Fluctuations in Waste Flow Rate

Starting with nominal steady state operation of the boiler, the waste flow rate was varied in a periodic manner such that the waste heat input was between 30% and 25%. The test results are shown in Fig. 8. Also plotted in Fig. 8, for comparison, are the relevant baseline results. The variation in waste flow rate may have caused a combination of poor atomization (due to pulsating flow to the nozzle) and oxygen deficiency per mole of POHC to decrease the DRE. It is worth noting that the POHC DRE went down below 99.99% for the tests performed.

Individual POHC DRE Comparisons

To explore the effect of molecular structure of POHC on DRE, DREs for the individual POHC are cross-plotted in Figs. 9–11. These plots suggest that the PCE was destroyed more easily than CCl₄, while CCl_4 was destroyed more easily than MCB. Thus MCB seemed to be the hardest to destroy among the POHCs tested.

Performance Indicators (DRE versus NO, CO)

Carbon monoxide (CO) and nitric oxide (NO) are emitted from all combustion systems in varying amounts. As CO is an indicator of the degree of completion of combustion, and NO is an indicator of temperature/stoichiometric ratio conditions in the furnace, these measures have been considered as possible indicators of boiler performance. Several studies have been conducted on this aspect [14, 15], and it











FIG. 9 CCI4 DRE VERSUS MCB DRE

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FIG. 12 POHC DRE VERSUS NO

has been concluded that the relationships between DRE and these parameters are, in all likelihood, facility specific.

In this study, correlations between DRE and CO/ NO emissions were attempted. The results are plotted in Figs. 12 and 13. Best-fit correlations were developed for the data in these figures. These correlations are also plotted in Figs. 12 and 13. Both the plots and the best-fit curves indicate that DRE increases with increasing NO emissions, perhaps due to increasing temperature, and DRE decreases with increasing CO emissions due to worsening combustion conditions.

PIC Emissions

Table 1 summarizes the chlorinated PIC and POHC emissions for the various data points analyzed by mini-VOST during this study. It can be seen that the PIC concentration increases with an increase in POHC concentrations. For the range of parameters tested the



FIG. 13 POHC DRE VERSUS CO

PIC/POHC ratio varied between 0.03 and 8.87, giving mean and median values of 1.14 and 0.67, respectively, thus indicating that PIC concentrations were of the same order of magnitude as the POHC concentrations. As chlorinated PICs could be just as hazardous as POHCs and their emissions are of the same order of magnitude, they should be paid as much attention as POHCs from an environmental pollution standpoint.

CONCLUSIONS AND RECOMMENDATIONS

Table 2 summarizes all the experimental conditions at which the POHC DRE was found to be below 99.99%.

Analysis of the results of the various tests performed in this study yielded the following conclusions and recommendations:

(a) As load and waste heat input were increased, and stoichiometric ratio was decreased, the POHC DRE was observed to decrease within the range of parameters tested.

(b) Stoichiometric ratio, or oxygen available per mole of POHC, was the most sensitive parameter affecting the POHC DRE under steady state, good atomization conditions. At a stoichiometric ratio below 1.1, the POHC DRE can be expected to be below 99.99%. The effect is especially noticeable with MCB.

				TABLE	1 PIC AN	D POHC EN	VISSIONS					
Data Point	ر (ایترا مالیا	ر ار در الله (ال	ر <mark>ار 100 ما</mark> ل (پرورکیار)	A POBC (uc/a*)	R CBCLa (µ@/W ^a)	LCHaCla (ug/b)	t Ca BC1a (µg/w ^a)	£Ca HaCla (μ∉/m ^a)	Other PICe (ug/m ²)	дРІС (µ g/₩ ³)	4 P.IC	ÅPOHC (lbm/min)
C W 62 E06	2.7	9.05	40.6	7.6	8.0	1	1	1			1	0.0254
303.21.MV.1	<0.6	<0.6	<0.6	1.6		Trace			-			0.0254
303.21.MV.2	<0.6	<0.6	<0.6	1.5		0.0				<1.0	0.67	0.0279
303.21.MV.3	<0.5	<0.6	<0.6	1.6	-	0.8		1		<1.3	0.69	0.0279
303.21.MV.4	<0.5	<0.5	<0.5	1.6	<0.6	2.6	-	-		<3.1	2.07	0.0254
303.21.MV.5	<0.5	<0.5	<0.6	1.6	<0.6	12.6		1		<13.1	8.73	0.0263
303.17.MV.1	1.2	<0.5	<0.5	2.2		6.1				6.1	2.32	0.0254
303.22.MVI	1.4	3.6	0.7	6.6	2.4	10.2	1	1	1	12.6	2.25	0.0559
2VN. 22. EOE	<0.5	2.6	<0.6	3.6	<0.6	0.4	1	1	1	<8.9>	2.47	0.0547
303.18.MV1	<0.6	0.6	<0.6	1.6	<0.6	<0.6	1	-	1	<1.0	0.63	0.0517
303.18.MV2	0.9	1.1	<0.5	2.6	<0.6	<0.6				<1.0	0.40	0.0617
306.37.MV2	1.3	0.7	0.6	2.6	3.9	1	-		1	3.9	1.60	0.0271
302. 14. MV2	2.3	125	3.2	130.6	3.3	86		7.1	8.4	83.8	0.64	0.0550
302.13.MVI	0.8	2.1	<0.6	3.4	<0.6	0.9				41.4	0.41	0.0288
302.09.MV1	0.8	\$0.6	<0.6	1.8	0.6	0.7	-	١	1	1.2	0.67	0.0263
302.09.MV2	2.0	0.1	\$0.6	3.2	0.8	0.0			2.0	3.7	1.16	0.0263
302.16.MV1	BB. 1	148.6	4.0	238.7	2.1	31.2			29.0	62.3	0.25	0.0616
302.16.MV1	2.6	146.0	2.0	149.6	3.6	63.8	-		24.6	91.9	0.61	0.0599
302.14.MVI	2.8	122	6.4	130.1	4.0	104	١		24.6	162.6	1.25	0.0569
302.14. MV1	12.4	117.8	0.0	136.2	<1.0	147			64.6	<187.2	1.30	0.0628
402.14.MVI	20	309	110	430	9.9	8	136	174	30.2	047.6	1.26	0.0663
403.21.MVI	1.4	0.0	7.8	59.2	0.8	.1.6	3.9	1	142	16.6	0.28	0.0282
601.4.MVI	91.4	0.6	<0.6	32.4	TTOO		Trees	-	10.3	-		0.0197
602.2.MV1	48.9	1.1	<0.6	60.6	0.7	.0.8	0.7	1	1	2.2	0.04	0.0209
601.2.MV1	1.8	3.9	<0.6	6.2	0.0	1.1				3.8	0.61	0.0620
602.2.MV1	0.0	3.6	<0.6	4.0	6.6	<0.6	-		1.0	<8.6 <	1.36	0.0607
602(R).2.MV1	10.6	2.0	<1.0	13.6	2.2	1.6		1	<0.8	10 ° 10	0.20	0.0493
601(R).2.MV1	2.6	<1.0	<1.0	4.6	1.2	2.0	1	1		3.2	0.70	0.0521
601.2.MV1	6.03	6.8	1.2	70.9		-		١	1.9	1.0	0.03	0.0286
602.2.MV1	29.8	198.2	16.2	243.2	3.1	16.8	-	7.8	36.7	63.4	0.25	0.0667
701.2.MVI	81.0	8.1	3.7	92.8	0.9	2.3		1	1.0	4.2	0.00	0.0296

Lond (Percent)	Waste bont input (percmat)	88	Atomisation	Description	POSC DEB
80	60	1.0	Good	Steady state	99.991266
80	50	1.0	Good	Stendy state	99, 990645
90	50	1.0	Good	Steady state	99, 9E3066
90	50	1.0	Good	Standy state	99.989031
80	25	1.1	Poer	Standy etete	99.9000 01
80	50	1.0	Poor	Standy state	99, 967805
70 -> 90	-	1.1	Good	Damping up of firing rate	99.983461
90 -> 70	-	1.1	Good	Pumping down of firing rete	99.990426
80	25	1.1 <-> 1.0	Good	Transient SR	99. 98885 3
80	50	1.1 <-> 1.0	Good	Trunsiest ER	99,980111
		1.1 <-> 1.0	Good	Trunsient weste feedrate	99.985517
90 -> 70		1.1	Good	Higher resping rate (down) of	99.998797

(c) Under the conditions investigated, MCB was the hardest to destroy among the three POHCs tested. This may suggest that aromatic chlorinated hydrocarbons could potentially pose emission problems in cofiring. However, this observation needs to be further corroborated by careful experimentation.

(d) Based on the two conditions tested, the degree of atomization seemed to affect the POHC DRE very drastically. Even at excess air levels of 10%, poor atomization caused the POHC DREs to be of the order of 99.9%. Thus, it would seem useful to study the effect of atomization on POHC DRE in more detail.

(e) There seemed to be a direct relationship between POHC DRE and NO emissions, and an inverse relationship between POHC DRE and CO emissions. However, much more data would be needed to determine if there is a strong correlation between these parameters.

(f) For the conditions tested, transient firing rates never resulted in POHC DREs being less than 99.99%. There was no conclusive evidence that upward or downward ramping yielded significantly different DREs. Furthermore, the ramping rate did not seem to significantly affect the DRE. However, more experimentation is recommended to corroborate this conclusion.

(g) For both test points with transient stoichiometric ratios the POHC DREs were below 99.99%. Thus, transient stoichiometric ratios seem to have a major influence on DRE.

(h) At the one condition tested with a transient waste flow rate, the POHC DRE was found to be below 99.99%, perhaps implying that transience in flow rates is a critical parameter as well.

(i) Summarizing for the treatment conditions tested, waste flow rate and stoichiometric ratio seemed to have a greater impact on DRE than did a transient firing rate. More data could corroborate this.

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