



Project Summary

PIC Formation Under Pyrolytic and Starved Air Conditions

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A comprehensive program of laboratory studies based on the non-flame mode of thermal decomposition produced much data on Products of Incomplete Combustion (PIC) formation, primarily under pyrolytic and starved air conditions.

Most significantly, laboratory results from non-flame studies were compared to those from various field tests to evaluate incinerability relationships. Measurement of gas-phase thermal stability in an atmosphere of low oxygen concentration yielded results of incinerability ranking that were far more consistent with the findings from field tests than any one of several common methods applied in the past such as those that employed heat of combustion, autoignition temperature, etc.

The results of four experimental studies were presented as significant contributions to developing/expanding the data base on Principal Organic Hazardous Constituent (POHC) stability and PIC formation for pure compounds and mixtures.

This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, 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

The ultimate goal of incineration research is to understand the process of incineration to the extent that one can accurately predict incinerator emissions and to determine the effect of changing design and operational parameters upon pollutant emission rates.

Emissions of hazardous organic compounds fall into two general categories, those compounds in the waste feed that

are not totally destroyed and those compounds formed from the partial degradation of the waste compounds. Designations for these classes are Principal Organic Hazardous Constituents (POHCs) and Products of Incomplete Combustion (PICs), respectively. Since regulation of incineration will always require some type of testing or monitoring of the actual incinerator, a desirable product of research would be information that can be used to simplify the testing procedure and ensure that the proper emissions and operating parameters are being monitored that can provide environmentally safe waste disposal.

The complexity of the incineration process, the differences in incinerator designs, and the difficulties in monitoring changing operating conditions make the accurate prediction of *absolute* incineration performance an essentially impossible task. A more reasonable goal is to be able to predict the *relative* destruction efficiency of POHCs and the relative emission rate of PICs for a given incinerator. This goal is consistent with that of reducing the need for incinerator testing, since one could then simply conduct tests focusing on the least "incinerable" POHCs and the PICs of greatest yield as predicted by laboratory testing and research. If these compounds are found to meet regulatory requirements then presumably so would the other POHCs and PICs. Of course, one must have sufficient knowledge of the effect of incineration parameters on POHC and PIC emissions to correctly define the conditions for the laboratory and field studies and allow for subsequent changes in these conditions on the incinerator. Laboratory and field testing under "worst" case conditions would appear to be the best means of assuring continuing

incinerator compliance. Once initial compliance has been established, a method of monitoring for continuing compliance is also necessary. This defines a second goal of the research program, which is to identify appropriate species or operating parameters for continuous compliance monitoring.

Both of the above-mentioned goals can gain considerable support from development of a simple, qualitative incineration model for determining the major effects upon emissions from changing incinerator conditions.

In determining the destruction efficiency (DE) of hazardous organic materials by incineration, primary emphasis is put on the gas-phase chemistry, although the nature of the physical change of material from the condensed phase into the gas-phase may be important. The overall gas-phase reactions and interactions depend upon both direct flame and thermal decomposition modes of the combustion process.

Flame-mode and also thermal decomposition mode studies indicate that any known organic waste can be destroyed in an incinerator to greater than 99.99% DE if it is operating under theoretically optimum conditions. Excursions from the optimum (fault modes) are probably the controlling phenomena for incineration efficiency. Only a very small fraction of the total volume of the waste needs to experience these less than optimum conditions to result in significant deviations from the targeted destruction efficiencies.

The two modes are found in a two-zone incineration model such as a simple one-stage combustor where a waste feed mixture is fed directly into a turbulent flame and the hot gases evolving from the flame zone pass on through a relatively long, high temperature hold-up zone prior to exiting from the system. Because of various destruction failure modes in the flame zone, it is assumed in this model that about 1% of the waste feed escapes the bulk reaction conditions in the flame. This 1% enters the post-flame zone. The overall measured DE at the stack is the weighted averages of the DEs of the flame and the post-flame zones.

Calculated DEs for representative hazardous organic compounds are presented in Table 1. The table shows that each compound is destroyed to essentially the same efficiency in the flame, i.e., greater than 99.99%. It is the significant differences in thermal stability of the organic compounds in the post-flame zone that can affect the overall DE as adversely as shown.

Table 1. *Calculated Destruction Efficiency for Representative Hazardous Organics*

Compound	A (s ⁻¹)	E _a (kcal/mole)	Calculated Destruction Efficiencies		
			DE (Flame)	DE (Post-Flame)	DE (Overall)
Acetonitrile	4.7 × 10 ⁷	40	99.999+	66.357	99.664
Benzene	2.8 × 10 ⁸	38	99.999+	99.999+	99.999
Chloroform	2.9 × 10 ¹²	49	99.999+	99.999+	99.999
Tetrachlorobenzene	1.9 × 10 ⁶	30	99.999+	98.556	99.986
Tetrachloroethylene	2.6 × 10 ⁶	33	99.999+	77.127	99.771
Trichlorobenzene	2.2 × 10 ⁸	38	99.999+	99.968	99.999

The applicability of this qualitative model has been confirmed by a more complex model of hazardous waste incineration developed by the Energy and Environmental Research Corporation (EERC). Pseudo-first order thermal decomposition kinetics developed by the University of Dayton Research Institute (UDRI) were used as inputs for the EERC model. Modeling results for three pilot-scale hazardous waste thermal destruction systems have been obtained; in each case the predicted relative destruction efficiencies correlated almost perfectly with the values for T_{99.99}(1) (temperature for 99.99% destruction at 1.0 sec residence time) of the test compounds that were developed from the UDRI results using pseudo-first order kinetics. The excellent agreement between the ranking according to T_{99.99}(1) and the EERC model was as predicted by the two-zone incineration model, thus illustrating the importance of post-flame reaction kinetics.

Comparisons of UDRI generated laboratory flow reaction (non-flame) data with laboratory flame-mode data indicate the similarity in the reaction mechanisms for both zones, i.e., a free-radical degradation mechanism. These results suggest that many PICs can be formed from simple feed mixtures and the POHC DEs and the PIC yields may depend much upon the waste composition and oxygen level of the reaction atmosphere. A detailed comparison of field and laboratory studies further reveals the importance of PIC emissions in determining incinerator performance and how laboratory data can be used to predict PIC formation.

Experimental Procedure

The bulk of the experimental laboratory data presented throughout the full report was generated at UDRI by use of the Thermal Decomposition Analytical System (TDAS) and the Thermal Decomposition Unit-Gas Chromatograph (TDU-GC) system. A block diagram, Figure 1, illustrates the general arrangement of equip-

ment in the TDAS. The same arrangement applies to the TDU-GC, except for the coupled Mass Spectrometer (MS) and its accessory equipment that was used in the TDAS for identification of the emission components. Each system is a closed in-line combination of two basic units, the thermal reactor and analyzer.

The thermal reactor incorporates a capillary quartz tube within a furnace with three heating zones that are independently controlled to produce temperatures up to 1150 °C in the central zone.

The sample insertion chamber is fitted with any one of several probes adapted to handle gas, liquid or solid samples. In a test, the sample enters the thermal reactor in the gas phase. A heating jacket around the insertion chamber tube provides elevated temperatures programmed by a controller to convert liquid and solid samples to the vapor phase. The vapor is conveyed to the reactor by a measured flow of carrier gas which is selected according to the nature of the atmosphere required in the high-temperature zone of the reactor. According to the temperature and pressure measured in the reactor tube, the carrier gas is regulated at the instrument console to result in a precise residence time of the vaporized/gaseous sample in the closely controlled high-temperature zone. The gaseous emissions from the reactor pass to a cryogenic trap at the head of the chromatographic column.

The analyzer, a gas chromatograph (GC) which may be coupled with a mass spectrometer, is fitted with a fused silica capillary column leading to a flame ionization detector (FID) in the case of the TDU-GC system, or a coupled mass spectrometer in the case of the TDAS system. A 30:1 splitter between the furnace and the GC directs only a small portion (~3%) of the effluent sample to the capillary column that is needed for high-resolution analysis.

The auxiliary units of computer and recorder provide a means of storing the output from the analyzer detector and depicting it in a chromatogram or spe-

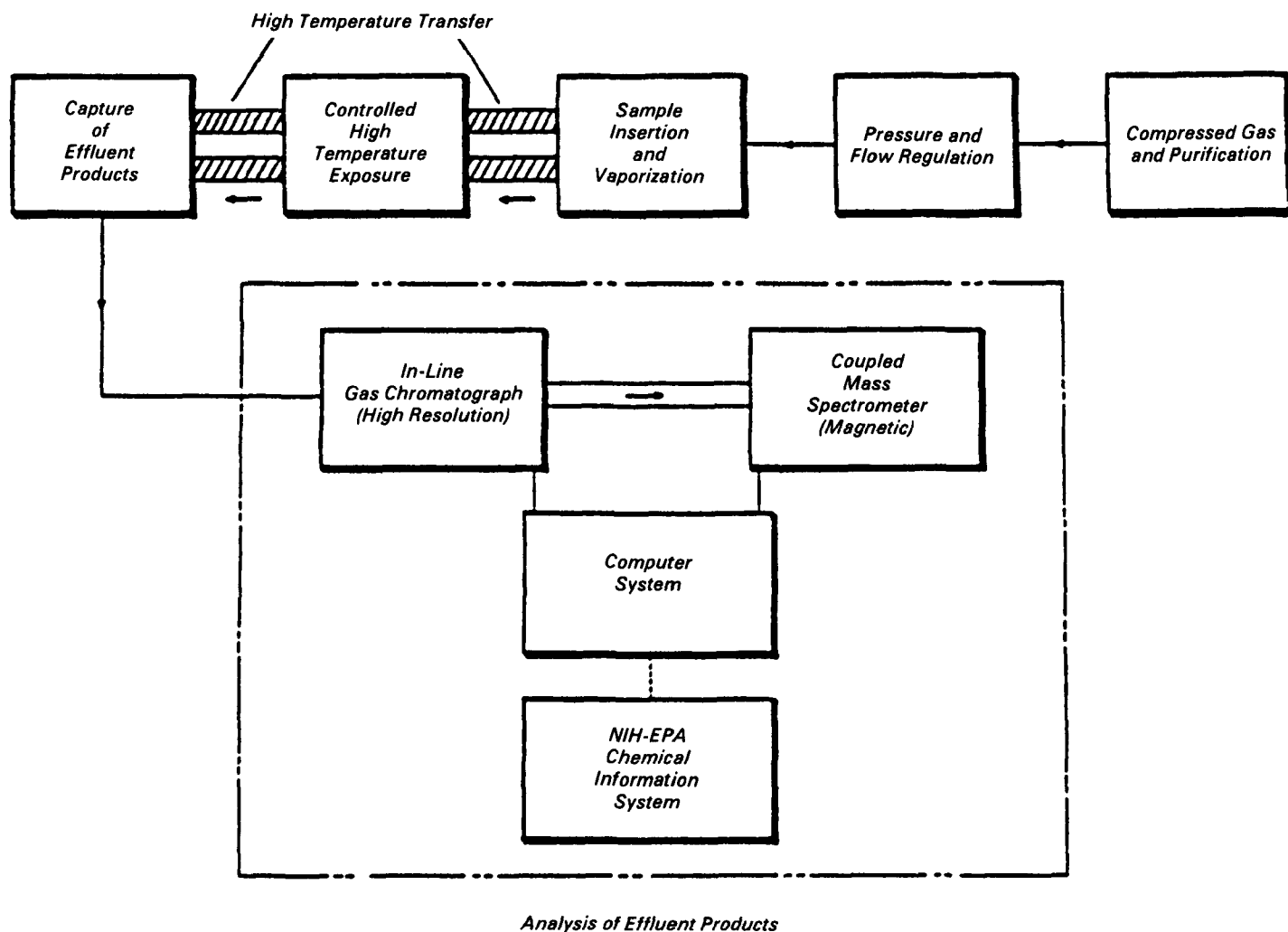


Figure 1. Block diagrams of the TDAS.

trum according to the nature of the data processor.

Each test run yields a single point on the thermal decomposition plot (quantity of compound in the effluent vs. temperature of the thermal reactor, with the residence time kept constant) for the POHC material. Corresponding single points for each PIC material formed during the thermal treatment run are simultaneously obtained. Runs made over a series of temperatures can produce a thermal decomposition profile of the POHC and formation-decomposition profiles for various PICs, within the temperature limits investigated. Runs made over a series of residence times provide data that can be used to determine the Arrhenius equation values of the constant, A , and the so-called activation energy, E_a .

Results and Discussion

Results are reported for three major studies, (1) comparison of flame-mode and thermal decomposition (non-flame) mode results, (2) correlation of laboratory-based predictions and field study results, and (3) expansion of data base on POHC stability and PIC formation for pure compounds and mixtures.

Comparison of Flame and Thermal Decomposition Results

For the first study, 13 compounds of wide interest to hazardous waste incineration were combusted in a laboratory diffusion flame, from which the relative burning rates of the compounds were determined based on their flame front velocities. For the six compounds for which thermal decomposition data are

available from the UDRI flow reactor systems, the non-flame ranking obtained from $T_{99.99}(2)$ (temperature for 99.99% destruction at 2.0 seconds residence time) was determined. Comparison of flame with non-flame data showed that the ranking of those six compounds was in the same order for all six as listed among the relative burning rates that were determined in the diffusion flame experiment.

In a second flame experiment, various combinations of dichlorobenzene, benzene and hydrogen chloride were combusted at 40% of stoichiometric air. Most ($n = 23$) of the observed PICs ($n = 33$), as complex as some of them were, were also found as PICs from the thermal decomposition of a mixture of carbon tetrachloride, toluene, chlorobenzene, trichloroethylene and Freon 113. The production of like PICs

from dissimilar molecular mixtures but similar atomic ratios of carbon, hydrogen and chlorine, in flame and in thermal decomposition environments suggests that similar reaction mechanisms are operative in both processes. At temperatures above 450°C, a free-radical mechanism appears to predominate the attack of molecular species, such as peroxide, that has been observed at lower temperatures.

The correlation between flame-mode and non-flame flow reactor POHC and PIC data indicates free radical decomposition reactions taking effect in both instances. The good agreement in identical PICs, even for dissimilar feed mixtures, supports the case of free-radical mechanisms. The majority of the products are due to recombination of free-radical fragments or of radical addition to aromatic substrates. The lack of oxygen-containing products even under oxidative conditions suggests that abstraction of H by OH and O dominates over addition reactions.

Correlation of Laboratory Predictions and Field Results

A comparison of various proposed scales of incinerability with recently available field test results was developed that included "thermal stability" values determined from the UDRI flow reactor studies.

Six methods of ranking the relative incinerability of hazardous organic compounds were considered in this specific evaluation:

1. Heat of Combustion (Hc/g)
2. Auto-Ignition Temperature (AIT)
3. Theoretical Flame-Mode Kinetics (TFMK)

4. Experimental Flame Failure Modes (EFFM)
5. Ignition Delay Time (IDT)
6. Gas-Phase Thermal Stability [T_{99} (2) (99% destruction at 2.0 seconds residence time), TSHiO₂ (high oxygen concentration), TSLoO₂ (low oxygen concentration)].

The TSHiO₂ (oxygen-rich) and TSLoO₂ (oxygen-deficient) data were considered when recently generated data showed that relative thermal stability varied with the waste feed/oxygen ratio.

To ensure a valid comparison of predicted results as obtained from the laboratory study with its precisely controlled, well-defined conditions and of the more general results of field study reports, the following data validation and reduction criteria were used:

- Compare only POHC Destruction and Removal Efficiencies (DREs) for a given incinerator.
- Compare only POHC DREs when they are fed to the system at a common point.
- Use averages of DREs when no significant run-to-run variation in relative POHC DRE is observed.
- Use only data where the majority of the POHC DREs are less than 99.995%.
- Include data from non-concurrently fed POHCs if other key parameters are held constant.
- Conduct the correlation of observed

field vs. predicted results on a rank/order basis with a minimum of four data points.

The observed incinerability rankings of the test compounds at each source were compared with the prediction of each proposed ranking method using a rank/order correlation approach. The rank-correlation coefficient, r_s , was used to judge if a correlation existed at the 90% confidence level for a number of test compounds. Table 2 summarizes the results of such analysis for ten studies judged to meet the data validation criteria.

Of all the ranking methods proposed above, only Hc/g, AIT, T_{99} (2), TSHiO₂ and TSLoO₂ had a sufficient data base to make predictions for a significant number of sources. Of these, only the experimentally predicted order under low oxygen conditions, TSLoO₂, had a reasonable success, i.e., 70%. The other four methods only correlated with field observation 10-20% of the time.

Observed deviations from laboratory predicted rankings of incinerability might be attributed to product formation ("contamination" of the stack effluent by volatile POHCs that did not pass through the destruction zones of the incinerator or even perhaps to volatile POHCs stripped from scrubber waters at the time of measurement of stack gas concentrations.

The following conclusions are offered:

- Measured POHC DREs and relative stabilities of all but the most stable compounds are influenced by the formation as products from other components of the waste feed and/or fuel.

Table 2. Results of Statistical Analyses of Observed Versus Predicted Thermal Stability Rankings

Study	Hierarchy							
	H _c /g	AIT	TFMK	EFFM	IDT	T_{99} (2)	TSHiO ₂	TSLoO ₂
A	-0.300/5 ¹	-0.200/4	—	—	—	—	0.000/5	0.900/5
B	-0.190/8	0.200/4	—	—	—	-0.057/6	0.533/10*	0.529/10
C	-0.500/5	—	—	—	—	0.500/5	0.400/5	0.600/5
D	-0.100/9	-0.060/	—	—	—	-0.800/4	0.386/9	0.493/9
E	0.589/7*	0.428/6	—	—	—	-0.300/5	0.425/8	0.429/8
F	0.343/15	0.571/7*	-0.100/5	—	—	-0.425/9	0.041/15	0.073/1
G	0.400/4	—	—	—	—	0.800/4*	0.800/4*	0.900/4
H	-0.333/7	0.457/6	—	—	-0.300/4	-0.161/7	-0.036	0.655/6
I	-0.077/10	-0.262/8	0.600/4	0.600/4	-0.100/5	-0.217/9	-0.318/11	0.536/1
J	-0.291/10	0.147/8	0.800/4*	0.600/4	-0.100/5	-0.202/9	-0.114/11	0.523/1
# Of Successes	1	1	1	0	0	1	2	7
# Of Failures	9	8	2	2	3	8	8	3
% Success*	10	11	33	0	0	11	20	70

¹ r_s/N

*Correlation was statistically significant at the 90% confidence level.

- Only DREs for very stable POHCs or POHCs difficult to form as reaction products (e.g., acetonitrile) are expected to be unaffected by PIC formation and these stabilities are predictable from pure compound thermal decomposition kinetics.
- The stack emissions and observed DREs of the very volatile compounds (e.g., methylene chloride, chloroform, di- and trichloroethanes) may be influenced by fugitive emissions in the ambient air or stripping of these compounds from contaminated scrubber water.
- Thermal decomposition, not in-flame destruction, determines relative POHC DREs and the identity and yield of products of incomplete combustion.
- Pyrolytic conditions in the incinerator are responsible for most emissions and control the relative DREs of POHCs and the formation of products.
- Results from laboratory thermal decomposition testing of pure compounds and mixtures can be effectively used to predict relative POHC DREs.
- Laboratory testing under pyrolytic conditions on actual waste streams or closely simulated waste streams is a potentially effective and reliable method for predicting relative POHC stabilities and PIC emissions.

Expansion of Data Base on POHC Stability and PIC Formation for Pure Compounds and Mixtures

Contributing to an expanding data base that can be used to predict the effect of changing reaction atmosphere and waste composition, the results of experimental studies like the following can be quite useful.

1. Thermal Decomposition of "CRF Soup-1"

Thermal degradation of a mixture of Freon 113, carbon tetrachloride, trichloroethylene, chlorobenzene and toluene was conducted in three reaction

atmospheres: oxygen-rich ($\phi = 0.06$), stoichiometric oxygen ($\phi = 1.0$) and oxygen-starved (pyrolysis). The $T_{99}(2)^\circ\text{C}$ (temperature for 99% destruction at 2.0 seconds residence time) thermal stability values for each compound in mixture and as pure compounds were compared. It was clear that carbon tetrachloride and Freon 113 were little affected by the differences in oxygen concentration in the test atmosphere. The other three compounds (trichloroethylene, chlorobenzene and toluene), however, showed considerable differences in absolute and in relative thermal stabilities as a function of both oxygen concentration and of feed composition (pure compounds vs. mixture).

Unimolecular decomposition by simple bond ruptures would explain the independence of the thermal stability of carbon tetrachloride and Freon 113 from changes in the reaction atmosphere. In contrast, the degradation of trichloroethylene, toluene and chlorobenzene is more likely to be caused by their interaction with free-radicals such as OH, O and H. Since the absolute and relative concentrations of these species will vary with the oxygen concentration and waste composition, the measured thermal stabilities will also vary with changing reaction atmosphere.

2. Formation of PCDFs and other PICs from PCBs

Thermal degradation of 2,3',4,4',5-pentachlorobiphenyl (2,3',4,4',5-PCB) was conducted in various reaction atmospheres (oxygen equivalence ratio $\phi = 3.0, 1.0, 0.2$, and 0.05 , oxygen-starved to oxygen-rich concentration, respectively) at a gas-phase residence time of 2.0 seconds, and at temperatures ranging from 500 to 1000 $^\circ\text{C}$.

With the increase in oxygen concentration through the range shown, the yield of total PCDFs increased by a factor of 7.

Thermal decomposition profiles based on the yield data showed that the degradation rate of the feed 2,3', 4,4',5-PCB rapidly increased above approximately 750 $^\circ\text{C}$. With the degradation of the PCB, there was an increasing production of the PCDFs. According to pseudo-equilibrium calculations of the concentration of small reactive species, the concentration of reactive radicals such as OH and O increases rapidly between 700 $^\circ\text{C}$ and 900 $^\circ\text{C}$. Since incorporation of oxygen is needed to form PCDFs from PCBs, it is likely that the OH and O radicals are the

predominant reactive species responsible for PCDF formation. The subsequent degradation of the formed PCDFs, starting at 850-875 $^\circ\text{C}$ and undergoing total elimination along with the parent PCB at 1000 $^\circ\text{C}$ indicates still some other reaction mechanism taking hold to destroy the PCDFs at the relatively high temperature range of 850-1000 $^\circ\text{C}$.

3. Formation of PICs from Chloroform

Thermal decomposition of chloroform (CHCl_3) at an equivalence ratio $\phi = 0.76$ and at 2.0 seconds residence time showed formation of pentachloroethane (C_2HCl_5) at lower temperature levels and shortly afterwards the formation of tetrachloroethylene (C_2Cl_4). However, with increasing temperature the pentachloroethane then decomposed at a rate approaching that for the chloroform and in the same temperature range, indicating comparable thermal stability for these two compounds. The tetrachloroethylene, on the other hand, increased to yields almost equaling the initial quantity of parent chloroform. It is likely that the product pentachloroethane plays an intermediate role in the chloroform thermal decomposition pathway that eventually produces the tetrachloroethylene.

In the initial step it is indicated that the biradical dichlorocarbene ($:\text{CCl}_2$) is formed along with HCl. The dichlorocarbene may then react with chloroform through insertion in the C-H bond to form pentachloroethane. Another proposed reaction of dichlorocarbene is its combination with another such radical to form tetrachloroethylene.

4. Formation of PICs from Polychlorinated Phenols

The thermal decomposition of chlorophenols is of intense interest because of the potential formation of polychlorinated dibenzodioxins (PCDDs) as PICs. Thermal decomposition profiles were developed for pentachlorophenol (PCP) in nitrogen, pentachlorophenol in air, and 2,4,5-trichlorophenol (2,4,5-TCP) in nitrogen.

While there were various major PICs observed at selected reaction temperatures on the TDAS, the production of octachlorodibenzo-p-dioxin (OCDD) was determined by retention time on the TDU-GC, after which identification was confirmed by examining low-level peaks on the TDAS. The maximum yield in air ($\sim 1\%$) was seen at 500 $^\circ\text{C}$, while the maximum

*Simulated Hazardous Waste Mixture #1 tested recently at EPA's Combustion Research Facility (CRF) in Pine Bluff, Arkansas.

yield in nitrogen (~1.5%) was seen at 550°C.

5. Expansion of Pure Compound Kinetic and Thermal Stability Data Base

Pseudo-first order oxidation kinetic data was generated for various pure compounds. The E_a and A values were calculated for 23 compounds ranked by the $T_{99}(2)$ calculated from those values.

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Robert E. Mournighan is the EPA Project Officer (see below).

The complete report, entitled "PIC Formation Under Pyrolytic and Starved Air Conditions," (Order No. PB 86-145 422/AS; Cost: \$11.95, subject to change) will be available only from:

National Technical Information Service

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