

Observations on Waste Destruction in Liquid Injection Incinerators

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Abstract—Various factors affecting the performance of a subscale liquid injection incinerator simulator are discussed. The mechanisms by which waste escapes incineration within the spray flame are investigated for variations in atomization quality, flame stoichiometry, and the initial waste concentration in the feed.

A turbulent spray flame reactor is fired on No. 2 fuel oil which is doped with an equimolar mixture of various compounds, including chloroform, chlorobenzene, acrylonitrile, benzene, and 1,1,1-trichloroethane. In spite of the fact that the compounds all are initially at the same concentration, certain operating conditions repeatedly yield a consistent ranking in the extent of compound destruction. This "destructibility" ranking is an important tool in identifying the mechanisms responsible for compound release. In the present work we identify two mechanisms as potential explanations for the compound release behaviour. The findings are applied to the problem of using CO and unburned hydrocarbon emissions as indirect indicators of waste destruction performance. The results also offer insight into the correlation between waste destruction efficiency and initial waste concentration in the feed that has been observed in field data.

Key words: incineration, liquid waste, incinerator monitoring, thermal destruction.

INTRODUCTION

Liquid injection incineration offers an appropriate means of permanently eliminating organic liquid waste. Incineration will gain acceptance, however, only if the waste emissions can be controlled to desired levels, if byproduct emissions are likewise controlled, and if means exist to detect operational upsets. At present, most liquid injection incinerators are capable of meeting the present waste destruction performance regulations (Trenholm *et al.*, 1984).

In spite of the generally good performance on organics emissions, a number of issues are of concern. First, even in the best of units, some small fraction of the waste still escapes incineration (waste release) and is either emitted or it contaminates the residue from the flue gas cleaning equipment. The mechanisms by which this occurs are not well defined. Secondly, significant waste emission can occur during upsets in incinerator operation. These transient upsets are a result of a number of causes, ranging from simple operational changes (e.g., an auxiliary fuel flow rate change) to equipment malfunctions, such as a plugged or eroded nozzle. The mechanisms that cause waste release during upsets are also not well known.

A third issue involves real-time monitoring of incinerator performance. The present manual methods for measuring waste emissions are too slow to be used as a basis for immediate corrective action. This has motivated considerable interest in indirect means of monitoring incinerator performance. One approach involves the addition of a non-toxic, surrogate compound whose exhaust concentration can be detected on a real-time basis to very low concentrations. Sulfur hexafluoride is the most common example of such a surrogate. Alternatively, the measurement of combustion by-products, such as CO or total hydrocarbons, has been proposed. These are used under the assumption that a flame environment that yields low emissions of these intermediates is favorable for organic waste destruction. Obviously, the nature of the waste

release mechanism will determine the degree to which these indirect approaches parallel the waste release behavior.

The fourth issue involves the formation of combustion byproducts. If incineration is viewed as a means of reducing the risk associated with a waste stream through a reduction in its volume, then byproduct formation can exert a negative influence through a potential increase in the specific toxicity of the products. Any quantitative theory of byproduct formation must include an understanding of the waste release mechanisms, for it is within these specific environments that the byproduct formation chemistry will take place.

In summary, there is considerable practical and scientific motivation for identifying the mechanisms that allow waste release to occur in real incineration systems. This includes identification of the specific thermal and compositional environments within which partial destruction of the waste occurs, and byproduct formation takes place.

The thermal destruction of hazardous wastes has been extensively examined under non-flame conditions (*e.g.*, Dellinger *et al.*, 1984) and for individual burning and non-burning droplets (Kramlich *et al.*, 1984b). These measurements indicate that complete waste destruction is possible under moderate temperatures. If extrapolated to flame temperatures, these results predict that waste compound lifetimes would be much shorter than mean flame residence times. Some escape, however, always occurs from practical incinerators. This implies that the basic release mechanism involves a failure of the transport mechanisms to fully contact the waste with a flame environment. The critical issues are therefore as follows: (1) identify the appropriate transport inadequacies that occur in liquid injection incinerators, (2) specify the thermal environments and composition provided by each of these environments, and (3) develop the response of the waste compounds to these environments, with respect to both waste destruction and byproduct formation.

The general problem just posed is extremely complex. Reliable predictions of even CO emissions from simple turbulent diffusion flames are presently beyond the state of the art (*e.g.*, see discussion in Karagozian and Nguyen, 1986). Even a complete understanding of the process fundamentals (*e.g.*, the detailed waste chemistry) may not be sufficient to predict global spray flame incineration behavior. The complex coupling between the turbulent hydrodynamics, the droplet dynamics, and the chemistry can yield behavior that is not intuitively obvious. The only means by which the behavior of the full process can be understood is through a detailed process model that mathematically simulates this coupling. Since such a model does not yet exist, an alternative is to gain insight through a simplified, subscale experiment that includes all of the phenomena of interest.

The objective of the present work is to gain an improved insight into the mechanisms that govern waste release from spray flames that are doped with model waste compounds. By perturbing the flame in a variety of ways, the changes in relative destruction rates of the various compounds are observed. This information is used, along with byproduct information, to test various hypothetical waste release mechanisms for consistency. The goal is to identify the most probable mechanisms, and their associated implications.

EXPERIMENTAL

Turbulent Flame Reactor

The design of the turbulent flame reactor has been described in detail elsewhere (Kramlich *et al.*, 1984a,b), so only a brief overview will be presented here.

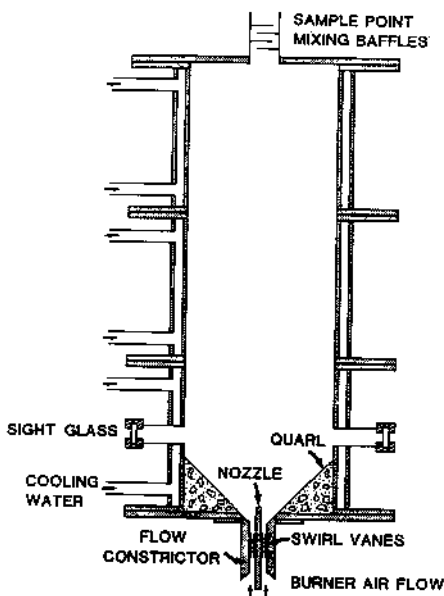


FIGURE 1 The turbulent flame reactor.

The design is based on the reactor used by Baker *et al.* (1975). This selection was made so that the detailed aerodynamic information developed in Baker's paper would be available to interpret the results of the present design. The reactor consists of a swirling air/liquid spray burner firing into a 30.5 cm-diameter by 91.5 cm-long water-cooled cylindrical enclosure, as shown in Figure 1. The water-cooled cylinder is made of 304 stainless steel formed into three interchangeable segments which are joined by flanges and gasketing.

The burner consists of a pressure-atomized hollow-cone nozzle (Delevan WDA 60° Series) located level with the bottom plate of the reactor as shown in Figure 1. The main burner air is introduced through the annular space around the nozzle. A swirl block arrangement is used to vary the inlet swirl number and air velocity. To provide a smooth entry of air into the burner and to prevent corner recirculation, a castable refractory quarl is placed in the lower water-cooled segment. As shown in the figure, this has the form of a 45° cone.

Analytical Techniques

Sampling for the waste compounds is accomplished with the standard volatile organic sampling train (VOST, Nutek Corp.). The contents of the Tenax/charcoal traps are recovered by thermal desorption during backflow onto an EPA Method 624 trap. The 624 trap is then thermally desorbed and the contents are analyzed by flame ionization gas chromatography. The procedure is detailed in LaFond *et al.* (1985) with the exception of the Method 624 trap (Kramlich *et al.*, 1989) which has been added for the more recent data to improve gas chromatograph injection sharpness for the more volatile compounds. The analysis of CO (via a non-dispersive infrared analyzer) and total hydrocarbons (via a total flame ionization analyzer) are as described in LaFond *et al.* (1985).

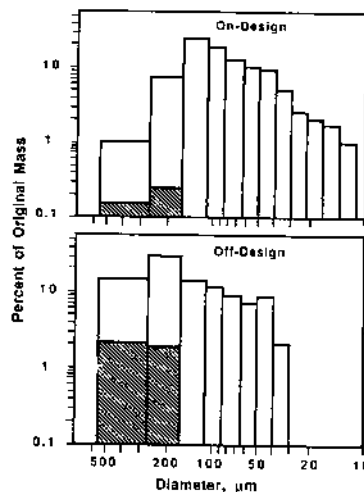


FIGURE 2 Laser diffraction measurements of droplet size distributions. Shaded portion represents that fraction that is estimated to escape the flame without evaporation (Kramlich *et al.*, 1986).

RESULTS AND DISCUSSION

Atomization

Previous work has shown that atomization quality has a first order influence on waste efficiency (Kramlich *et al.*, 1984a,b; LaFond *et al.*, 1985; Kramlich *et al.*, 1986). By deliberately degrading atomization quality, enhanced emissions of waste compounds occurred. Also, although equal amounts of waste compounds were used in the feed, a consistent concentration ranking developed in the exhaust. In this section we explore the relationship between hypothetical escape mechanisms and the compound exhaust ranking implied by these mechanisms. The goal is to identify the means by which release occurs under poor atomization.

Figure 2 illustrates the droplet size distribution obtained at 0.922 gm/sec fuel flow (Kramlich *et al.*, 1986). These measurements were obtained through laser diffraction (Malvern 2600 HSD) as a line of sight average through the center line of the spray. These data are under cold flow conditions, and were obtained at a sufficient axial distance to prevent the distortion of the size distribution due to the persistence of the droplet - velocity correlation in the near field of the nozzle.

The data set labeled "On-Design" was obtained for a 0.922 gm/sec capacity nozzle (nominally 1 gallon/hr) and thus represents the size distribution resulting from correct operation. The "Off-Design" data set is for the identical flow rate, but an oversized nozzle (1.38 gm/sec or 1.5 gallons/hr). The use of oversized pressure jet nozzles results in low fluid pressure (1360 vs. 600 kPa) and reduced droplet velocity. Figure 2 shows that the principal influences of reducing the fluid pressure are (1) the elimination of the fine component under 30 microns, and (2) a significant increase in the larger droplet sizes. In particular, the largest "bin" increases over an order of magnitude. In spite of this large increase, the Sauter mean diameter increases only from 70 to 113 microns.

These two atomizer conditions were applied to the turbulent flame reactor. A No. 2 fuel oil doped to 3.0 weight percent with an equimolar mixture of model waste compounds was fired. These compounds were acrylonitrile, chloroform, benzene, and

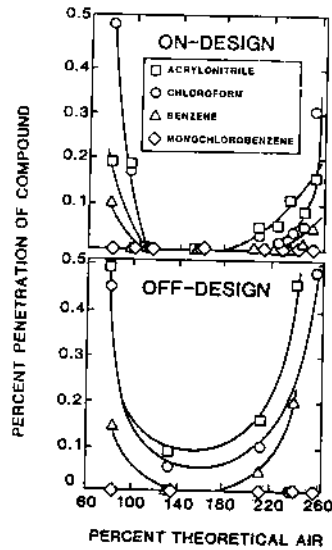


FIGURE 3 Percent of each compound that escaped the reactor.

monochlorobenzene. The reactor was operated with an air inlet velocity of 7.8 m/s (at stoichiometric) and a swirl number of 0.8.

Figure 3 shows the fraction of each of the waste compounds that escaped destruction as a function of percent theoretical air (Kramlich *et al.*, 1986). The on-design condition shows three general regimes of behavior. These include: (1) a range of high waste destruction between 110 and 200 percent theoretical air, (2) a significant decrease in efficiency below 110 percent theoretical air, most likely associated with extensive oxygen-starved regions, and (3) another decrease in efficiency above 200 percent theoretical air that is probably caused by excessive flame quench.

Comparison of the on-design and off-design data shows that the penetration below 110 percent theoretical air is not significantly different. Penetration above 200 percent theoretical air is similar, although values are increased by a factor of 2–3 over the on-design case. However, in the nominal operating range of 110 to 200 percent air the penetration is substantially increased for the off-design condition.

The compound concentration in the "on-design" exhaust exhibited consistent rankings. Chlorobenzene was not detected under any condition. Under fuel-rich conditions chloroform had the highest exhaust concentration, followed by acrylonitrile and benzene. For fuel-lean failure acrylonitrile had the highest exhaust concentration, followed by chloroform and benzene. Under poor atomization conditions the exhaust ranking did not change significantly.

For poor atomization, the increase in waste emissions in the 110–200 percent theoretical air range can be explained in two ways. First the significant increase in mass associated with large droplet size can lead to enhanced droplet penetration to the wall, or through the flame. Second, the shift in size distribution, and particularly the elimination of the fine droplets, can change the flame shape or aerodynamics in a way that increases waste escape.

The first option can be evaluated by estimating the fraction of droplets that are expected to escape the flame. A simple model was constructed in which the initial

TABLE I
Liquid-phase transport and volatility parameters for the waste compounds

Compound	Lewis Number	Normal Boiling Point °C
Acrylonitrile	12.0	77.7
Benzene	14.4	80.1
Chlorobenzene	15.6	132.
Chloroform	13.5	61.2

velocity of the droplets leaving the nozzle was estimated from an energy balance using an orifice coefficient of 0.8. Using the known flame shape, the in-flame residence time of each of the droplet size classes can be calculated. The fraction of each size class that evaporates within the flame is then estimated according to the transfer number theory of Spalding (1953). These results are shown as the shaded bars on Figure 2, which represent the fraction of the original total fuel mass associated with each size bin that escaped the flame. This indicates that approximately 0.4 percent of the droplet mass escapes for the on-design case, and 3.9 percent escapes under the off-design condition.

Under this scenario, the ranking of the waste compounds could be determined by the relative rate at which the various compounds are vaporized within the flame; the most easily vaporized compounds are destroyed in the flame, and the least easily vaporized compounds will escape the flame because they are enriched in the droplets. The initial approach of treating multicomponent droplet vaporization as a batch distillation process, in which the relative vaporization rate of the components is set by their relative volatility, has long been known to be inadequate (Law, 1982). This occurs because in the liquids under consideration here, the Lewis number (here defined as the ratio of thermal to mass diffusivity) is large, implying that heat transfer and surface regression due to evaporation are much faster than the rate at which the droplet can internally adjust its concentration profile. This implies that, after a short initial transient in which the volatile components are depleted in a thin region near the droplet surface, the droplet completes vaporization without a significant change in composition. Mixing within the droplet caused by ballistic droplet slip through the flame fails to improve the situation. Hill's vortices are established which maintain a stratified structure within the droplet, although on a smaller length scale than the droplet radius (Sirignano, 1983).

Experimental measurements on evaporating multicomponent droplets by Randolph *et al.* (1986) have suggested that for Lewis numbers below 10–15, the liquid phase diffusion becomes sufficiently rapid to permit bulk depletion of the droplet in the diffusing component. This suggests a ranking in which compounds with lower diffusivities are enriched in the escaping droplets. Under the present conditions, however, Table 1 shows that the Lewis numbers with respect to the individual components are not sufficiently widely separated to cause preferential vaporization (Randolph *et al.*, 1986). Also, this means of ranking suggests that acrylonitrile is the most easily vaporized compound in the flame, which is inconsistent with its higher emission concentration. As expected, Table 1 also shows that the relative exhaust ranking of the compounds fails to agree with volatility.

The conclusion for this set of conditions is that under atomization failure the principal waste release mechanism is not the transport of droplets from the flame, followed by evaporation and emission. Rather, flame or thermal decomposition failures appear to be responsible. Specifically, note that the rankings do not change significantly in moving from the on-design to the off-design condition. This implies

that it is through a perturbation on the flame structure that atomization failure causes enhanced emissions. The presence of significant post-flame chemistry is suggested by the fact that 3.9 percent of the droplet mass is shown to escape the flame in Figure 2, but only 0.1 percent of the acrylonitrile appears in the exhaust. Thus, the critical mechanism for this case appears to involve inadequacies in the turbulent diffusion flame. These are explored in the next section.

It should be noted that although no evidence for droplet dynamic effects were found in the emission rankings, this may not always be the case. Volatility differences will be important during the initial depletion at the surface of the droplet. Volatility can also be important if gasification is sufficiently slow to allow liquid phase diffusion more time to proceed (Makino and Law, 1988). Also, droplet gasification effects might become apparent for mixtures whose components have more widely varying Lewis numbers or volatility.

Performance Monitoring

The present regulatory approach to licensing incinerators is to perform an extensive trial burn, and to verify performance through detailed measurements. This approach, however, fails to ensure long-term performance because it does not provide for detection of transient failures and long-term operability degradation. The goal of indirect performance monitoring is the real-time indication of incinerator performance, for which the direct manual waste measurement techniques are not suitable. The study of the correlation between waste destruction and the various monitoring approaches offers some insight into waste release mechanisms.

Four general monitoring approaches have been suggested (Dellinger and Hall, 1986). These include (1) measurement of CO emissions, (2) measurement of total hydrocarbon emissions, (3) measurement of the most stable waste compound in the feed stream, and (4) the use of additive surrogates. The use of the most stable compound in the feed does not solve the real-time measurement problem, however, and it requires the selection of an "ease of destruction" ranking procedure to allow a general determination of the most stable compound. Not only is there no agreement on an appropriate procedure, but rankings in multicomponent systems change with flame conditions (Kramlich *et al.*, 1984 a,b) and can be changed by the presence of trace quantities of other waste compounds (Graham *et al.*, 1986).

The additive surrogate approach uses a non-toxic compound whose thermal behavior is refractory relative to the waste compounds, and whose exhaust concentration can be measured in real-time to a high sensitivity. Sulfur hexafluoride is the most frequently suggested surrogate, and its application has been the subject of extensive research (Dellinger and Hall, 1986; Taylor and Chadbourne, 1987; Pandompam *et al.*, 1989).

The hypothesis that CO and total hydrocarbon emissions (termed THC hereafter) correlate with incinerator performance arises from the assumptions that the process which favors waste destruction also favors burnout of these intermediates. Subscale spray flame data suggest a correlation when waste and auxiliary fuel are premixed (Kramlich *et al.*, 1984 a,b). It is not clear if this would be the case for separate injection of waste and fuel because the CO and THC emissions could be dominated by processes in the auxiliary fuel flame that are independent of the environment experienced by the waste.

Two data sets have been published on the correlation between CO emissions and waste destruction in subscale turbulent spray flames. One set was obtained in the

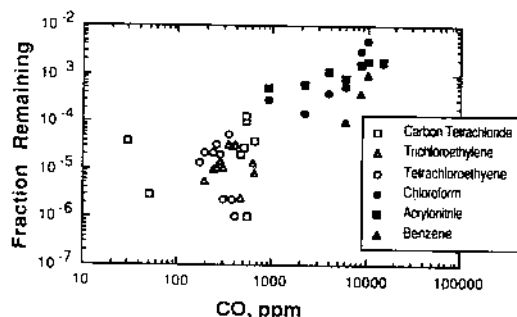


FIGURE 4 Correlation of CO with waste emissions from turbulent flame reactors. Open symbols are from Staley *et al.* (1989) and closed symbols are from LaFond *et al.* (1985).

reactor shown in Figure 1 (LaFond *et al.*, 1985) while the other is from an almost identical unit (Staley *et al.*, 1989). These data sets are plotted as Figure 4.

On first examination, the figure suggests a gross correlation between CO and waste emissions which covers several orders of magnitude, but which includes at least one order of magnitude of scatter. Closer examination shows that the data of Staley *et al.* exhibit essentially no correlation for any of the waste compounds. The data from LaFond *et al.* do indicate a correlation, although its characteristic is different for each compound.

How are the differences between the data sets to be reconciled? One approach is to examine the "on-design" portion of Figure 3. Our work with theoretical air as a variable has shown two regions of markedly different behavior in plots such as Figure 3. These are:

1. In the regions above 200 percent theoretical air and below 110 percent, emissions of both CO and wastes are elevated, and the waste emissions are repeatable to an accuracy commensurate with the precision of the analytical techniques.
2. Between 110 and 200 percent theoretical air, the waste emission is low, below 0.01 percent of original feed. Furthermore, repeat measurements under the same condition show that waste emission values are not repeatable, and actually scatter randomly over an order of magnitude.

This non-repeatability cannot be attributed to the analytical technique. Rather, it suggests that under high efficiency operation the waste that escapes the flame is due to a small number of individual turbulent events. Since the waste measurement represents an integrated average over a 20 minute period, then the number of these release events must be small enough to yield the observed scatter. This is indirectly supported by the observation that relatively minor, momentary changes in operating parameters during the course of a run can increase the measured waste emission over the 20 minute base by factors of 100 to 1000 above expected levels (Kramlich *et al.*, 1984a).

Since the data of Staley *et al.* (1989) were obtained under high efficiency conditions, they also would be expected to show the same random fluctuations in waste destruction efficiency, and therefore show no correlation with CO. We term this mode of waste emission *Random Failure* and define it as that waste release that occurs only under isolated turbulent events. The CO emissions are unlikely to correlate with waste emissions, for CO emission is a much more continuous process under these conditions, *i.e.*, the random events that give rise to CO release are much more numerous

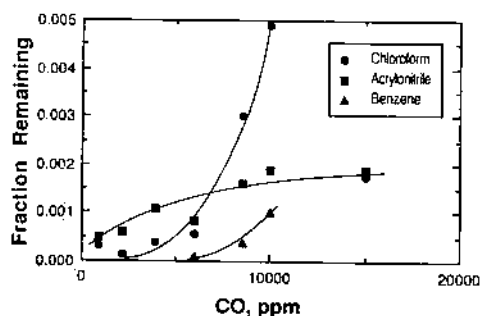


FIGURE 5 Linear scale plot of waste release vs. CO from LaFond *et al.* (1985).

than the number that allow release of individual waste compounds. Thus, the destruction of individual waste compounds in high efficiency flame zones does not appear to correlate with CO emissions.

Figure 5 replots all of the data of Figure 4, but on a linear axis. Note that this compresses the data of Staley *et al.* (1989) into the origin. This figure thus focuses on the low waste destruction efficiency zone of Figure 3. This region is characterized by highly repeatable waste emission measurements. Also, CO and waste emissions correlate, although on a compound specific basis. In this region the flame has been sufficiently perturbed to open a bulk, time-steady pathway for waste release. We have term this *Gross Failure*.

As discussed above, mean flame temperatures are capable of effecting an essentially complete destruction of waste compounds in times many orders of magnitudes shorter than the mean flame residence time. However, turbulent diffusion flames are inherently made up of broad ranging distributions of temperature, age, and composition (*e.g.*, see Borghi, 1988 for a review of the complexities involved in modeling these phenomena). As suggested by Dellinger *et al.* (1986), the waste escaping from a liquid injection incinerator is most likely due to the extreme tails of the residence time, oxygen, or temperature distribution function. The key is to examine behavior under conditions representative of the tails of the distributions.

Two extreme limits of behavior can be envisioned. In one limit, a pocket of gas remains sufficiently fuel-rich to yield a family of pyrolysis products. These could approach a thermochemical equilibrium composition. In the other limit, fuel-lean or cold gases could permit only partial reaction of the waste, or could allow the pocket to escape without reaction. Yang *et al.* (1987) examined the thermochemical equilibrium approach, but for a range of conditions much more representative of the mean flow. Figure 6 shows the results for some species of thermochemical equilibrium calculations for a variable stoichiometry. Note that below 10 per cent theoretical air the concentration of many waste-type compounds rises to high levels. These consist principally of aromatic compounds along with chlorinated methanes, and chlorinated C_2 compounds.

This suggests the following scenario for waste escape. Unmixed fuel or droplets are convected through the flame, and a fraction of these are mixed with hot, vitiated combustion products. These fuel-rich pockets approach thermochemical equilibrium in composition, and therefore contain a whole family of waste-type products in addition to light hydrocarbons. If these are convected out of the flame and quenched, the high local concentrations noted in Figure 6 will be diluted to the low levels of the family compounds found in incinerator exhausts.

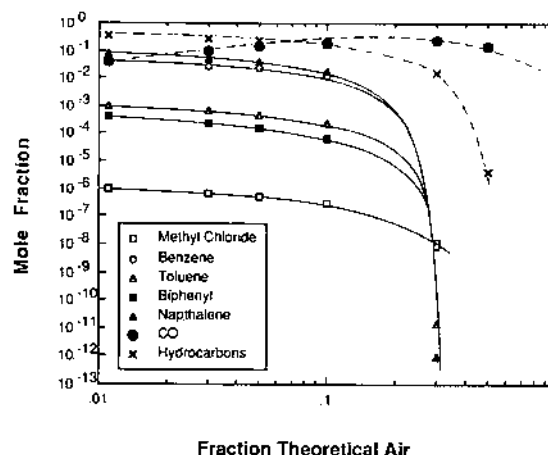


FIGURE 6 Species from a thermochemical equilibrium calculation at 727°C.

The alternative limit represents a similar scenario, but under fuel-lean conditions. The original fuel pocket is either mixed to sufficient dilution to prevent reaction, or is mixed such that partial reaction occurs. These processes would yield both the original waste compound, and specific reaction intermediates. The ranking would be similar to that suggested by thermal decomposition data.

From Figure 5, it is clear that CO must rise to a significant level before chloroform and benzene concentrations begin to increase. This would be expected because, as shown in Figure 6, the severity of unmixedness required to yield CO emissions is much less than that required to yield waste compounds. Acrylonitrile stands out as an exception, with relatively high emission reported for low CO values. Figure 3 shows that these high acrylonitrile values are associated with fuel-lean conditions. Thus, the elevated acrylonitrile concentration appears to be associated with fuel-lean failure. In fact, the thermal stability ranking reported by Hall *et al.* (1986) places acrylonitrile in the most refractory position in the series: acrylonitrile > benzene > chlorobenzene > chloroform. Chloroform is the only inconsistency in this ranking. Previous data show, however, that chloroform is formed as a byproduct in these flames at concentrations consistent with those observed here (Kramlich *et al.*, 1989).

These results suggest that two sources dominate the emission of waste-type compounds. In the first, rich pockets allow the generation of a family of pyrolysis products. Their speciation will not depend strongly on the composition of the initial waste, but rather will be governed by the approach towards thermochemical equilibrium. In a rate limited situation, one would suspect that simple chlorinated hydrocarbons would be favoured over complex aromatic compounds that require time to form. The second source would occur in fuel-lean pockets where partial waste destruction would occur. Both situations would generate byproducts, but the latter case these byproducts would be much more specific to the waste compound.

Figure 6 also shows the concentration of THC. (This was estimated as the signal expected from a flame ionization detector that had been calibrated on methane. The non-methane species were converted to equivalent methane response using flame sensitivity factors.) These estimated total hydrocarbon concentrations appear to be

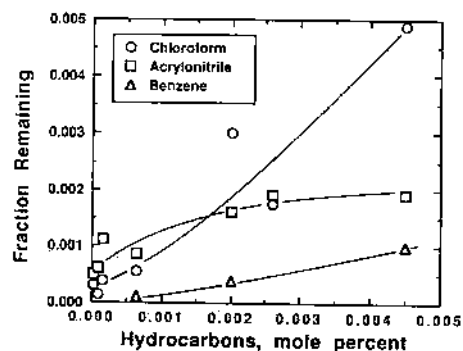


FIGURE 7 Correlation of total hydrocarbons with waste emissions from the turbulent flame reactor (LaFond *et al.*, 1985).

better than CO in approximating the waste yield as a function of stoichiometry. Figure 7 shows that the flame data are much more linearly related to THC than they were to CO in Figure 5. Note that this is not because the escaping wastes are detected as THC, but rather because the fuel hydrocarbons are destroyed by qualitatively the same mechanisms that destroy the waste.

Compound Concentration

One of the most interesting observations from field data is the correlation between efficiency and waste concentration in the fuels (Trenholm *et al.*, 1984). Figure 8 shows a compilation of field data illustrating the correlation and also showing that scatter within the correlation covers at least an order magnitude. The correlation shows that

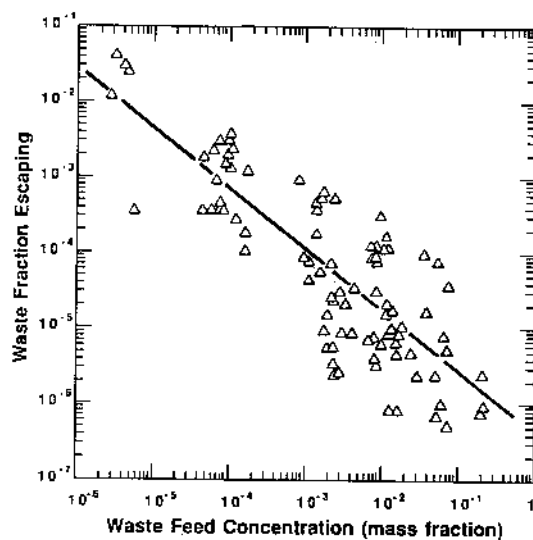


FIGURE 8 Field data compilation showing the correlation of waste destruction efficiency with waste concentration in the feed (Trenholm *et al.*, 1984).

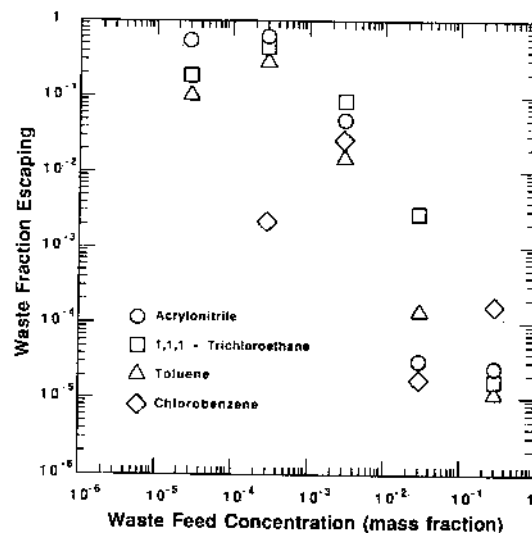


FIGURE 9 Influence of waste concentration in the feed on waste destruction efficiency in the turbulent flame reactor.

waste emissions are constant (within the scatter) at approximately 7 ppb. No elementary reaction kinetic order is capable of reproducing this behavior, so a more complex mechanism must be sought.

An attempt was made to replicate this behavior in the turbulent flame reactor. Figure 9 shows the waste destruction efficiency as a function of initial waste concentration in the feed for a mixture of acrylonitrile, 1,1,1-trichloroethane, toluene, and monochlorobenzene. The results show a trend that is very similar to the field data.

Two hypotheses have been offered to rationalize the correlation (Oppelt, 1987). The first states that the constant emission level is due to a constant byproduct formation that is independent of feed concentration. The second presumes that the correlation is an artifact due to measurement limitations.

One explanation that is consistent with the data is the equilibrium hypothesis developed in the previous section. It is the only means kinetically that emissions can be independent of waste feed. The argument would be that the mixing processes within practical incinerators are similar, to within an order of magnitude. Thus, the number and intensity of pyrolysis regions within which some kind of equilibrium state could be approached would also be similar, within the same order of magnitude. If the waste feed concentration is varied over five orders of magnitude, as shown in Figure 8, then the rich, pyrolysis zone process would yield the behavior shown in Figure 8.

Recent data (Fuerst *et al.*, 1989) using an enhanced analysis technique on practical incinerators, shows the emissions stream to be made up of three organic components. These are: (1) the original waste compound itself, (2) specific byproducts that are related to the waste, and (3) a background of many trace organic compounds that nominally in the 0.2–10 ppb range. Both the wastes and the specific intermediates are at much higher concentrations. This suggests that in practical incinerators where the wastes and specific byproducts are destroyed to high efficiencies, the only remaining emissions would be due to the products of the pyrolysis pockets that are approaching

thermochemical equilibrium. If the family of feed wastes were sufficiently broad, then these non-specific emissions would appear to be independent of the feed concentration.

SUMMARY

Incineration data and subscale spray flame results have been reviewed to postulate the mechanisms responsible for waste release. Understanding of these complex mechanisms is necessary to identify the factors which cause one waste compound to be more resistant to incineration than another, given the same environment. They must also be understood to evaluate the applicability and limits of the various approaches proposed for continuous, indirect performance monitoring of incinerators.

Mechanisms governing the release of hazardous constituents from multicomponent droplets were reviewed and were not found to correlate with the waste compound rankings in the exhaust. This occurred even under conditions in which a significant fraction of the droplet mass penetrated the flame. Such heterogenous effects may, however, become apparent if mixtures of more widely varying Lewis numbers of volatility are used.

Flame measurements showed two distinct modes of operation. *Gross Failure* was characterized by a time steady release of waste from a perturbed flame. It represents the opening of a major pathway for waste escape. *Random Failure* governed waste release under high efficiency conditions. The release appeared to involve the occurrence of a relatively small number of transient waste releasing events. The number of these events appeared to be sufficiently small that the normal 20 minute sampling period did not allow sufficient time to obtain a good statistical average of the long-time behavior. Under gross failure, consistent compound rankings were observed in the exhaust. For random failure the rankings are random and not repeatable.

Evaluation of CO and total hydrocarbons as indirect incineration performance monitors was also undertaken. Under random failure, no correlation was observed between CO and waste emissions. For gross failure, the CO would generally rise to a significant level before waste emission began to increase from the low, random levels. In this instance, acrylonitrile was a notable exception in that its concentration correlated almost linearly with that of CO. Total hydrocarbon emissions were much more linearly correlated with waste emissions. This is expected because CO will be formed and maintained in any local environment that is fuel-rich, while the fate of hydrocarbons and wastes are much more closely coupled in that a much more severe local departure from mean flow conditions is necessary to cause emission.

The data give evidence of two principal release mechanisms. Both occur in the extreme tails of stoichiometry, residence time, and temperature distributions. Under sufficiently rich conditions, most of the smaller waste-type molecules (e.g., chlorinated methanes, chlorinated C_2 's) can reach high concentrations at equilibrium. If these are quenched and mixed into the exhaust gases, they can cause the ubiquitous background of species concentrations in the 1-10 ppb range that are prevalent in the exhaust. The second mechanism involves partial thermal decomposition and by-product formation in cool, lean fluid elements. In the present experiment, the acrylonitrile results are more consistent with the second hypothesis.

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