

MODELING AEROSOL EMISSIONS FROM THE COMBUSTION OF COMPOSITE MATERIALS

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The use of advanced composite materials (ACM) in the B-2 bomber, composite armored vehicle, and F-22 advanced tactical fighter has rekindled interest concerning the health risks of burned or burning ACM. The objective of this work was to determine smoke production from burning ACM and its toxicity. A commercial version of the UPITT II combustion toxicity method developed at the University of Pittsburgh, and subsequently refined through a US Army-funded basic research project, was used to establish controlled combustion conditions which were selected to evaluate real-world exposure scenarios. Production and yield of toxic species varied with the combustion conditions. Previous work with this method showed that the combustion conditions directly influenced the toxicity of the decomposition products from a variety of materials.

INTRODUCTION

Introduced in the 1960s, advanced composite materials (ACM) are expected to compose 40-60 percent of future airframes. Figure 1 illustrates the increased use of ACM in US Air Force aircraft. During the 1990s, several events focused attention on the human and environmental consequences resulting from fabrication and incidental combustion of ACM. In addition, although the fibers and epoxy resins of advanced composites appear to be safe in their original state, the chemical transformation to a hazardous substance during combustion is not well characterized. These resins, such as epoxies, polyimides, phenolics, thermosets, and thermoplastics, may release potentially lethal gases, vapors, or particles into the atmosphere when burned.

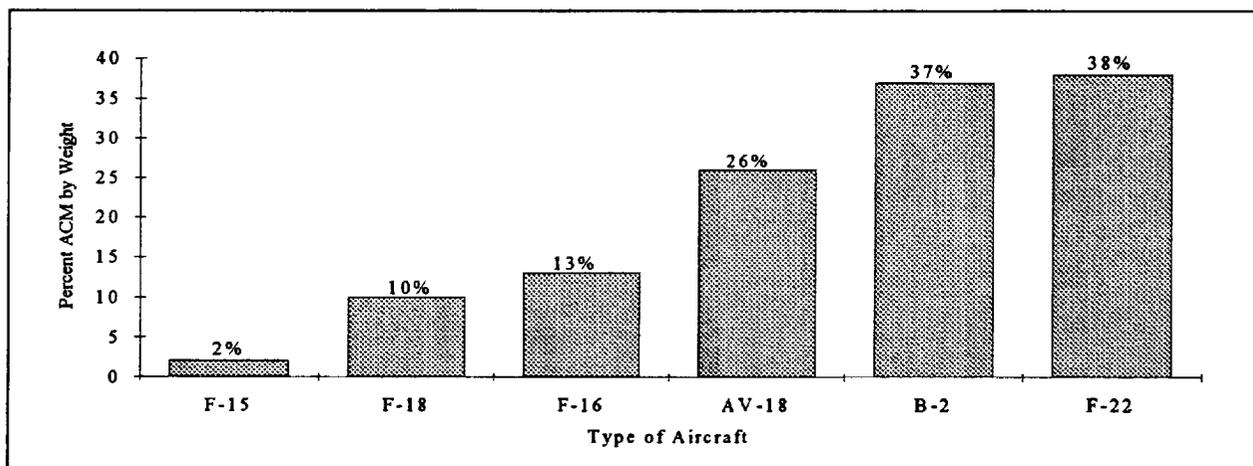


Figure 1 Percent of Aircraft by Weight

As the use of composites increase, so do the potential risks to the environment and those exposed to the smoke and combustion gases during aircraft mishaps. The objective of this work was to determine smoke production from burning ACM and predict its toxicity.

The apparatus used to establish controlled combustion conditions is a commercially available version of the cone heater combustion module of the UPITT II method developed at the University of Pittsburgh. Previous work with this method showed that the combustion conditions directly influenced the toxicity of the decomposition products from a variety of materials. Not only will the toxic potency of the thermal decomposition products be determined, but the time to toxic effect will also be obtained over a variety of combustion conditions selected to enable evaluation of real-world exposure scenarios.

Development of test methods to evaluate smoke from burning materials has been an aspect of fire science which has received much attention. Two approaches exist, the first is the analytical approach which attempts to predict smoke toxicity based on the toxicity of each component found in the smoke. The major drawback of this approach is that limited information exists for only a few chemicals while many unknown chemicals are typically generated during combustion of most materials. Even when the major toxicants in a combustion atmosphere can be identified, the possibility of biological interactions between these chemicals would render any prediction of toxicity speculative. For these reasons the second approach, the bioassay, is preferred. The use of animals is necessary in combustion toxicity tests of materials to detect the presence not only of unusual or uncommon toxicants but also of biological interactions between common gases. All currently used test methods, including the UPITT II method, share lethality as the common endpoint of toxicity and typically determine the LC_{50} for a material. We have incorporated alternate endpoints (such as incapacitation) into the UPITT II method. Thus, we not only measure toxic potency in terms of smoke concentration, but also determine the time to effect, be it lethality, incapacitation, or any other selected endpoint. This research will result in the selection of safer materials for new and existing weapons systems.

DESCRIPTION OF EXPERIMENT

Materials

A carbon fiber/modified bismaleimide resin advanced composite material (approximate 2:1 ratio by weight) was used in these studies. Specimens were 108 mm square by 2.5 mm thick with a mass of 53.90 ± 0.36 g.

Combustion Module

A commercial version of the UPITT II combustion toxicity apparatus (1) was used to establish controlled combustion conditions selected to evaluate real-world exposure scenarios. For these experiments the heat flux (Q) was set at 38, 44, 57, or 84 kW/m^2 ; the airflow was maintained at 19, 28, 35, or 41 L/min. The time to ignition (T_{ign}), duration of flaming (T_{FI}), and mass loss rate (\dot{m}) were determined as previously described (1) except that a 10-minute period was used instead of a 30-minute period. The smoke concentration (SC) was calculated by dividing the mass loss rate by the airflow through the apparatus.

Combustion Product Identification

A Perkin-Elmer Model 1600 FT-IR spectrometer was used to obtain transmission spectra of the filtered smoke produced by the burning specimen. The major toxic species were qualitatively identified from these spectra.

RESULTS

Results from experiments conducted under flaming conditions are presented in Table 1. The T_{ign} decreased as Q increased, while the mass loss rate increased with increasing Q (2). Table 1 represents the time to ignition, and mass loss rate for 0.01m^2 ACM specimens irradiated for 10 minutes.

Table 1 Preliminary Experiment Results

| Q kW/m^2 | T_{ign} seconds | m g/min |
|------------------------|----------------------|-----------------------|
| 38 | 255 | 1.2 |
| 44 | 60 | 1.2 |
| 57 | 35 | 1.5 |
| 84 | 15 | 1.7 |

Consolidated results of the coupon burn experiments find that the average mass loss of the ACM is 29.1%. Further review of the results from these controlled experiments suggest that, at constant air flow, the mass loss rate increases with heat flux. The graphical representation of these data points and regression line are found in Figure 2. Conversely, Figure 3 demonstrates that, at constant heat flux, the mass loss rate is not significantly related to increasing air flow.

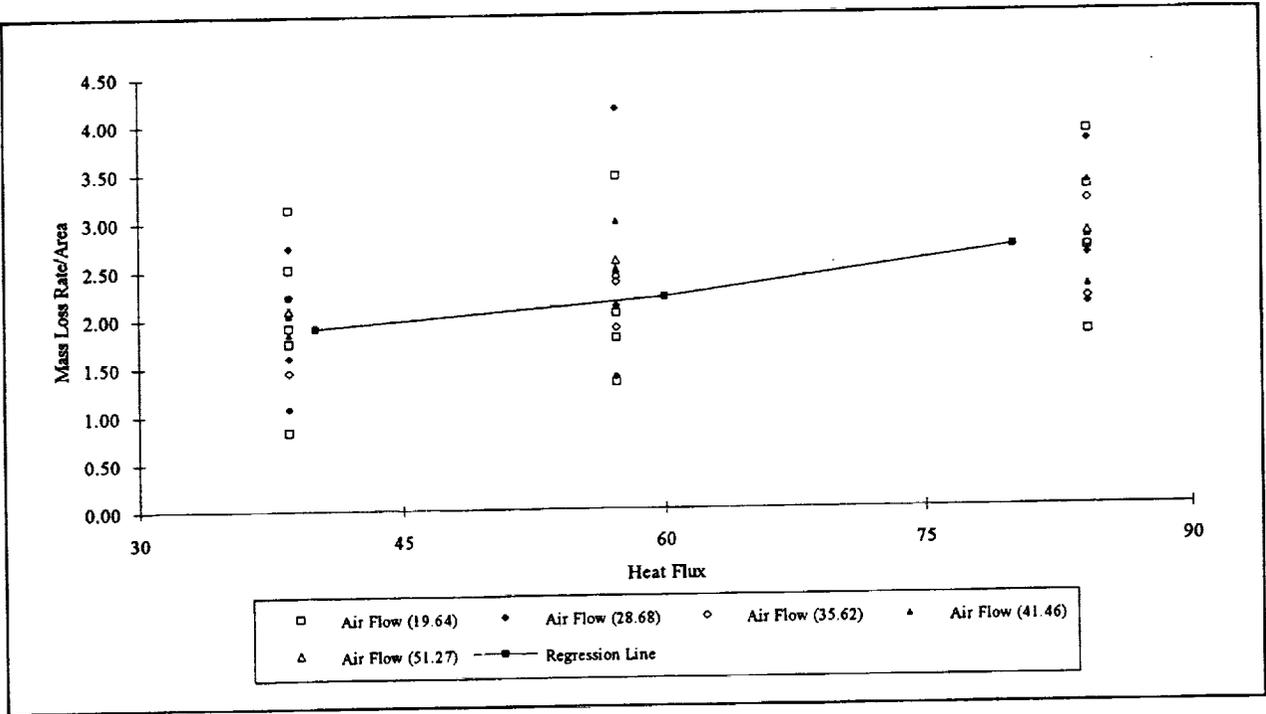


Figure 2 Coupon Mass Loss at Constant Air Flow

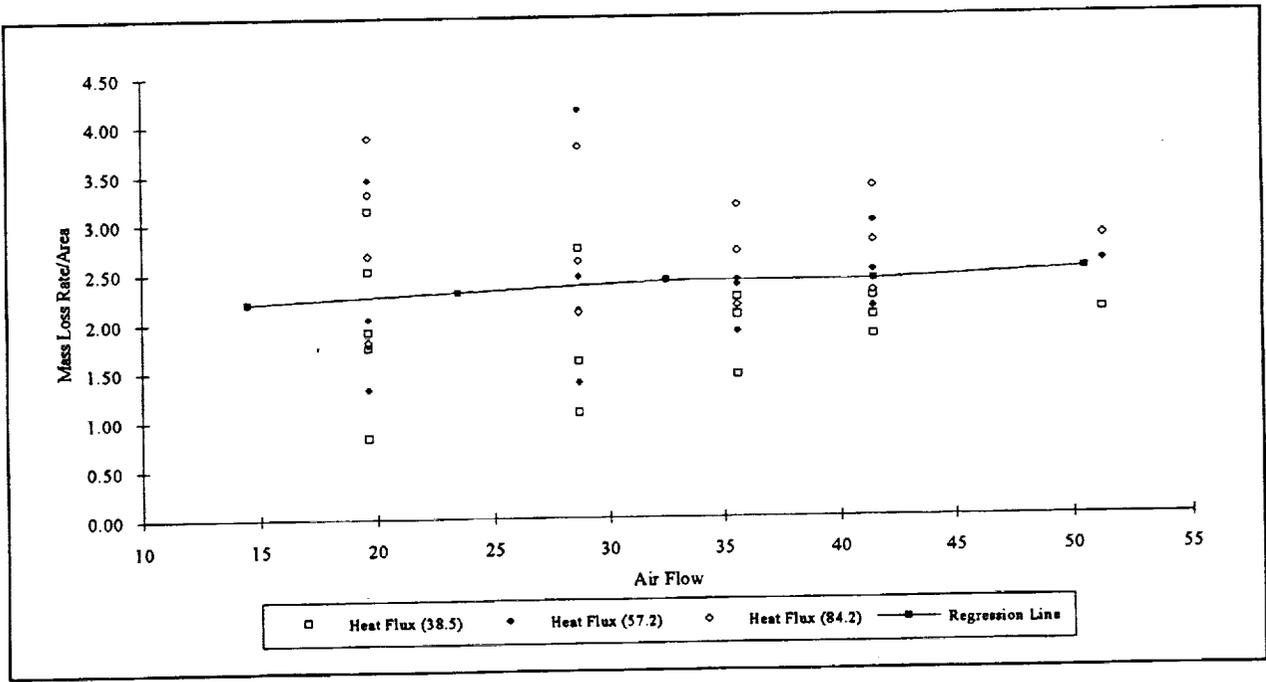


Figure 3 Coupon Mass Loss at Constant Heat Flux

Smoke and Aerosol Characterization

The composition of the smoke and properties of the aerosol particles was evaluated. Initial results find the smoke is composed of phenol groups, aniline groups, carbon monoxide, and carbon dioxide. Major spectrum peaks from a representative FT-IR spectrum of smoke from an experiment conducted at 50 kW/m² are identified in Table 2.

Table 2. Peak identification from representative FT-IR spectrum.

| CM-1 | Height | Identity |
|-------------|---------------|-----------------|
| 3708 | 17.64 | Aniline |
| 3628 | 19.23 | Aniline |
| 3596 | 25.35 | Aniline |
| 3566 | 53.31 | Aniline |
| 3324 | 53.36 | Phenol |
| 2510 | 81.09 | Carbon Dioxide |
| 2174 | 50.68 | Carbon Monoxide |
| 2116 | 56.36 | Carbon Monoxide |
| 1526 | 10.45 | Aniline |
| 1304 | 29.53 | Aniline |
| 1164 | 47.28 | Phenol |
| 1138 | 53.65 | Phenol |
| 730 | 10.25 | Phenol |

Two samples were analyzed by GC/MS with the results summarized below in Table 3. The quantitative figures were obtained by using the Response Factor = 1 approximation as specified in the CLP Statement of Work. A vapor aliquot was collected using a cold trap. The collection conditions were two runs at 30L/min for 10 minutes. The following compounds were qualified:

Table 3 Quantification of Identified Compounds

| Identified Compound | Soln Conc ($\mu\text{g/ml}$) | Air Conc ($\mu\text{g/m}^3$) |
|---------------------------------|--------------------------------|--------------------------------|
| Aniline | 342.4 | 0.57 |
| Phenol | 961.8 | 1.60 |
| 4-methylphenol (o-cresol) | 63.7 | 0.11 |
| 2-methylphenol (p-cresol) | 74.7 | 0.12 |
| 3-methyl-1-isocyanobenzene | 5.9 | 0.01 |
| quinoline | 24.9 | 0.04 |
| Biphenyl | 6.8 | 0.01 |
| Diphenyl Ether (diphenyl oxide) | 114.0 | 0.19 |

The aerosol particle density (ρ_p) was determined using standard laboratory practice and found to be 0.29 mg/mL. The air samples, analyzed by electron microscopy identified a range of aerosol diameters from 0.5 to 1.5 μm . Given this density and the observed range of particle diameters the gravitational settling velocity ranged from 6.5×10^{-6} to 3.8×10^{-4} m/sec. Due to this small velocity, the aerosol emissions were found to have no significant affect on the downwind concentrations.

Approximately 1.4g of the soot was extracted with 50:50 Methylene Chloride:Acetone solution. It was apparent, upon examination of the injection port liner, that many of the extracted compounds were not suitable for analysis by GC/MS, as there was obvious evidence of pyrolysis and deposition in the liner. The major compounds identified are shown in Table 4 below.

Table 4 Identification and Quantitation of Major Compounds Extracted from Soot

| Identified Compound | Soln Conc ($\mu\text{g/ml}$) | Conc in Soot ($\mu\text{g/Kg}$) |
|--------------------------------------|--------------------------------|-----------------------------------|
| Aniline | 215.5 | 2994.4 |
| phenol | 156.5 | 2174.6 |
| 2- and 3-methylaniline | 45.0 | 1204.0 |
| quinoline | 250.2 | 3476.3 |
| 5-methylquinoline | 86.4 | 1200.3 |
| Diphenylether | 75.8 | 1053.6 |
| 2-methoxyethoxybenzene | 119.7 | 1662.7 |
| 1,2-dihydro-2,2,4-trimethylquinoline | 159.2 | 2212.3 |
| 1-isocyanonaphthalene | 158.9 | 2208.2 |
| dibenzofuran | 97.6 | 1356.7 |
| 1-Isocyanonaphthalene | 119.6 | 1661.5 |
| Anthracene | 122.2 | 1698.1 |
| N-Hydroxymethylcarbazole | 92.5 | 1285.1 |
| Fluoranthene | 93.3 | 2129.6 |

From experience, the quantification is probably low. Several other comments need to be made. As these identifications were made by mass spectroscopy, it is quite probable that some of the isomers may be some other isomer. That is one of the weaknesses of the technique. There were a number of PAH peaks in the soot extract which were of too low an intensity to characterize properly, and were not included in the above. Additionally, as mentioned above, there are probably a considerable number of compounds which either did not extract in the first place or did not make it out of the GC injection port. The key point is that many of these compounds are known carcinogens.

DISCUSSION

ACM Emission Rate

The primary objective of these combustion experiments was to obtain a mass loss rate for the ACM. However, one significant limitation to this study is the lack of research on the heat transfer properties of composite materials. Therefore, we assume that the flame spread characteristics demonstrated by this bench-scale combustion equipment accurately simulates those of a full-scale aircraft. The results, under controlled heat flux and air flow conditions, identified a linear relationship between the mass loss rate and the area of the burning composite.

Multi-variable linear regression of the mass loss rate data with the sample coupon area was preferred. The equation for the regression line is found below in Equation 1-1. The regression results provide a linear equation ($R^2 = 0.99$) that allows accurate prediction of an emission rate for a full-scale aircraft.

$$\dot{m} = \beta_1 (Area) + \beta_2 (HeatFlux) - 0.01 \quad (1-1)$$

where:

$$\beta_1 = 1.98$$

$$\beta_2 = 1.86 \times 10^{-4}$$

These findings enable regression analysis of a linear equation for the emission rate given constant heat flux, air flow, and area conditions. Aerosol properties were identified which enabled calculation of the gravitational settling velocity. This, in turn, will serve to better estimate the downwind plume characteristics. The combined results allow for accurately modeling the smoke and aerosol smoke plume generated during the combustion of composite material aircraft.

Thermogravimetric Analysis

The way heat was applied to the samples in the thermogravimetric analyzer was a little different than that in the larger unit. The TGA uses a cup design, with the sample in the center of a small furnace. It wasn't possible to shield the sample during the heatup cycle from the heat, as is possible in the UPITT II apparatus. Despite this difference, and the much smaller sample size, the weight loss measured by the two units was quite similar. During the first two to three minutes,

the sample lost approximately 25% of its weight. What happened in the TGA after this is a direct result of the differences between the TGA and the larger burn unit. The TGA has the capability to heat in a nitrogen atmosphere or in air. The atmosphere made a significant difference in the weight loss characteristics.

Burns in Nitrogen: After the initial weight loss due to the polymer pyrolysis, the weight stabilized at a little over 75% of the initial weight, and stayed there for the rest of the thirty minute test run. There was no significant change with extended time.

Burns in Air: The specimen mass never stabilized after the initial pyrolysis mass loss (due to the polymer resin loss). The mass loss curve changed with temperature, the slope of which increased as temperatures increased. Given enough time, the graphite fibers completely disappeared, i.e., at 950°C all mass is lost within 15 minutes, while at 650°C the time required increased to 60 minutes.

We suspect that the graphite fiber was being "eroded" by the oxygen in the air. Unpublished work on diamond showed a molecular surface effect (R. Langford, personal communication). Apparently, when the material is given enough energy (heated), the impact of an oxygen molecule is enough to pull off a carbon atom and form CO₂ or CO. This is supported by infrared spectroscopy data, which show evolution of these gases until the weight goes to zero.

Modeling the Plume Corridor

The Industrial Source Complex Short Term 2 (ISCST2) Model results were used to identify deposition values, downwind concentrations, and plot the potential plume concentration corridor.

These results provide a review of the modeling scenarios described below. Following the scenario are figures that portray the ISC plume corridor concentration results in a plan view or contour plot, and a 3-Dimensional surface plot. Given the very unstable conditions in Scenario 1, Figure 4 suggests a small area of potential contamination, but a large concentration. Further review indicates a maximum concentration of 1400 µg/m³ occurring approximately 500 m downwind from the source. A significant difference in the plume area is identified in Figure 6 where the maximum concentration is 1300 µg/m³ at 400 m downwind of the source. This should be expected due to the changing meteorological conditions used in the scenario

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The following describes the parameters for Scenario 1:

- JP-4 Pool Fire Centerline Temperature: 873.5 °C
- Emission Rate: 870.98 g/sec
- Stability Class: A
- Wind Speed: 5 m/sec
- Release Height: 0
- Effective Stack Height: 972 m
- Model: Particle Deposition over a 1 and 3 hour period.

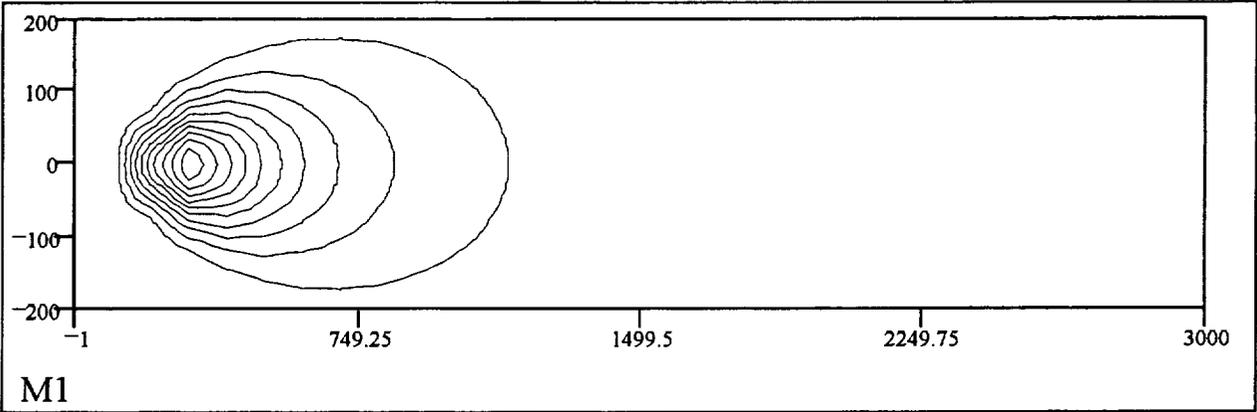


Figure 4 A Contour Plot of Plume Corridor for Scenario 1

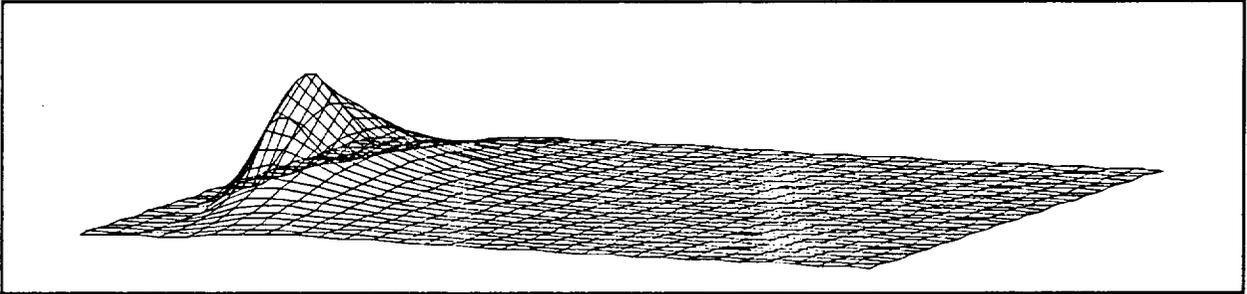


Figure 4.5 A 3-Dimensional Surface Plot of Plume Corridor for Scenario 1

The following describes the parameters for Scenario 2:

- JP-4 Pool Fire Centerline Temperature: 873.5 °C
- Emission Rate: 870.98 g/sec
- Stability Class: Varying
- Wind Speed: Varying
- Release Height: 0
- Model: Particle Concentrations over a 1 and 3 hour period.

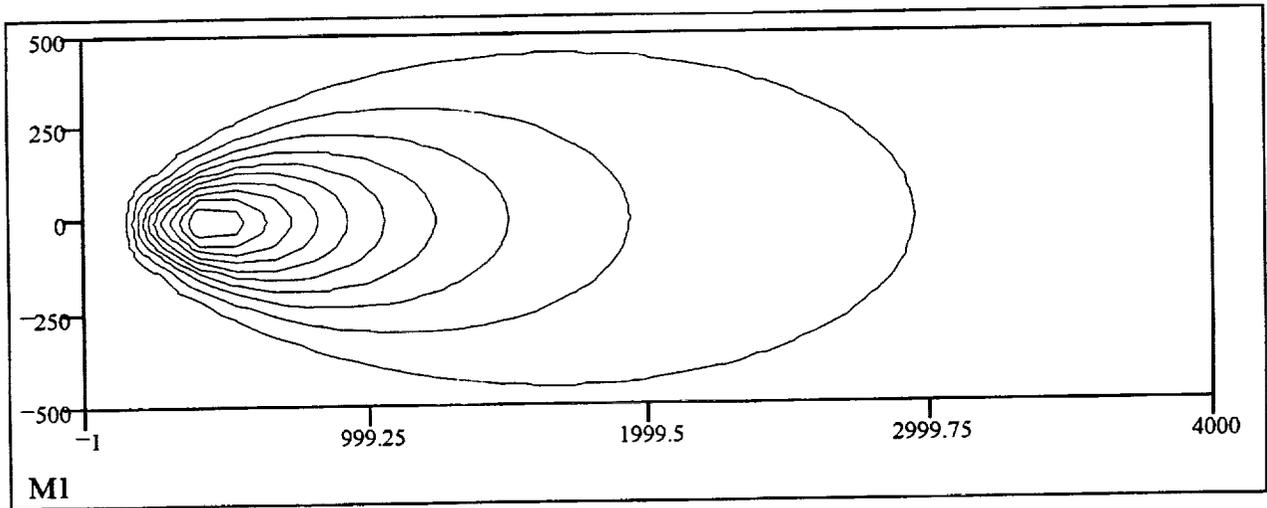
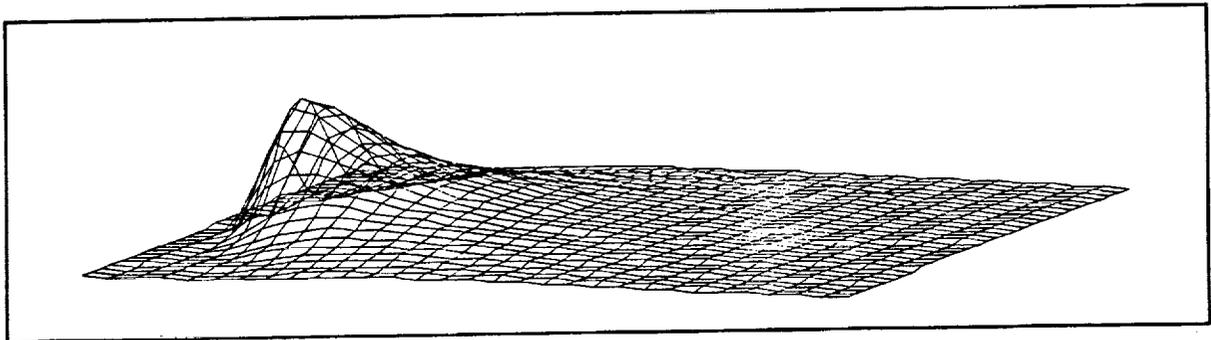


Figure 4.6 A Contour Plot of the Plume Corridor for Scenario 2



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Figure 4.7 A 3-Dimensional Plot of the Plume Corridor for Scenario 2

The previous plots suggest that the ACM plume corridor is extremely dependent upon the atmospheric conditions at the time of the mishap. The concentrations will be higher with a nominal plume spread on a turbulent day, whereas the converse will occur during a calm day.

Other Observations from the TGA runs

Once the resin was pyrolysed off the fiber matrix, the fibers separated and puffed to several times the original volume and lost any cohesion or tendency to group together. After a burn where the graphite was not completely consumed, there was a considerable difficulty getting fibers out of every nook and cranny of the instrument. This phenomenon happened whether the burn was in nitrogen or air.

This leads to a couple of speculations. In general, even after a long burn, the fibers remain visible and therefore not respirable. It is, however, possible that some are being eroded to the point where they could be respirable. At this point, the answer is unknown, however, there are clear hazards associated with what is known to be contained in the soot particles and that these present the greater hazard to life and property than does the physical shape (i.e., particle or fiber).

The fibers are extremely fluffy, and potentially electrically conductive. They could travel a significant distance in a mild breeze, and have the potential to short out everything from computers to power lines. It is probably critical that measures be taken in fighting a fire involving these materials to reduce dust and aerosols.

CONCLUSIONS

Smoke production and yield of toxic species varied with the combustion conditions. This finding is consistent with previous work with this method which showed that the combustion conditions directly influenced the yield and toxicity of smoke produced by a variety of materials (3).

Although no animal exposures were performed during this preliminary series of experiments, an estimate of the potential toxicity of the smoke can be made based on the analytical results and the smoke yield from the burning ACM.

Future work will incorporate animal exposures to determine the toxic potency of the smoke and evaluate alternate non-lethal endpoints such as incapacitation. We can not only measure toxic potency in terms of smoke concentration, but also determine the time to effect, i.e. lethality or incapacitation. This approach will result in the selection of safer advanced composite materials for new and existing weapons systems.

REFERENCES

1. D. J. Caldwell and Y. C. Alarie, *J. Fire Science*, **8**, 23-62 (1990).

2. J. A. Roop, *Modeling Aerosol Dispersion from Combustion of Advanced Composite Materials During an Aircraft Mishap*, Master's Degree Thesis (AFIT/GEEM/ENV/94S-21), Air Force Institute of Technology (1994)
3. D. J. Caldwell and Y. C. Alarie, *J. Fire Science*, **9**, 470-518 (1991).