Experimental Determination of Vapor Species from Laser-Ablated Carbon Phenolic Composites

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The thermal loadings approximating those to be encountered by heat-shield materials at peak heating during vehicle entry into the atmospheres of the outer planets have been simulated with laser irradiation. The relative concentrations of the resulting vapors as they emanate from the ablating material have been measured, and the technique for vaporizing the surface of bulk samples by laser irradiation while measuring in situ the vapor species by mass spectrometry is described. Results from carbon phenolic show that vapor composition varies with irradiance level and with depth of heating (or extent of pyrolysis). Attempts are made to compare these experimental results with the theoretical predictions from computer codes.

Introduction

IN view of the paucity of measurement data identifying the chemical species generated by vaporization of heat-shield materials, the objective in this work has been to determine experimentally the composition of blow-off gasses produced by carbon phenolic composites when subjected to the level of incident thermal energy encountered during entry into planetary atmospheres. This information is important as a basis for predicting the blockage factors for incident thermal radiation, and as a means of verifying the computer codes that predict chemical mole fractions on the basis of thermodynamic and chemical equilibrium. The approach in this work has been to measure the vapors in situ as they emerge from the surface of the heated material prior to striking container walls or condensing on any surfaces, thus making possible a more complete determination of the chemical composition of the gaseous components including the free radicals and condensables as well as the more stable molecules.

Although carbon/phenolic heat shield materials are not new, heretofore the amount of experimental work that has been done to define the vaporization products of the composite material has been limited both in extent and in instrumentation employed. In most cases, the heating has been accomplished by placing the sample on a resistively heated surface or by putting it in a furnace, and the gas analysis carried out subsequently by gas chromatography or mass spectrometry. This inherently limits analysis to the stable vapor species. The major contribution of the work reported here lies both in the results and in the technique used to heat ablation materials by incident thermal radiation in an attempt to simulate the thermal levels encountered under vehicle flight conditions, while simultaneously sampling the gaseous products by instrumentation that can best determine the initial pyrolysis species, including the transient intermediates.

Experimental

As in earlier work,[1] the technique used for studying the materials of interest has been to vaporize an area of the sample surface by laser irradiation while measuring the vapor products using a mass spectrometer as the in situ diagnostic tool; the sample and spectrometer are within the same high-vacuum chamber and are positioned so that the ion source of the mass spectrometer is in a line-of-sight, collision-free path from the heated surface.

The instrumentation used in this work is shown in Fig. 1; it has been described previously along with the associated data acquisition system.[2] A time-of-flight (TOF) mass spectrometer was selected because of its unique ability to present up to 50 complete mass spectra per millisecond plus its capability of measuring quantitatively several vapor species simultaneously, thereby permitting an in situ analysis during each laser-induced vaporization process. When the pulsed laser was employed, mass spectra were recorded only as the initial vapor cloud passed through the ion source; this insured equal measurement of the condensables and short-lived species along with the fixed gases. Although absolute calibration of the instrument has not been achieved at this time, sensitivity factors for the various gases were derived from the literature and from experimentation so that relative concentrations could be determined.

Two types of laser heating have been employed: 1) a pulsed Nd:glass laser in the normal (or burst) mode, and 2) a continuous wave (cw) carbon dioxide laser operating at a wavelength of 10.6 μm. Although pulsed lasers operating in the burst mode characteristically produce a highly irregular time-intensity distribution of output energy, their lower power densities and longer radiating periods better simulate the heating encountered by planetary probes than would those operating in the Q-switched mode. Furthermore, it is necessary to minimize any laser beam-vapor interactions that produce plasma, etc.—typically a result of the very high power intensities associated with Q-switched lasers. The pulsed laser heating conditions used here are shown in Table 1.

Earlier work[3] has shown that under the given conditions a laser beam having a uniform cross section and focused onto a planar surface—thereby vaporizing material in a circular spot within a reduced ambient pressure (or vacuum)—produces a gas-dynamic phenomenon which is a quasisteady, supersonic, free-jet expansion of the vapor products. Thus, the spot acts as a sonic orifice for the vapors and produces isentropic flow with streamlines appearing to radiate from a point source.

Table 1 Pulsed laser heating conditions

Wavelength	1.06 μm
Operating mode	Normal (burst)
Pulse duration	400-800 μs
Energy density on target	25-80 joules/cm^2
Beam diameter on target	3-6 mm
Peak irradiance	50-270 kW/cm^2
Beam cross section	Uniform (non-Gaussian)

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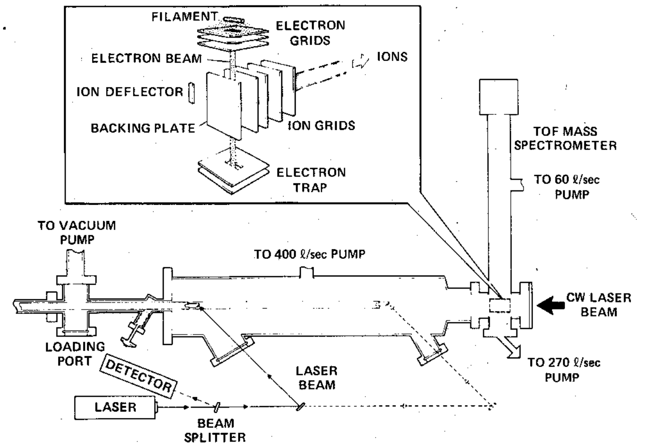

Fig. 1 Mass spectrometer and vaporization chamber for laser-heated samples.

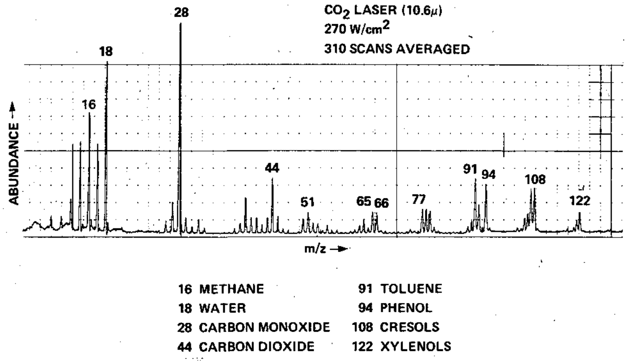

Fig. 2 Mass spectrum of vapor from cw laser-heated carbon phenolic composite.

Table 2 The cw laser heating conditions

Wavelength	10.6 μm
Pulse duration	0.1-3 s
Beam diameter on target	1-3 mm
Power density on target	90-270 W/cm^2

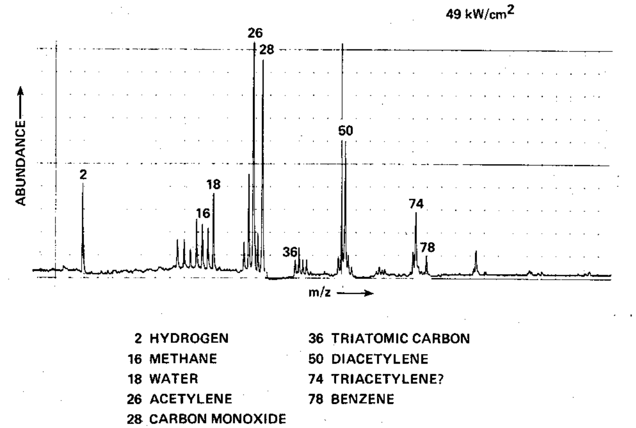

Fig. 3 Mass spectrum of vapor from pulsed laser-heated carbon phenolic composite.

Table 3 Mole fractions of major vapor species from laser heating of carbon phenolic composite

	Pulsed 58 kW/cm^2	Continuous 270 W/cm^2
CH_4	0	0.12
H_2O	0.10	0.48
C_2H_2	0.026	0
C_2H_4	0.021	0.05
CO	0.065	0.14
C_3	0.69	0
CO_2	0	0.030
C_4H_2	0.088	0
Toluene	0	0.023
Phenol	0	0.031
Cresols	0	0.028
Xylenols	0	0.012
C_3H	0.02	0

Although the local pressure at the vaporizing surface can be quite high, the rapid gas-dynamic expansion quickly "freezes" the components in a collisionless regime so that we have reasonable confidence that the species detected by the mass spectrometer many centimeters away are, indeed, the same as those existing near the surface-gas interface.

Inasmuch as the emphasis in this paper is on the response of materials to thermal radiation, it would be well to note briefly some of the salient features of high-intensity, pulsed radiant heating. When the irradiance level is extreme on an opaque body of high surface absorptance, energy deposition is limited to material very near the exposed surface, and ablation effects predominate over the relatively inconsequential diffusion of heat into the solid. Thus, under the conditions described earlier the heating is effectively one-dimensional and only the exposed surface is vaporized during each laser pulse. The surface absorptance of FM 5055G carbon phenolic composite is assumed to be over 0.9 at the laser wavelength and after initial exposure.

The cw laser operates at a much lower power output level. The heating conditions are shown in Table 2.

Ideally, the simulated heating would be performed at irradiance levels equal to those from the pulsed laser and extended for many seconds. However, even if such a laser were available, its use for this application would require enormous vacuum equipment to avoid overloading the vacuum system. Consequently, under present laboratory limitations we are constrained to a trade-off between irradiance level, vaporization area, and exposure time. Thus, the results presented here highlight the differences and the similarities in vapor species produced by these two different heating rates.

Results and Discussion

Although the cw laser heats the material for a much longer period than its pulsed counterpart, it might be expected that the orders of magnitude lower irradiance would produce lower ultimate temperatures. This appears to be borne out by the results from heating carbon phenolic composite (FM 5055G TWCP) with the cw laser; the results reveal that the major vapor products are those corresponding to the pyrolysis of the polymer—methane, water, carbon monoxide, ethylene, carbon dioxide, toluene, cresol, benzyl alcohol, and some xylenols (Fig. 2). Evidently, the longer exposure yields greater in-depth heating but produces only pyrolysis reactions of the resin in the composite, and carbon species are noticeably absent in the spectra. This indicates that the temperatures are too low to vaporize any of the carbon present in the filler or the fibers. On the other hand, the results presented in Fig. 3, obtained from the first in a series of pulses heating the same area on a TWCP sample at fluxes corresponding to entry conditions, reveal some vaporized carbon present as the C_3 species, and, in general, the vapor population is comprised of smaller molecules, which is typical of polymer varporization occurring at higher heating rates (i.e., higher incident heat flux). This is also evident in Table 3.

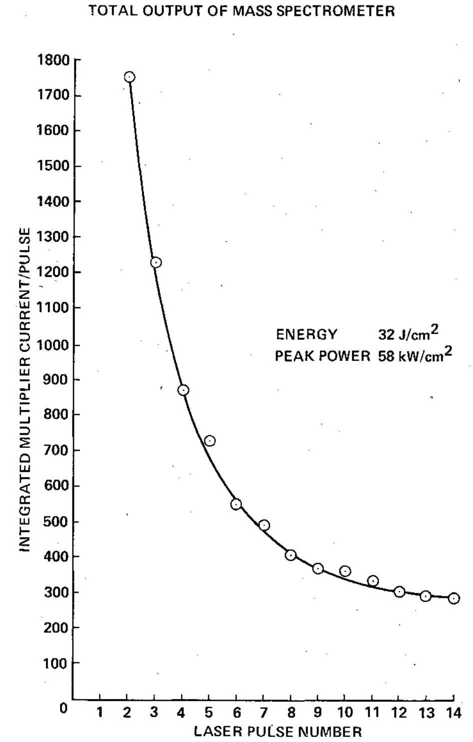

Fig. 4 Total vapor yield per laser pulse.

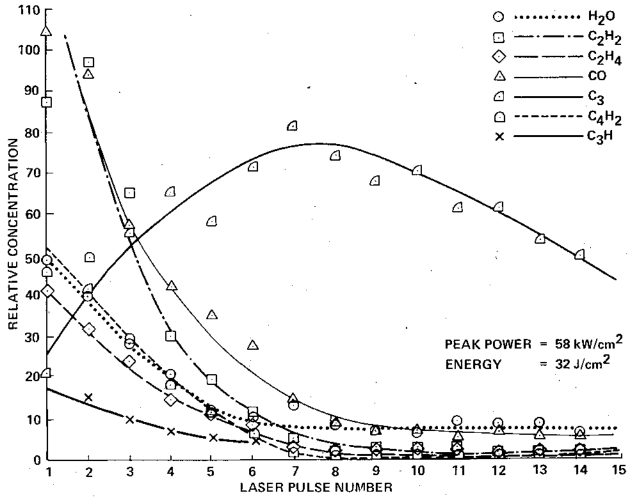

Fig. 5 Vapors from pulsed laser-heated carbon phenolic composite.

An important aspect of vaporization by pulsed energy is demonstrated in Figs. 4 and 5, which are results from the same series of laser pulses. (Also detected but not shown here were large amounts of H_2 plus small amounts of C_2H from the first several pulses.) at these fluence levels (and much higher ones) the pulses of incident energy vaporize a very thin surface layer each time, and the first one or two pulses may dislodge (chiefly) the absorbed surface gases. For this reason it has been our practice to mechanically shave off the outer surface to be exposed and immediately place the sample in the high vacuum chamber for an extended period of time before exposing it to the laser beam. The fresh surface is then hit with a number of laser pulses in order to reach a condition such that the blow-off gases represent vaporization from the bulk material which, after all, is the goal in predicting ablation characteristics. These data came from a phenolic composite that includes graphite fibers as well as the carbon filler; therefore, it is not surprising that the major vapor component is vaporized carbon in the form of C_3 after the initial pyrolysis is completed.

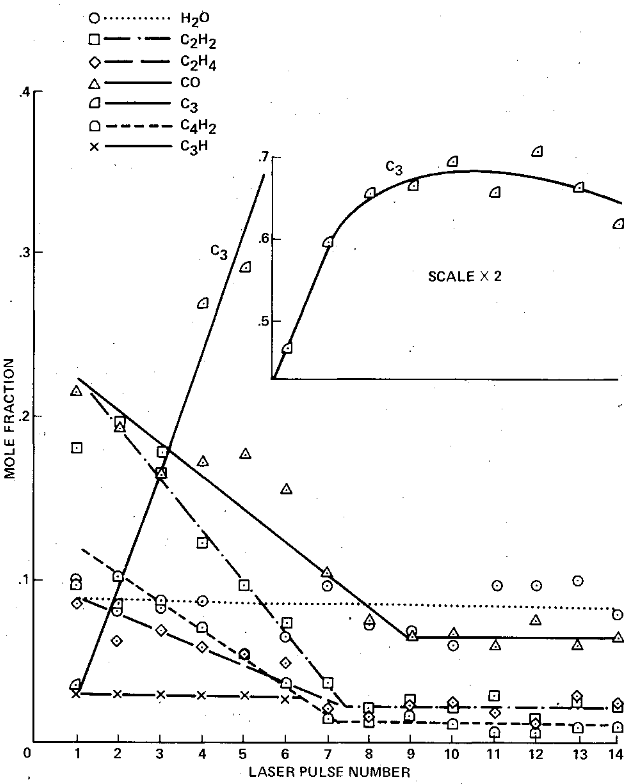

Fig. 6 Mole fractions of major vapors from pulsed laser-heated carbon phenolic composite.

Table 3 compares the vapor products resulting from low irradiance (the spectrum of Fig. 2) with those resulting from high irradiance (hydrogen not included); the latter are averages from pulse numbers 10, 11, and 12 in Figs. 4 and 5 where the vapor generation has reached nearly a constant value. This table, along with the other data, confirms that the incident thermal loading on the heat shield material makes a profound difference in the vapor products; however, the experimental work thus far also indicates that the species produced is fairly independent of irradiance down to above 5 kW/cm². It appears from Fig. 5 that the vapors produced by the first few pulses are mostly pyrolysis products from the phenolic component, and it is reasonable to assume that they were produced at a lower surface temperature (but not as low a temperature as that with the cw laser) than the later pulses from which the products correspond to those from graphite.

Unfortunately, attempts to compare these data with the theoretical calculations for the Jupiter entry probe are not straightforward. The calculations assume that vaporization occurs under thermodynamic and chemical equilibrium at pressures of several atmospheres. Although the laser vaporizations are carried out in a vacuum, measurements (using the technique described in Ref. 3) indicate that the pressure at the surface of TWCP reached about one-fourth atmosphere and the temperature range was 3400-4000 K at the peak of the laser pulses. Figure 6 shows the data of Fig. 5 expressed in mole fractions; comparisons of these data with predictions from the CMA Code[4] show some differences. CMA (310 kg entry probe, stagnation point at peak heating, 89% H_2/11% He atmosphere) predicts significant amounts of the transient species C_4H, C_3H, and C_2H at and near the surface; however, the experimental work shows very little of these and large amounts of the stable species such as CO, C_2H_2, C_4H_2, and H_2O—at least from the first few pulses. Early on it was assumed that the experimental conditions corresponding to the later laser pulses where vapor generation has approached a constant value would most nearly simulate the steady-state ablation; however, the best correlation with the theoretical calculations evidently occurs with the second or third pulse. More study is needed to resolve this detail.

Concluding Remarks

The chief contribution of this work has been to provide some experimental data on the relative concentrations of vapor species produced by carbon phenolic heat-shield material under conditions approximating those expected at peak heating during entry into the atmospheres of the outer planets. Attempts to compare these data with predictions from theoretical calculations run into several difficulties.

1) It is not practicable to completely simulate entry conditions in the laboratory and make these kinds of measurements.

2) The experimental work is lacking in information on mass loss or mass loss rates accompanying the vaporization reported here, but future measurements might fill this gap.

3) The theoretical calculations begin with the elemental compositions of C, H, and O found in the material and assume that thermodynamic and chemical equilibrium prevails during ablation, whereas the mass spectrometric measurements clearly show the presence of many aromatic compounds in the solid material. It is reasonable to believe that these compounds influence the final species distribution and lower the wall temperatures during pyrolysis; this explanation can be added to those suggested by Green and Davy[5] for the discrepancy between the predicted and measured recession rates for carbon phenolic.

4) Experiments show that as the charring and ablation of carbon phenolic composite proceeds, there is no single, clearly defined interface between solid and vapor and, consequently, there is no single wall temperature at any point along the interface. These are factors which can also contribute to differences between calculated and observed vapor species.

It is hoped that these experimental data will prove useful in enhancing the design calculations for future planetary probes.

Acknowledgment

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