SHOCK-TUBE MEASUREMENTS OF CARBON TO OXYGEN ATOM RATIOS FOR INCipient SOOT FORMATION WITH C₂H₂, C₂H₄ AND C₂H₆ FUELS

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April 1971

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FLUID MECHANICS LABORATORY

DEPARTMENT OF MECHANICAL ENGINEERING
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SHOCK-TUBE MEASUREMENTS OF CARBON TO OXYGEN ATOM RATIOS
FOR INCIPIENT SOOT FORMATION WITH C_2H_2, C_2H_4 AND C_2H_6 FUELS

by

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This work was supported by NASA
Grant NGL 22-009-378.

March 1971
Abstract

The critical atomic carbon to oxygen ratios, $\phi_c$, for incipient soot formation in shock-heated acetylene, ethylene, ethane/oxygen/argon mixtures has been measured over the temperature range 2000$^\circ$K to 2500$^\circ$K for reactant partial pressures between 0.1 and 0.4 atmos. Absorption of light from a He-Ne laser at 6328Å was used to detect soot. It was observed that the values of $\phi_c$ for all three fuels increased uniformly with temperature such that at the highest temperatures $\phi_c$ was considerably greater than unity, i.e. greater than the value of about unity at which solid carbon should have been precipitated on a thermochemical equilibrium basis. Observations were made over periods extending up to about one millisecond, which was well in excess of the time required for the major heat release of the combustion reactions. The relevance of these experimental findings to the problem of soot formation in gas turbine combustion chambers is discussed.
I. INTRODUCTION

There are a number of recent publications (Faitani 1968, Sawyer 1970, Heywood et al. 1970, Linden and Heywood 1971) in which the problem of smoke formation in gas turbine combustion chambers has been qualitatively discussed. It appears that the carbon particles (soot) are formed in regions of the primary zone where the local equivalence ratio is very high, and, on passing through the secondary zone, do not have sufficient time to be completely oxidised (Heywood et al. 1971). They therefore end up in the jet exhaust and give rise to a visible trail.

Although considerable reductions in jet engine smoke emission have been effected by intuitive design changes of the combustion chamber, generally resulting in leaner primary zone combustion, quantitative descriptions of the primary zone combustion are hampered by our inability to properly describe the complicated flow patterns, and mixing processes, and by our very imprecise knowledge of the kinetics of soot formation (see, for example, Homann (1967)).

Numerous studies carried out in premixed laboratory flames have demonstrated the nonequilibrium nature of the soot formation problem. For example, measurement of $\phi_c$, the ratio of the numbers of carbon atoms to oxygen atoms present in the mixture at the limit of observable sooting at some point within the flame, have shown it to be considerably less than the equilibrium value of close to unity for a wide variety of hydrocarbon fuels (Street and Thomas 1955). It also seems
that, at least for aliphatic fuels, soot appears somewhat after the completion of the flame front reactions (Millikan 1962) on a characteristic time scale which is comparable with particle residence times (typically 4m sec) in the primary zone of the combustor.

In this report we have addressed ourselves to measuring the value of $\phi_c$ for the appearance of soot within approximately one millisecond of the initial combustion reactions. The study was carried out for three fuels - acetylene, ethylene and ethane - in the reflected shock region of a shock-tube over the temperature range of interest to gas turbine combustion chambers, approximately $2000^\circ - 2500^\circ K$. Soot was detected by monitoring the absorption of light from a continuous wave He-Ne laser at 6328Å. The advantage of this method is that, since the soot particles will be assumed to absorb light according to the small particle limit of the Mie theory (Foster 1963), it should give a threshold for soot detection which is approximately independent of temperature, in contrast to the method of visual observation of soot luminosity used in most flame studies (Homann 1967).

The most significant result of this investigation was the observation that at high temperatures $\phi_c$ can be considerably greater than unity, e.g. $\phi_c \approx 1.8$ for acetylene at $2500^\circ K$. The values of $\phi_c$ were observed to increase uniformly with temperature from the less-than-unity values suggested by flat flame experiments (Fenimore et al. 1957, Flossdorf and Wagner 1967, Homann and Wagner 1965, Millikan 1962).
In Section II of the report we describe the experimental technique and some tests which were performed to establish the validity of the method of soot detection. Section III contains an account of the observations which were made, and the results are discussed and compared with other work in Section IV.

II. EXPERIMENTAL TECHNIQUE

A. General

The general arrangement of the apparatus is shown in Figure 1. The laser soot detection apparatus, which we shall describe later, was located so that the axis of the beam passed diametrically across a 7.5 cm i.d. stainless steel shock tube at a position about 5 mm in front of the endwall. The shock tube is a conventional pressure driven device which has been described previously (Appleton and Steinberg 1967). Pressure-time profiles behind the reflected shock were recorded on an oscilloscope using a Kistler pressure transducer system. Platinum film heat transfer gauges placed upstream of the main observation station and coupled to microsecond time counters provided incident shock velocity measurements and oscilloscope triggering.

The test gas mixtures were made in Lif-0-Gen one liter steel Chemispheres (Lif-0-Gen Inc. Lumberton, N. J.). The component High Purity Grade gases were estimated to be present in the mixture to better than 1 percent of their intended concentration. After filling the Chemispheres, generally to 500 psi total pressure, they were left to mix for a minimum of 12 hours.
Before each run the driven section of the shock tube was evacuated to better than $10^{-4}$ torr, and then filled with test gas to a typical pressure of 300 torr. Following each run any diaphragm material and soot which had been deposited were removed from the tube.

B. Soot Detection

The absorption of the beam from a 5 milliwatt continuous wave He-Ne Spectra-Physics laser (6328Å) was used to detect the presence of soot (see Figure 1). The laser light was spread across the cathode of the 1P28 photomultiplier by two Mylar diffusers about 3 cm apart. A 100Å halfwidth interference filter centered on the laser wavelength ensured that the major fraction of the light which reached the photomultiplier originated from the laser. For a sooting mixture typical of the high temperature runs in the main body of experiments, the emission signal at $2450^\circ$K was measured to be 1.5 percent of the absorption signal so that, over the temperature range of the experiments (2000-2500$^\circ$K), the effects of emission were quite negligible.

The probable nature of the newly formed soot particles in the reacting gas makes it possible to roughly calibrate the absorption system in terms of the mass concentration of soot in the dispersed phase. Observation of soots sampled from just behind flame fronts (Bonne et al. 1965) indicate that they are composed of spherical particles with diameters less than about 350Å; agglomeration to long chain-like structures appears to be a late stage in particle growth. The light absorption by soot in the present experiments was therefore assumed to
be described by the small particle limit of the Mie theory (Foster 1963). It can be shown that the spectral absorption coefficient, $k_\lambda$, is proportional to the volume fraction, $f_v$, occupied by the soot and is independent of particle shape. The absorption coefficient, $k_\lambda$, is a function of the refractive index of the soot particles which, in turn, depends on their hydrogen content. Table 1 gives values of $(k_\lambda/f_v)$, where $\lambda = 6328\AA$, for acetylene and propane soots which have been examined by Dalzell and Sarofim (1969). Also shown in Table 1 is the mass density $\rho_{10}$, defined as the mass of soot per cm$^3$ of gas for a 10% absorption signal in our experiments; the particle density was taken as 2 gm/cm$^3$. The linear proportionality of $\rho$ with absorbed light fraction, $(1 - I/I_0)$, is correct to within 5 percent up to 20 percent absorption. One consequence of assuming that the particles are small is that the contribution of scattering to the extinction of the incident beam is small and, hence, the effects of forward scattering may be neglected.

<table>
<thead>
<tr>
<th></th>
<th>Acetylene Soot</th>
<th>Propane Soot</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic C/H</td>
<td>14.7</td>
<td>4.6</td>
</tr>
<tr>
<td>$(k_\lambda/f_v)$ (cm$^{-1}$)</td>
<td>$6.13 \times 10^4$</td>
<td>$7.27 \times 10^4$</td>
</tr>
<tr>
<td>$\rho_{10}$ (gm/cm$^3$)</td>
<td>$4.58 \times 10^{-7}$</td>
<td>$3.87 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

The primary purpose of the absorption apparatus in the present experiment was as an indicator of when soot was no longer being formed. Its overall sensitivity was somewhat less than 0.5 percent,
the limitation arising from mode changing in the laser cavity and random movement of the apparatus relative to the laser beam. A sensitivity of 0.5 percent implies a threshold detection for soot of about $2 \times 10^{-8}$ gm/cm$^3$ using the absorption properties given in Table 1. By assuming that the optical properties of soot do not change over the present temperature range (2000-2500°K), the sensitivity of our absorption technique was taken to be approximately constant. Thus, using typical values of hydrocarbon concentration behind the reflected shock (1.0 percent hydrocarbon at 2500°K and 20 atmospheres total pressure) we see that it was possible for us to detect when about 0.08 percent of the carbon atoms were in the dispersed phase.

C. Preliminary Experiments

Two preliminary experiments were performed to confirm, as far as possible, that the absorption apparatus was indicating the appearance of dispersed soot particles within the volume of the shocked gas.

(a) Emission Check on the Absorption Profile

Figure 2 displays oscilloscope traces recorded during a run into a 1.0 percent acetylene mixture. In the upper photograph, which displays pressure and absorption signals, it is seen that the absorption increases with time up to 3 milliseconds after the shock wave. The increase continued through a large part of an expansion process as indicated by the pressure trace and, therefore, did not follow the gas density variation. The expansion was caused by the arrival of the
unsteady expansion wave from the driver end of the shock tube. Although it was not our primary intent to investigate soot formation processes in expansion waves, it was considered desirable to check by another method this surprising absorption profile of soot formation.

The simultaneous output signals of two 1P28 photomultipliers observing light emission at the same station as the absorption measurement was made are shown in the lower photograph. The photomultipliers were fitted with 100Å halfwidth interference filters centered at 3800Å and 6100Å. By assuming that the radiation was mainly blackbody emission from soot particles which closely followed the gas temperature, we calculated the relative change in the effective surface area of the emitter. The corrections for optical thickness were neglected, since the absorption was always less than 20 percent. Values of the reflected shock pressure and temperature calculated from the pressure transducer reading and incident shock velocity agreed to within 1 percent, and were calculated to be 5.63 atmospheres and 2305°K respectively. The gas temperature and density change through the expansion was obtained from the measured pressure profile and the isentropic ideal gas relations. The relative amounts of soot formation as obtained from the 3800Å and 6100Å emissions, and the 6328Å absorption profiles were normalised at the head of the expansion wave, 600 microseconds after the shock. These normalised profiles were then plotted, together with the gas density variation, as a function of time in Figure 3.

It can be seen from the results contained in Figure 3 that the emission data confirm the shape of the absorption profile, at least
until the emission was too small to be measured accurately. Table 2 gives a comparison between the experimental values of the ratio of the 6100Å and 3800Å photomultiplier output signals (again normalised at the head of the expansion wave) and the theoretical ratio calculated assuming a blackbody source. The assumption that the emission was primarily blackbody in nature over most of the profile is justified.

(b) Window Sooting

To confirm further that absorption was occurring due to changes in the transparency of the volume of shocked gas and not to heterogeneous reaction leading to deposition on the walls and windows of the shock tube, the following experiment was carried out. The laser beam was split into two parallel beams separated by a distance of about 5 mm. One beam was allowed to pass through the shock tube observation station in the normal way, the other was arranged to pass through an additional thin glass fin located in the center of the shock tube with its plane normal to the beam axis. By comparing the absorption signals of the beams, the separate absorption due to volume
and window sooting could be distinguished. It was found that for periods up to 50 milliseconds window sooting forms a negligible part of the absorption. In fact, window deposition was only found to occur after about 1 second, and to amount at most to 30 percent of the maximum gas absorption.

III. MAIN EXPERIMENTS

A. Introduction

The main experiments were carried out in the following way. For the first set of runs the reflected shock temperatures were set near 2500°K, and the changes in absorption profiles observed as increasing quantities of oxygen were added to each hydrocarbon fuel. In each case the oxygen concentration was noted at the point where the absorption signal had decreased to zero over the duration of the shock tube test time; the value of $\phi_c$ was thus determined. The values of $\phi_c$ at temperatures between 2000°K and 2500°K were then found for each fuel.

In order to prevent detonation and to obtain a reasonable estimate of temperature in the reflected shock, the reacting gases were highly diluted with argon. The hydrocarbon concentration was generally about 1.0 percent and the oxygen concentration was varied over the approximate range 0 - 1.0 percent. The temperatures which were used in presenting the experimental data were calculated from the measurements of the incident shock velocity and the Rankine-Hugoniot relations for a monatomic gas. Based on an equilibrium computation of the composition and specific heats of the reacted gas mixtures, the temperature rise at
constant pressure due to exothermicity was estimated to be always less than $240^\circ K$.

B. Determination of $\phi_c$

The oscilloscope records shown in Figure 4 illustrate the changes in the absorption profile produced by a 1.0 percent ethylene mix when increasing amounts of oxygen are added. Absorption and pressure increase upwards and time increases from left to right. The arrival of the shock wave is indicated by the sharp increase in pressure and by the Schlieren spikes on the absorption trace. It is apparent that the absorption, as shown by the almost linear profiles in the sequence, fell uniformly to zero as the concentration of oxygen was increased. The reflected shock temperature was estimated to vary over the sequence between 2457 and $2514^\circ K$. The most significant observation is that the critical oxygen concentration lies between 0.55 and 0.60 percent, implying a $\phi_c$ value of about 1.7 in this case, i.e., a value considerably greater than the equilibrium value of about unity.

A short period immediately following the shock wave during which there was no absorption is clearly observed in the case where no oxygen was present in the mixture (see Figure 4(a)). A similar "induction" period was also noted when we used ethane mixtures, but was not observed for acetylene where the absorption increased immediately from behind the shock wave. The induction time is interpreted as being the time required for significant decomposition of ethylene and ethane to acetylene and equivalent amounts of hydrogen. Our measurements of the induction
times were found to correlate with the shock tube measurements of Kozlov and Knorre (1962) for decomposition of these hydrocarbons.

A few runs were made with each mixture, and it was noted that those with lower temperatures had larger absorption profiles. For example, a run into 1.0 percent ethylene, 0.7 percent oxygen mixture at 2469\textdegree K gave zero absorption as would be expected from Figure 4(d). However, when two runs with temperatures of 2355\textdegree K and 2340\textdegree K were made into the same mixture, sooting profiles similar to Figure 4(c) resulted. Thus, the $\phi_c$ determined in these experiments seems to have a temperature dependence in the same sense as observed in the flame work (Homann 1967). For each mixture, therefore, the final determination of $\phi_c$ involved making several runs, some showing slightly sooting profiles and some showing no sooting, so that the critical condition could be located. The actual runs used for data points in the present experiments showed no detectable absorption for periods of observation ranging up to at least 800 usec, and extending in some cases for several milliseconds into the expansion wave region.

Our laser absorption observation that soot formation was being suppressed by oxygen addition was qualitatively confirmed by visual inspection of the walls of the shock tube and of the gases remaining in it after a run. When the absorption profile was large, as in Figure 4(a), copious quantities of soot were seen, but none could be detected when the absorption signal was small or zero.

In Figure 4(a) it is observed that the endwall pressure increases with time before the arrival of the expansion wave; this is typical of
runs into high downstream pressures (about 300 torr) and is due to boundary layer effects in the shock tube flow. Assuming the compression to be isentropic indicates that the gas temperature increases by about 100°K from the initial shock to arrival of the expansion wave. The height of the initial pressure step when reactants were present in the test gas was found to be detectably greater than when, at the same incident shock velocity, no reactants were present. This difference, which amounts to about 6 percent in the extinction run of Figure 4(d), indicates exothermicity due to reaction. For runs with more oxygen than was necessary to just suppress soot, a pressure overshoot was observed, lasting typically 200 microseconds at 2500°K.

C. Variation of $\phi_c$ with Temperature

The final stage in the experiments was to determine $\phi_c$ at other temperatures and at other partial pressures of the hydrocarbon fuels.

The effect of reactant partial pressure variation on $\phi_c$ was examined only with acetylene. The results of this, and the dependence on temperature are shown in Figure 5. It is seen that, apart from the runs with a post-shock partial pressure of acetylene of about 310 torr, the points are scattered among one another and no obvious trend is distinguishable. We were unable to determine whether the 310 torr data indicated a real variation of $\phi_c$ with pressure, or whether they arise because the absorption apparatus was able to detect a smaller fraction of carbon atoms in the dispersed phase. If it is a pressure
dependence, it is in the same sense as that observed by Fenimore et al. (1956) (FJM) for several hydrocarbon-air flames at about 1600°K. The temperature variation seems clear, however. We find that \( \phi_c \) decreases from its high temperature value with decreasing temperature and tends in the general direction of the flat flame observations of FJM and of Homann and Wagner (1965) (HW). The bar on the data of FJM includes the \( \phi_c \) they determined at all flame pressures in the range 10 to 60 torr; the data of HW were taken at 20 torr. The observation by Street and Thomas (1955) (ST) at atmospheric pressure is plotted in this Figure, and in Figures 6 and 7, assuming the adiabatic flame temperature of a stoichiometric mixture (Mavrodineanu and Boiteux 1965). The scatter of the present data represents the accuracy of measurement.

The \( \phi_c \) variation with temperature which was found for ethylene is shown in Figure 6. In this instance the partial pressure of ethylene initially in the shocked gas was held at about 155 torr throughout the temperature range. A decrease of \( \phi_c \) with decreasing temperature from values greater than unity is again indicated, and reasonable agreement is shown with flame observations at lower temperatures. The flame measurements shown are due to Flossdorf and Wagner (1967) (FW), Millikan (1962) (M), FJM on two burners of 1.6 cm (S) and 3.2 cm (L) diameters at pressures in the range 60 to 300 torr, and ST.

Finally, the ethane results are presented in Figure 7 together with the flame data of ST and of FJM and FW at pressures between 10 and 210 torr.
If our data for each of the hydrocarbons are superimposed, it is found that, at the higher temperatures, the ethylene points lie between those of acetylene and ethane, and are somewhat closer to the acetylene measurements. At lower temperatures the points all scatter in the same vicinity.

IV. DISCUSSION

Before discussing the $\phi_c$ measurements we have made, we will estimate the extent to which the initial combustion reactions had occurred in our experiments. It seems quite certain that they were completed quite early in the available test-time. In support of this, the endwall pressure overshoot indicated that the exothermicity was essentially over within 200 microseconds at $2500^\circ\text{K}$ in the acetylene-oxygen mixture; at $2150^\circ\text{K}$ about 300 microseconds elapsed before it fell to the value calculated from the incident shock velocity. Gay et al. (1967), observing the change in species concentrations with time during shock heating of 1.5:1.0:97.5 ethylene:oxygen:argon mixtures, noted that oxygen had decreased to 10 percent of its initial concentration after 150 microseconds at $2190^\circ\text{K}$. In rich acetylene-oxygen-argon mixtures, Homer and Kistiakowsky (1967) observed the peak of $\text{CH}^*$ emission, identifiable with the main reaction zone, to occur no later than 300 microseconds after the shock. It is to be noted that in both of these investigations the absolute concentration of reactants and reflected shock pressure are typically 30 times lower than those of the present experiments. Thus, we believe
our measurements are applicable to the criteria for soot formation in the region immediately following the flame front.

The values of $\phi_c$ which we have measured for acetylene, ethylene and ethane in these experiments show fair agreement with those determined in flat flame experiments at the lower end of the temperature range, while being somewhat greater than Street and Thomas (ST) observed in bunsen flames at higher temperatures. In making these comparisons it must be remembered that the definition of the sooting limit varies between experiments (Homann 1967) so that part of the difference between the present results and the ST data may be because, at higher temperatures, the luminosity technique is a more sensitive measure of the soot concentration in the burned gases than the absorption method.

However, our main observation is the high value that $\phi_c$ may have at temperatures in the vicinity of 2500°K. This implies that, even with very rich mixtures, soot formation may be limited, at least for times on the order of 1 millisecond following the initial combustion reactions, to less than 0.1 percent of the carbon atoms in the fuel. The range of stoichiometries for which sooting does not occur, subject to these conditions, may thus be considerably extended beyond both the limit indicated by flame work and that suggested on the basis of thermochemical equilibrium. From comparison of the results for each fuel, we note that relatively more oxygen is required to suppress soot formation for fuel molecules containing higher proportions of hydrogen.
This general trend has also been found in flame work (Street and Thomas 1955).

The nonequilibrium characteristics of the region just following the main combustion reactions has been emphasised by Millikan (1962) who detected in it concentrations of the hydroxyl radical much greater than equilibrium, and therefore, postulated that the growth of soot particles was inhibited by OH oxidation. In our experiments, at somewhat higher temperatures, this nonequilibrium nature is demonstrated by the high values of $\phi_c$ which we found; they are such that, if equilibrium did exist soot would easily be detected. For example, at a temperature of $2500^\circ$K, $\phi_c$ for acetylene is about 1.8; at equilibrium the oxygen atoms would be preferentially bound as carbon monoxide, so that about 45 percent of the carbon atoms remain, probably as acetylene. Runs into mixtures with this concentration of acetylene and no oxygen gave rise to large soot absorption traces.

An interpretation of our results is possible on the basis of the scheme described by Millikan, but it would require that high hydroxyl concentrations were present, especially at higher temperatures. An experimental determination of OH concentration in these shocked gases would be most interesting.
REFERENCES


FIGURE CAPTIONS

Figure 1 - Schematic of Experimental Arrangement.

Figure 2 - Laser absorption, pressure and emission records obtained during a run to check the validity of the absorption technique. Test gas was 1 percent acetylene, 99 percent argon. Pressure and temperature behind the reflected shock were calculated as 5.63 atmospheres and 2305°K respectively.

Figure 3 - Relative soot formation as a function of time behind the reflected shock obtained from analysis of the records in Figure 2. Key: ○, laser absorption; □, 3800Å emission; ●, 6100Å emission; ▲, gas density. All points are normalized with respect to unity at the head of the expansion wave.

Figure 4 - Effect of oxygen addition on the absorption records of ethylene-argon mixtures. Time increases left to right at 200 μ second/major div. Upper trace at start of sweep is absorption; vertical sensitivity is (a) 5 percent/major div., (b), (c), (d) 2 percent/major div. Lower trace at start of sweep is pressure, with sensitivity of 4.13 atmos/major div. for all traces. Ethylene: Oxygen: Argon percentages and calculated reflected shock temperatures are (a) 1.0: 0.0: 99.0, 2505°K; (b) 1.0: 0.5: 98.5, 2457°K; (c) 1.0: 0.55: 98.45, 2514°K, (d) 1.0: 0.6: 98.4, 2475°K.

Figure 5 - Variation of $\phi_C$ with temperature for acetylene. Letter symbols are explained in the test. Present data shown
by the following symbols, indicating acetylene partial
pressure behind reflected shock; ○, 45 torr; ●, 55 torr; △, 115 torr; ▲, 155 torr; □, 310 torr.

Figure 6 - Variation of $\phi$ with temperature for ethylene. Letter meanings are explained in the text. Present results are indicated by the filled circles. Ethylene partial pressure behind reflected shock was about 155 torr.

Figure 7 - Variation of $\phi_c$ with temperature for ethane. Letter meanings are given in the text. The present data, shown by the filled circles, were taken at about 160 torr partial pressure of ethylene behind the reflected shock.
FIGURE 1
FIGURE 2

LASER ABSORPTION
5% PER MAJOR DIV.

PRESSURE
0.79 ATM. PER MAJOR DIV

6100 Å EMISSION
INCREASING DOWNWARDS

3800 Å EMISSION
INCREASING UPWARDS

SHOCK ARRIVAL

500μ sec
Figure 3

Soot Formation (Relative Scale)

HEAD OF EXPANSION WAVE

Time after Shock Arrival (milliseconds)

FIGURE 3
FIGURE 4
FIGURE 6

TEMPERATURE (°K)
Figure 7: Temperature dependence of \( \phi_c \) for ethane. The data points are labeled FJM and FW, with an additional marker labeled ST.