

## Oxidation of Soot in a Diffusion Flame

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### Introduction

In most practical systems, soot burn-out occurs at the end of the combustion process, reducing the amount of soot released in the atmosphere. We have determined the oxidative species involved and their effect on soot morphology.

### Experimental

A laminar and axisymmetrical methane-air diffusion flame was used. It was previously analyzed by Mitchell (1). Using experimental conditions described elsewhere (2) a steady 5.8 cm height diffusion flame was obtained.

An optical method using an ionized argon laser (3) was used to locally characterize soot particles inside the flame. Profiles of volume fractions ( $f_v$ ), equivalent diameters ( $D$ ) and number densities ( $N$ ) of carbon particles were deduced from elastic scattering at  $90^\circ$  and extinction measurements.

The three types of profiles were determined axially, along cross sections and along some streamlines. As the flame is stationary, streamlines correspond to particle trajectories. We have shown (2) that soot burnout exhibits three steps:

- in the first one, number density as well as volume fraction decrease while equivalent diameter increases: particles aggregation which began earlier is proceeding; the solid carbon oxidation, however, has already started.
- in the second step, carbon volume fraction continues diminishing but mean diameter is decreasing while number density is increasing. This step may be due to aggregate break-up.
- in the third and last step, volume fraction, equivalent diameter and number density decrease and finally cannot be measured anymore. The total duration of step 3 is ca. 5 ms.

As an example, Figure 1 shows the profiles of  $f_v$ ,  $D$  and  $N$  along flame axis versus time. The origin of time is taken at the flame front.

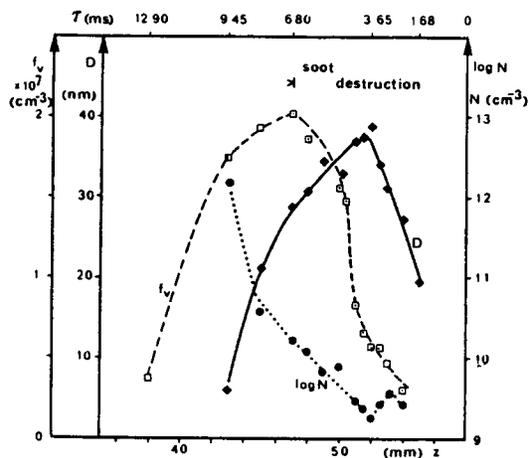


Figure 1.  $f_v$ ,  $N$  and  $D$  versus time.

### Interpretation and Conclusions

Let us call  $w$  (4) the specific soot burnout rate ( $\text{g cm}^{-2} \text{s}^{-1}$ ). It can be shown that  $w = -\rho \frac{D}{6} \frac{d(\text{Ln}f_v)}{dt}$  where  $\rho$  is the carbon density. It must be noticed that the definition of  $w$  is somewhat misleading as a variation of  $w$  results essentially from a variation of the nature and concentration of oxidative species and not necessarily from a variation of carbon surface reactivity.  $w$  versus time goes through a maximum equal to ca.  $10^{-3} \text{ g/cm}^2/\text{s}$  for a duration of 20 ms. Before the maximum aggregation of particles and burnout occur simultaneously. The total carbon surface area decreases. After, surface oxidation and rupture of aggregates have opposite effects on the total carbon surface area.

In works on secondary premixed flames, Neoh and Howard (5) emphasized the major role of hydroxyl radicals in soot burnout. Our interpretations are based on their results. The previous measurements of Mitchell (1) allowed us to calculate the local concentrations of the radicals O and OH by assuming the partial equilibrium of the reactive system ( $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ , O, OH and H), in a restricted range of local

equivalence ratio ( $\phi < 2.5$ ). Comparison of the profiles of major species concentrations brings the following remarks on soot destruction. The oxygen radical concentration is systematically smaller than the OH one; the profiles of O and OH decrease, when approaching the flame front. The molecular oxygen concentration, relatively small inside the flame, grows up. It is not negligible in the soot burnout zone. CO is the most abundant gaseous fuel. We have observed the simultaneous presences of oxygen and hydroxyl radicals, molecular oxygen and soot.

Several authors emphasized the molecular oxygen influence. They agree to evaluate this oxidation by the Nagle and Strickland-Constable formula (6). This correlation formula established for pyrolytic graphite, is based on the assumption of two different types of sites on carbon to be involved in oxidation.  $w_{NSC}$  is the corresponding soot burnout rate.  $w$  is the soot burnout rate obtained from our experimental results. Some axial values of  $w/w_{NSC}$  are reported on the following table.

Table I. Axial values of  $w/w_{NSC}$ .

| Z (mm) | $\zeta$ (ms) | $[O_2]$<br>$\times 10^3$ | $w$<br>$\text{gcm}^{-2}\text{s}^{-1}$<br>$\times 10^4$ | $w_{NSC}$<br>$\text{gcm}^{-2}\text{s}^{-1}$<br>$\times 10^6$ | $w/w_{NSC}$ |
|--------|--------------|--------------------------|--|--|-------------|
| 49     | 5.50         | 5.3                      | 1.39   | 4.10   | 33.9        |
| 50     | 4.85         | 5.55                     | 3.49   | 4.44   | 78.5        |
| 51     | 4.25         | 5.8                      | 10.02  | 4.75   | 210.9       |
| 52     | 3.65         | 6.05                     | 10.05  | 5.07   | 198.3       |
| 53     | 3.05         | 6.3                      | 8.3  | 5.40   | 153.8       |
| 54     | 2.45         | 6.6                      | 5.1  | 5.72   | 89.2        |
| 58     | 0            |                          |  |  |             |

(flame front)

The influence of molecular oxygen, predicted by Nagle and Strickland-Constable formula is much smaller than the measured soot destruction process. Only the presence of one or several other oxidants may explain such a difference. Soot burnout can be due to  $O_2$ , O and OH radicals,  $CO_2$ ,  $H_2O$  or NO. The literature allows to conclude that oxidations by  $CO_2$  and NO have a minor role.

In agreement with the work of Neoh (4) and of Mulcahy and Young (7), it is considered that OH and  $O_2$  are the main oxidants. Therefore,

$$\Gamma_{OH} = \frac{w - w_{NSC}}{w} \gamma_{OH} \text{ where}$$

$\Gamma_{OH}$  is the collision efficiency of OH (probability to oxidize one carbon atom by collision between a soot particle and one OH radical).

$\gamma_{OH}$  is the apparent collision efficiency of OH deduced from experimental results (diameter decreases in oxidation zone) in assuming that OH radical is the only oxidizing species.

The axial values of  $\Gamma_{OH}$  are summarized on Table II.

The maximum value is 0.099 which is identical to those given by Neoh (4), 0.10

Table II.  $\Gamma_{OH}$  values.

| Z (mm) | $\Gamma_{OH}$ | Z (mm) | $\Gamma_{OH}$ |
|--------|---------------|--------|---------------|
| 49     | 0.012         | 52     | 0.099         |
| 50     | 0.031         | 53     | 0.086         |
| 51     | 0.094         | 54     | 0.057         |

and by Fenimore and Jones (8), 0.10; using electron microscopy Mulcahy and Young (7) also obtained a maximum of 0.10. Using an in situ optical method for soot particle diameter measurement, Neoh found 0.27.

We have determined the number density as function of the weight percentage of soot burnout, on several trajectories close to the central axis. Results point out that aggregates breakup occurs when 70-80 % of soot has disappeared. On axis, breakup corresponds to a molecular ratio  $O_2/OH$  of ca.2. In the outermost streamlines where  $O_2$  contribution to oxidation is expected to be maximum, soot aggregates breakup occurs for the smallest values of soot burnout. These results agree with the assumption of Neoh and Howard (5) and of Donnet and Lahaye (9) on the major role of oxygen in the internal oxidation of carbon particles. Less reactive than OH, it should diffuse inside soot particle while hydroxyl radical induces preferentially surface oxidation.

#### References

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