

SOOT DEPOSITION FROM ETHYLENE/AIR FLAMES AND THE ROLE OF AROMATIC INTERMEDIATES. Joanne M. Smedley and Alan Williams. Department of Fuel and Energy, Leeds University, Leeds, LS2 9JT, UK.

ABSTRACT

The formation of soot is of interest as a pollutant but also because it forms deposits in combustion chambers. In this work a McKenna flat flame, water-cooled, premixed burner was used to study soot deposition from two rich ethylene/air flames ( $\phi = 2.52$ ,  $\phi = 2.76$ ). Rates of soot deposition for both cooled copper and uncooled stainless steel surfaces were investigated. Soot samples from these experiments were analysed for PAH by solvent extraction. Temperature profiles were taken using Pt/Pt 13% Rh thermocouples. A quartz microprobe sampling system was used in conjunction with a gas chromatograph to determine the concentration profiles of aromatic and polyaromatic species in the deposition region. Experimental results indicate that soot deposition occurs by a thermophoretic mechanism when cooled surfaces are used and that soot deposition rates increase as samples are taken further in the flame zone. If uncooled surfaces are used then direct surface deposition takes place. The chemical mechanisms involved are discussed.

INTRODUCTION

The formation and deposition of soot in any combustion system is undesirable. Soot deposits can have adverse effects on heat transfer characteristics or combustion behaviour which can cause performance or failure problems in a range of systems from rocket engines to diesels. The emission of soot particles from combustion chambers into the atmosphere is also of environmental concern due to the fact that soot particles can contain significant concentrations of PAH. There is thus a need to accurately predict under what conditions soot formation will occur and to quantify the amount of soot deposited in any part of a combustion system.

Over recent years more progress has been made in understanding the chemical route of soot formation but work in this area is difficult due to the complex interaction of aromatic species in sooting flames (1-5). Harris et al (1) have attempted to model single ring aromatic species but have only succeeded in modelling benzene because of the complexity of the subsequent growth steps. They encountered the problem that most of the rate constant data must be estimated since absolute values are not available. Minor species such as  $C_2H_2$  have been accurately modelled by Miller et al (2) and Harris et al (3) as more reliable data are available for these species. Even though these models exist, many gaps remain in the mechanism of the subsequent steps leading to soot formation. Whilst acetylene is recognised as a major growth species there is uncertainty about the level of participation of the PAH species. Soot deposition onto a cooled surface has been recently investigated by Makel and Kennedy (4) using a laser diagnostic technique to measure soot deposit thickness and free stream soot concentrations. A numerical model to make predictions of soot deposition rate was also developed by them.

EXPERIMENTAL METHODS

Two rich ethylene/air flames ( $\phi = 2.52$  and  $\phi = 2.76$ ) were studied using a flat flame, water-cooled, premixed burner (McKenna Industries). The gas flows in litres/minute for the  $\phi = 2.52$  flame were  $O_2 = 2.22$ ,  $N_2 = 8.36$ ,  $C_2H_4 = 1.79$  and the flows for the  $\phi = 2.76$  flame were  $O_2 = 2.36$ ,  $N_2 = 8.90$ ,  $C_2H_4 = 2.09$ . To investigate soot deposition rates an uncooled stainless steel plate and a cooled copper plate were used to support stainless steel and copper sample squares respectively within the flame. The sample plate dimensions were approximately

10 mm x 10 mm x 2 mm. Four flame heights were of interest, these were 5, 10, 15 and 20 mm above the burner surface. At each height weighed sample plates were inserted into the flame for intervals of 15 seconds (from 15 to 75 seconds) and were reweighed after to give the weight of soot produced.

The PAH content of some of the soot collected was determined using a solvent extraction process. Deposited soot from the metal plate and free steam soot which was collected on a Whatman glass microfilter GF/C paper from both flames was analysed using a pyrolysis chromatography. A Perkin Elmer 8320 gas chromatograph fitted with a Quadrax 007' series fused silica capillary column was coupled with a CDS Pyroprobe to desorb hydrocarbons from the soot. Approximately 2.5 mg of soot is heated at a rate of 0.1°C per millisecond up to 600°C. A quartz microprobe with a 6 mm outside diameter similar to that used by Harris et al (3) was used to obtain gas samples at various heights above the burner surface and a syringe method was used to transfer samples into a gas chromatograph (Perkin Elmer 8700 gas chromatograph fitted with a J & W megabore GS-Q column).

## RESULTS AND DISCUSSION

### Soot Deposition

Figures 1 and 2 give typical experimental data for the rate of soot deposition for the uncooled and cooled plates. In these each line represents different sampling heights above the burner. As expected the deposition rate of soot increases on an uncooled stainless steel plate as the plate is moved vertically away from the burner surface. However the deposition rate of soot at 20 mm above the burner surface is less than the deposition rate at 15 mm above the burner surface when the water cooled copper plate is used. This was found to occur in both flames ( $\phi = 2.52$  and  $\phi = 2.76$ ). It has been observed that the ultimate soot load on sample squares is approximately 0.7 mg regardless which plate is used. For the uncooled plate a 0.7 mg soot load occurs at 20 mm but when using the water cooled plate a soot loading of 0.7 mg is achieved at 15 mm when both had 75 seconds exposure in the flame. It is thought that above 0.7 mg the soot load is too great and the soot breaks off and is dispersed back into the flame. This is why a reduced soot deposition rate is seen for the 20 mm height samples when using the water-cooled plate. In general, for both plates the soot deposition rates are greater for the  $\phi = 2.76$  flame at all heights than for the  $\phi = 2.52$  flame. The exception for the metal plate is at 20 mm. Similar rates are experienced for both flames at this height and this again suggests that there is a limit to the amount of soot that can be deposited under these conditions.

When comparing the results from the uncooled plate and water cooled plate for  $\phi = 2.52$  flame it can be seen the soot deposition rate at 10 mm above the burner surface for the uncooled plate is much less than the soot deposition at the same height for the cooled plate. For example, at 75 seconds a soot load of under 0.1 mg is recorded for the uncooled plate. Whereas on the water cooled plate a soot load of approximately 0.4 mg is recorded at 75 seconds. The same is noticed at 15 mm above the burner surface at 75 seconds. The uncooled plate has a soot load of 0.4 mg while the cooled plate has a soot load of 0.55 mg. This is consistent with the thermophoretic transport of soot particles. From the results it also seems that thermophoresis is more prominent at lower regions in the flame. This may be because the soot particles are smaller earlier in the flame and as they become larger later thermophoresis has less influence on the movement of the soot particles. Makei and Kennedy (4) assumed that thermophoresis was the primary transport process for soot particles (-10 - 100 nm in diameter) although no allowance was made for variation in particle size. He also experienced the process of resuspension when the soot load increases to a certain limit. This was incorporated into his model to try and determine the final soot loading.

The soot mass flux to the surface can be expressed (4) as

$$J''_{\text{tot}} = \rho_s V_d \phi_{s,z} \quad (1)$$

where  $\rho_s$  is the particle density ( $1900 \text{ kg/m}^3$ ),  $\phi_{s,z}$  is the soot volume fraction at the edge of the diffusion sublayer and the deposit velocity,  $V_d$ , is equal to the thermophoretic drift velocity,  $V_t$ , given by

$$V_t = -0.55 \nu d (\ln T)/dy \quad (2)$$

where  $\nu$  is the viscosity and which is largely determined by the temperature gradient.

Experimental deposition rates were found to be  $1 \times 10^{-2} \text{ mg/cm}^2 \text{ s}$  at 15 mm above the burner using the water-cooled plate and  $0.75 \times 10^{-2} \text{ mg/cm}^2 \text{ s}$  using the uncooled metal plate. This is consistent with Makel and Kennedy's experimental data although they used a water-cooled cylinder to collect their samples. The calculated deposition value for our experiments using their theory is  $1.2 \times 10^{-2} \text{ mg/cm}^2 \text{ s}$  for the water-cooled plate and  $0.6 \times 10^{-2} \text{ mg/cm}^2 \text{ s}$  for the uncooled plates. The agreement is excellent.

#### PAH Content of the Soots

Deposited soot samples at 20 mm above the burner were collected from both flames after 75 seconds exposure within the flame. These soot samples were analysed in the Pyroprobe apparatus. Some results from this experiment are shown in Figures 3 and 4. Most of the peaks in the chromatograph were identified using a standard PAH mixture or by using retention indices (5-7). The major peaks are identified in Fig. 3. The gas chromatograph results for both the flames studied were very similar. Generally each PAH component was found in greater quantities in the richer  $\phi = 2.76$  flame. The  $\phi = 2.52$  flame contained much more volatile material which is expelled from the soot very early and is the first peak. The  $\phi = 2.52$  also contained more amounts of the larger components such as benzopyrenes and other 5-ring compounds which occur in the latter part of the chromatogram. Larger ring compounds also exist in both flames.

Free stream soot samples were collected on to Whatman glass microfibre filters were also analysed using the Pyroprobe system. Results from the  $\phi = 2.76$  flame are shown in Figure 4a. The collecting conditions for the free stream soot are identical to those quoted above for the deposited soot samples. When comparing the results from the free stream soot and the results for the soot deposited on the uncooled plate (Figure 4b) it is noted that the free stream soot always contains greater amounts of the 2 and 3 ring compounds such as acenaphthylene and the deposited soot always contains larger amounts of the 4 and 5 ring compounds like pyrene and also 6 and 7-ring compounds. This may be because the filter paper collection is at a lower temperature which favours the absorption of the smaller volatile gas phase material. If this is not the case there are important implications to the ability of soot to have varying compositions depending on whether it is in the gas phase or deposited on a surface.

#### Soot Formation Steps

Figure 5 shows the gas composition profiles obtained using the quartz probe sampling system. The reaction zone (based on  $\text{O}_2$  decay) is quite extended. Figure 6 shows profiles of some aromatic species and their precursors. The results show that as combustion takes place  $\text{C}_2\text{H}_4$  and  $\text{O}_2$  are depleted. In Fig. 6 it can be seen that  $\text{C}_2\text{H}_2$  peaks at about 5 mm above the burner after which it levels off to a fairly constant value between 10 and 20 mm.  $\text{C}_6\text{H}_6$  rises gradually at about 6 mm and begins to fall at 12 mm. Initially there was more  $\text{C}_6\text{H}_6$  in the  $\phi = 2.52$  flame but at 20 mm there was more in the  $\phi = 2.76$  flame. Laser beam

attenuation studies at 670 nm indicated that soot formation began at 6 mm above the burner. From the results it can be seen that as  $C_2H_2$  is consumed  $C_6H_6$  is produced as well as soot; this is consistent with the fact that  $C_2H_2$  is involved in  $C_6H_6$  formation and it is generally considered that  $C_2H_2$  is an important precursor to soot formation.  $C_2H_2$  and  $C_6H_6$  fall as soot is formed and other larger hydrocarbons are produced in the flame. In Fig. 5 both CO and  $H_2$  increase gradually as the probe is moved away from the burner surface. It was found that  $H_2$  was in greater concentration in the  $\phi = 2.52$  flame and CO was in a higher concentration initially.  $O_2$  was only found in small amounts in the  $\phi = 2.52$  flame. These increase as combustion takes place and are products of oxidation reactions. These trends were seen by Harris (3) et al but they only probed to about 3 mm above burner so they did not observe the fall in  $C_2H_2$  and  $C_6H_6$  in the later part of the flame. Miller (2) et al however undertook experiments up to 22.5 mm and also found similar profiles for CO,  $O_2$  and  $H_2$ .

The mechanism of soot formation from an ethylene flame involves the formation of acetylene and its polymerisation to single and then multi-ring species. The subsequent growth of the initial soot particles involves surface growth involving acetylene and polyaromatic species the relative extent of them being subject to different interpretation (eg. 5, 8 and 9). In the free stream soot samples taken here the product involves soot particles, surface adsorbed PAH and gas phase PAH. However the deposited samples can only contain PAH associated with the soot particles as adsorbed or growth species. The deposited samples are significantly different to the free stream soot in that the dominant PAH species are the 4+ ring species and smaller species are present in lower concentrations.

The suggestion must be implicit in these findings that the acetylene grows on the soot surface generating multi-ring compounds there which ultimately become part of the soot particle. During pyrolysis gc these compounds are desorbed as shown in the experimental results.

#### CONCLUSIONS

1. The deposition rate of soot increases with height above the burner surface (up to 20 mm) and sampling time (up to 75 seconds). More soot is deposited as  $\phi$  is increased, but there seems to be a limit in the amount of soot that can be deposited regardless of the method of deposition because of soot break off at relatively low loadings.
2. There is evidence that thermophoresis is involved in soot deposition on to a cooled plate and that it is more dominant earlier in the flame when soot particles are smaller. The measured rates are consistent with the values calculated using the model proposed by Makei and Kennedy.
3. Soot samples from the uncooled metal plate contain large aromatic compounds with 4 and 5 and larger rings. The  $\phi = 2.52$  had a higher concentration of some of these compounds.
4. Free stream soot samples contain a higher concentration of 2 and 3 ring aromatics than deposited soot. Higher concentrations of 4 and 5 ring aromatics were found in the deposited soot for the same conditions. This implies that these compounds are implicated in the soot growth mechanism.

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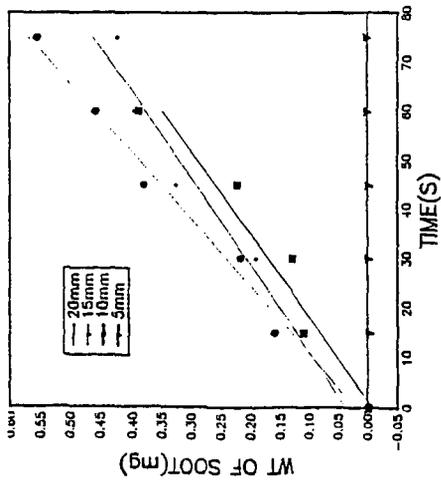


Fig. 1. Plot of soot deposition against time for water-cooled plate,  $\phi = 2.52$ .

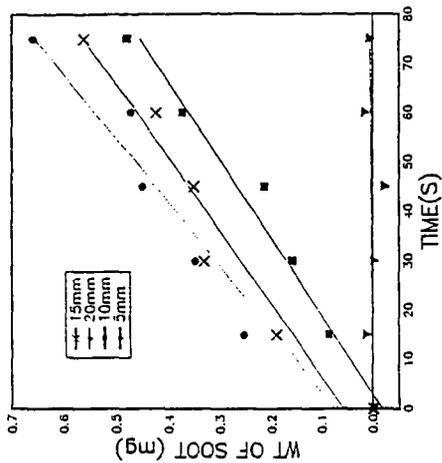


Fig. 2. Plot of soot deposition against time for uncooled metal plate,  $\phi = 2.76$ .

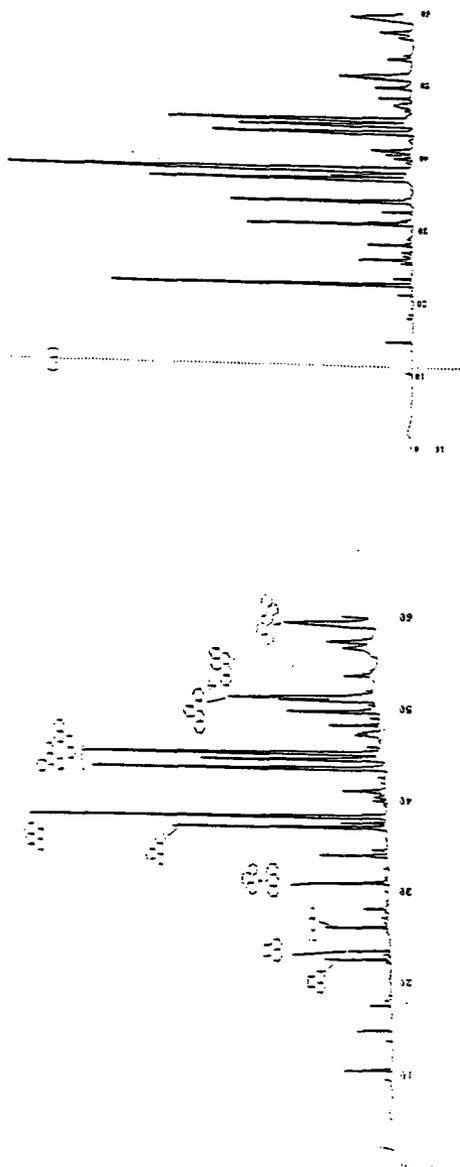


Fig. 3. Gas chromatogram with major peaks labelled sample for uncoated metal plate,  $\phi = 2.76$ .

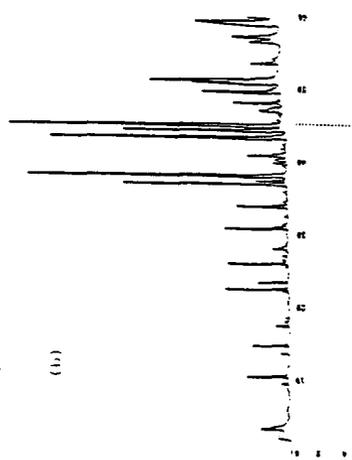


Fig. 4 (a) Gas chromatogram of free stream soot at 15 mm above burner,  $\phi = 2.76$ .  
 (b) Gas chromatogram of deposited soot at same conditions.

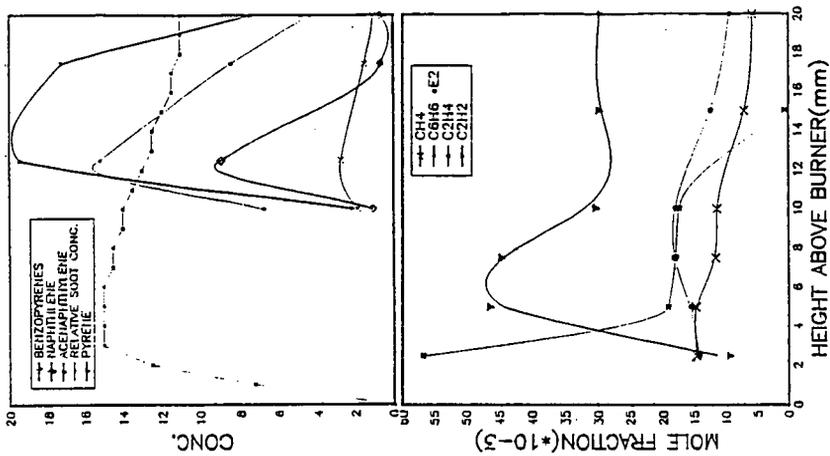


Fig. 5. Small molecule species profiles for  $\phi = 2.76$  flame (mol fraction).

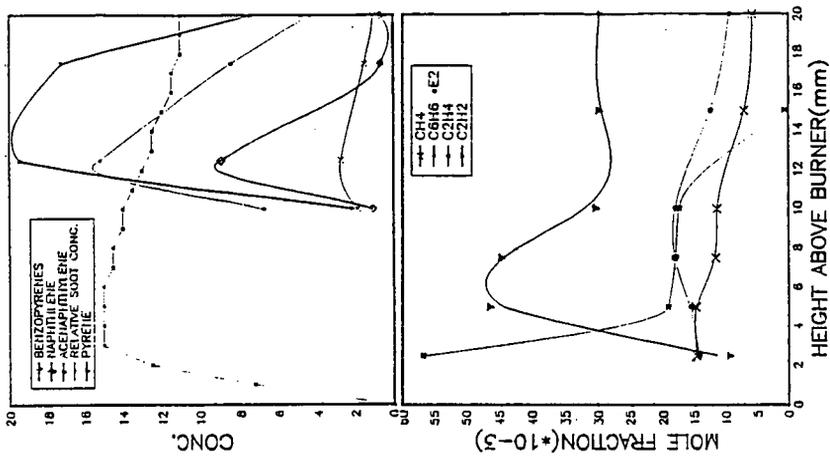


Fig. 6. Hydrocarbon species profiles for  $\phi = 2.76$  flame (arbitrary concentration scales) and  $\phi = 2.52$  flame (mol fraction).