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Premixed Flames by UV Scattering,  
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# Characterization of Nanoparticles in Premixed Flames by UV Scattering, Absorption and Fluorescence

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## 1) Introduction

Aerosols play a central role in the Chemistry and Physics of the atmosphere as demonstrated by recent research. Epidemiological studies point out their importance for the health effects in polluted areas and toxicological research suggest a critical role of particles smaller than 100 nm. In observed climate records, there is evidence of a response to forcing not only due to greenhouse gases but also to aerosols. Consequently, it is important to assess the role of human actions in the production of aerosols in terms of total quantity, size distribution function, and chemical and physical properties.

Combustion is considered responsible for the formation of the greatest part of the particulate in form of nanoparticles. Particles from combustion are either emitted directly in terms of elemental carbon (i.e. soot) or indirectly, through gas to particle conversion in the atmosphere, either from the sulfur content of the fuel leading to sulfate nanoparticles or from the gas to particles evolution of volatile organic compounds leading the secondary formation of organic carbon particles.

However, the formation of the organic carbon nanoparticles during combustion has not yet been object of systematic analysis. This study is of great importance and may contribute in a relevant way to assess the relative role of different technologies (gasoline and diesel engines, gas turbines, steam generators, incinerators, etc.) in the health/climate change effects.

Size, chemical functionalities and water solubility have a decisive role for establishing the interactions of aerosol with human tissues in the lungs. The same parameters establish their optical properties relevant to direct radiative forcing and to their ability to act as cloud condensation nuclei.

Different groups in Naples at the University and at CNR Institutions (Istituto Motori and Istituto di Ricerche sulla Combustione) have been involved in the characterization (mainly optical and spectroscopical) of combustion generated nanoparticles. Research is carried out in laminar flames [1-3] turbulent spray flames [4], optically accessible diesel engines [5, 6], and at the exhaust of uncatalyzed and catalyzed gasoline engines, diesel engines, and different stationary sources [7-9].

This paper describes the optical characterisation of slightly sooting premixed flames employing UV light scattering, absorption and fluorescence. More specifically, the early formation of nanoparticles of organic carbon and their transformation into elemental carbon (soot particles) followed as a function of residence time in the flame is analysed. In addition, the organic carbon particles are sampled from the flame and collected in water, which is also characterized optically, to explore their interaction with water.

## 2) Experimental Procedures and Measurements.

An overview of the experimental set-up is reported in fig. 1. Fuel rich premixed laminar ethylene/air flames are stabilized on a capillary burner. The flame temperature is measured by Na-D line reversal method employing a calibrated tungsten streak lamp. The fourth harmonic of a vertically polarized Nd:Yag laser source ( $\lambda = 266$  nm) is employed as the light source for scattering

and fluorescence measurements. A Xe lamp is the light source used for the absorption measurements, and a pre-dispersing monochromator is used to avoid stray light in the UV measurements. Signals are detected by means of a spectrograph coupled to a ICCD camera. The set up for isokinetic sampling is shown in fig.1B. A stainless steel probe is inserted in the flame at a height  $z$  above the burner, the sampled material is sent to a condenser where it bubbles in water and condensable material is stopped while the gaseous species are sent to the exhaust. The material collected in water is then analyzed optically with the same apparatus used for Laser induced in situ measurements while absorption spectra are measured with a spectrophotometer.

Fig. 2-3 show how the scattering and monochromatic absorption coefficients in the UV at 266 nm and in the visible at 532 nm change along the flame. In the early region, near the flame front, light scattering exceeds the gas phase contribution indicating the presence of small nanoparticles. Later on light scattering increases several orders of magnitude due to the formation of larger particles. The light absorption coefficient in the visible appears quite late in the flame almost in correspondence of the strong increase in the scattering. On the contrary UV absorption starts soon after the flame front and increases only slightly in the burned gas region.

Fig. 4 reports the absorption spectra of early nanoparticles produced in non sooting or slightly sooting conditions. The absorption decreases from the vacuum UV limit at 200 nm and is negligible beyond 300 nm.

Fluorescence spectra, excited at  $\lambda_0=266$  nm, reported in fig. 5, show the fluorescence of two bands: the first peaked at 320 nm is present either in presence or in absence of soot particles whereas the second broader feature centered in the visible becomes evident only when particles absorbing in the visible are present.

Absorption and fluorescence spectra strongly suggest that the transparent particles contain aromatic functionalities with no more than 2-3 rings although the presence of heteroatoms like oxygen can not be excluded.

"Ex situ" absorption and fluorescence spectra obtained in the water bubbled suspensions before soot inception are similar to those measured "in situ" (see fig. 6), thus showing the hydrophylic nature of these nanoparticles. More details on ex situ sampling are available elsewhere [10].

### 3) Interpretation of the results.

Light scattering and absorption measurements are interpreted quantitatively according to the Rayleigh theory of absorbing particles much smaller than the light wavelength. Light scattering and absorption coefficients are given by the expressions:

$$f_V = N \frac{\pi d^3}{6}$$

$$Q_{VV} = \frac{\pi^4}{4\lambda^4} \left| \frac{\tilde{m}_p^2 - 1}{\tilde{m}_p^2 + 2} \right|^2 N d^6$$

$$K_{abs} = -\frac{\pi^2}{\lambda_0} \text{Im} \left\{ \frac{\tilde{m}_p^2 - 1}{\tilde{m}_p^2 + 2} \right\} N d^3$$

From these equations the average size,  $d$ , number concentration,  $N$ , and volume fraction  $f_v$  of the nanoparticles may be obtained when the complex refractive index ( $m$ ) is known. The procedure which takes into account the variation of the optical properties passing from the initial nanoparticles to soot is reported in a previous paper [11] and just the results are reported in Fig. 7.

In this slightly sooting flame the first nanoparticles have typical size between 2 and 3 nanometers and their initial number concentration is higher than  $10^{13} \text{ cm}^{-3}$ . Later on, only when soot inception starts, the average size increases up to 25 nm and the number concentration decreases down to  $10^{10} \text{ cm}^{-3}$ . However, interestingly enough, the volume fraction remains almost constant, within 10% along the flame. It seems that the total amount of carbonaceous material is formed by a very early inception of organic carbon nanoparticles and soot inception is formed later on through a dehydrogenation and internal rearrangement of the organic carbon toward more aromatic graphitic structures.

Organic carbon nanoparticles have a very low coagulation rate, two orders of magnitude smaller than that predicted by the "meet and stick" model in the gas kinetic limit, as it is shown in fig. 8. Only after the dehydrogenation/graphitization process has progressed, does the coagulation reach and eventually exceed the gas kinetic limit (fig. 9). The atomic H/C ratio of the nanoparticles in fig. 9 is obtained also from optical measurements [12].

#### 4) Conclusions

A noticeable amount of organic carbon nanoparticles with typical sizes smaller than 3 nm are produced in rich premixed flames just downstream the oxidation front. At this stage the nanoparticles have a coagulation rate two orders of magnitude lower than the gas kinetic limit.

These results suggest that practical combustion sources operating in premixed regimes below the soot threshold, like gasoline engines and gas turbines, may emit a large number of nanoparticles much smaller than those normally detected with the current Electrical Low Pressure Impactor, ELPI, and Scanning Mobility Particle Sizer, SMPS instruments which are seldom able to detect particles smaller than 10 nm.

The formation of elemental carbon particles just above the soot threshold limit is due to relatively slow dehydrogenation and aromatization processes of the organic carbon nanoparticles followed by a fast coagulation which produces particles with typical size around 20 nm. Gas to particle addition processes do not play a significant role in this regime of premixed combustion.

The coagulation rate between organic and elemental carbon nanoparticles at lower residence times and at lower temperature as well as the surface growth kinetics of organic nanoparticles due to volatile organic compounds should be determined in order to establish the role of these processes in determining the amount and size distribution functions of nanoparticles at the exit of combustion source exhausts and in the atmosphere.

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# Final Consideration I

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- Formation of Organic Carbon (OC) aerosols is studied in premixed slightly sooting flames.
- OC is observed “in situ” and in water suspension with UV optical diagnostics.
- OC aerosols have a typical size (2-5 nm) much smaller than that of elemental carbon (soot particles, 20-50 nm) and have different chemical structures.
- OC is formed quite soon in the flame front while soot formation process is a much slower process.
- The total amount of carbonaceous material is constant with reaction time and soot is formed from the internal rearrangement of OC toward a more aromatic structure.

# Final Consideration II

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- Coagulation rate of the organic aerosol is much slower than that predicted by gas kinetic theory.
- Coagulation rate depends strongly on the H/C ratio of the carbon containing material.
- The fact that OC can be collected in water has implications for human and environmental health.
- The contribution of combustion generated OC must be considered in calculating the radiative atmospheric forcing function.

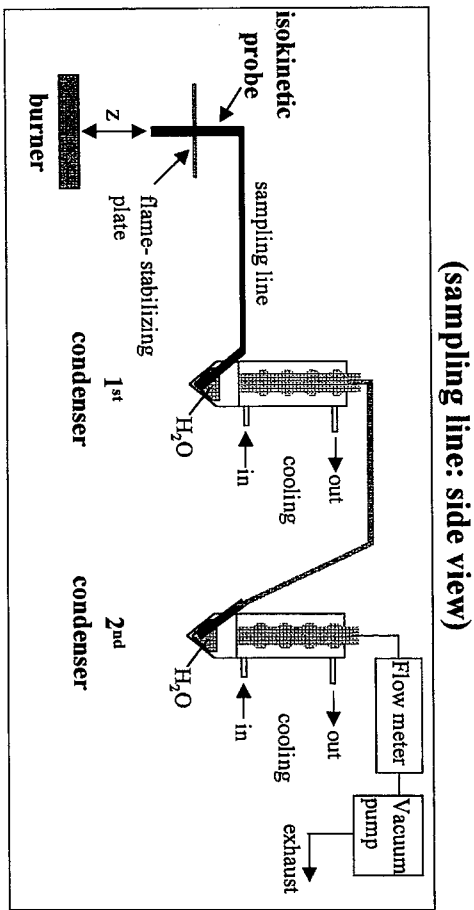
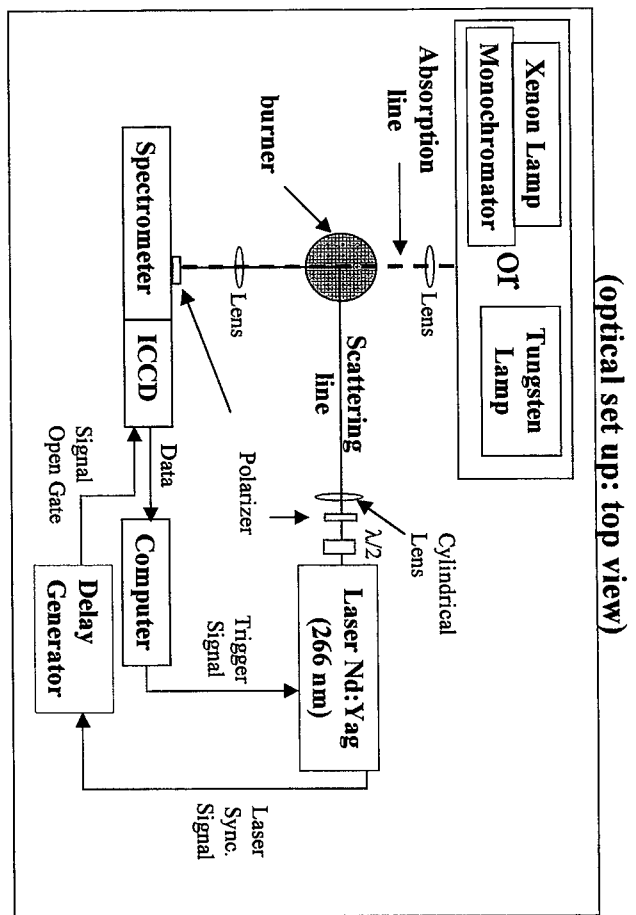
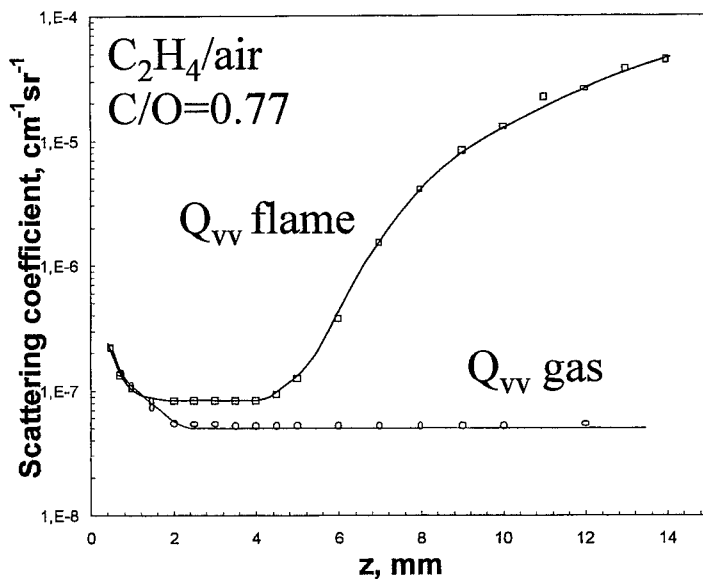


FIGURE 1: Experimental set up (A) for laser light scattering, light absorption and laser induced fluorescence for both *in situ* and *extra situ* measurements. (B) set up for isokinetic sampling.

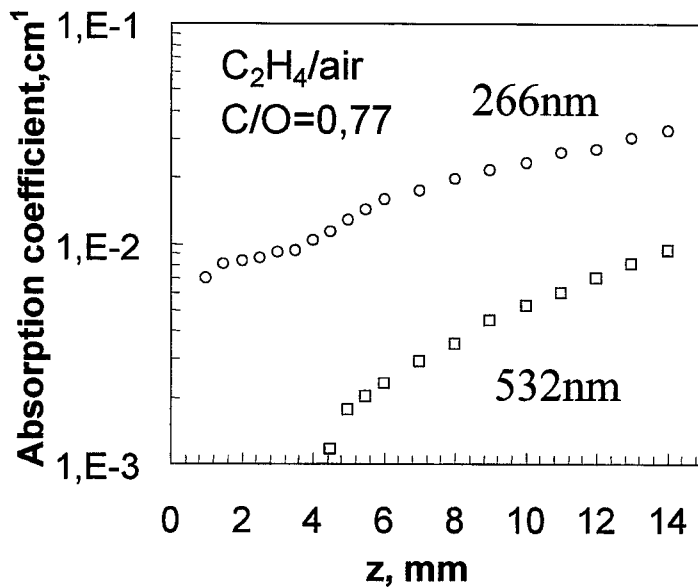
*Above the flame front the flame light scattering exceed the gas contribution*



- In the plateau region the excess scattering is due to small nanoparticles
- The strong increase of the excess scattering is due to soot particles

FIGURE 2: Light scattering coefficient versus the height above the burner for the flame ethylene/air with  $C/O=0.77$ . The scattering coefficient due to the gaseous compounds is also reported.

# Light absorption coefficient



•UV absorption starts soon after the flame front

•Visible absorption is delayed respect to the UV absorption

FIGURE 3: Light absorption coefficient in the UV (266 nm) and in the visible (532 nm) versus the height above the burner for the flame ethylene/air with C/O=0.77.

## Light absorption spectra in non sooting and near sooting flames: $K_{abs}(flame) - K_{abs}(CO_2)$

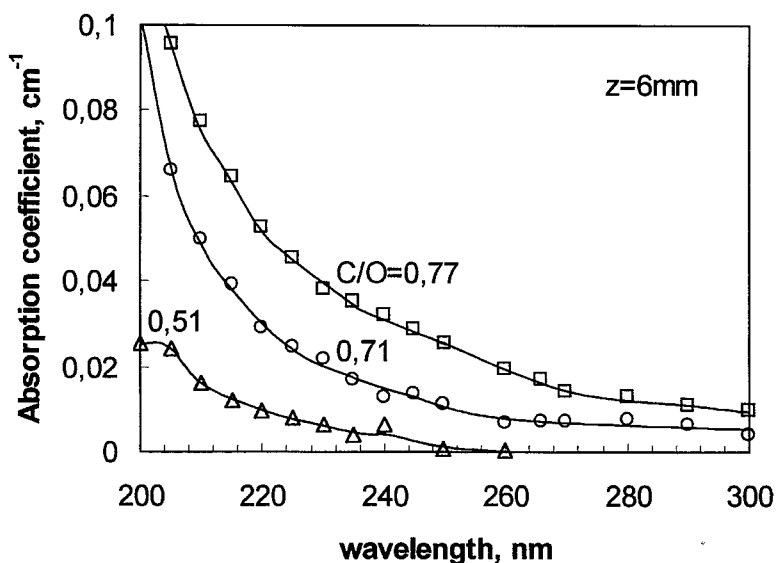


FIGURE 4: Light absorption spectra for the flames ethylene/air with C/O=0.51, 0.71 and 0.77 measured at z= 6 mm. The contribution to the absorption due to CO<sub>2</sub> has been subtracted.



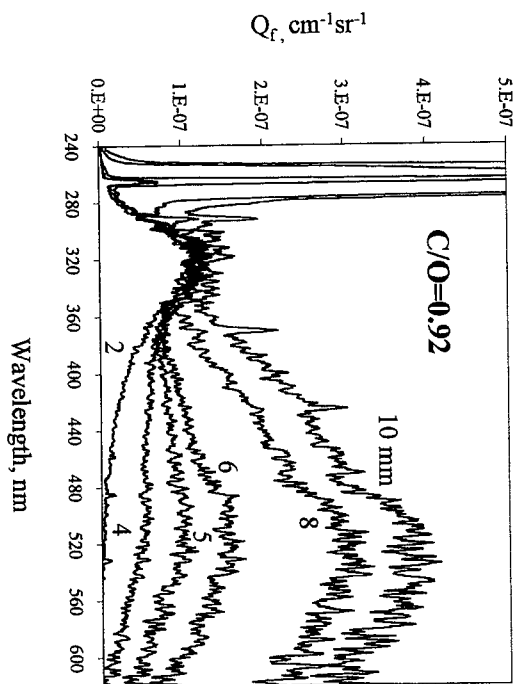


FIGURE 5: In situ laser induced fluorescence spectra measured in a strongly sooting (C/O=0.92) flame for different height above the burner (numbers near curves). The strong peak at the excitation wavelength (266 nm) is due to elastic scattering.

## *Ex Situ Absorption and Fluorescence*

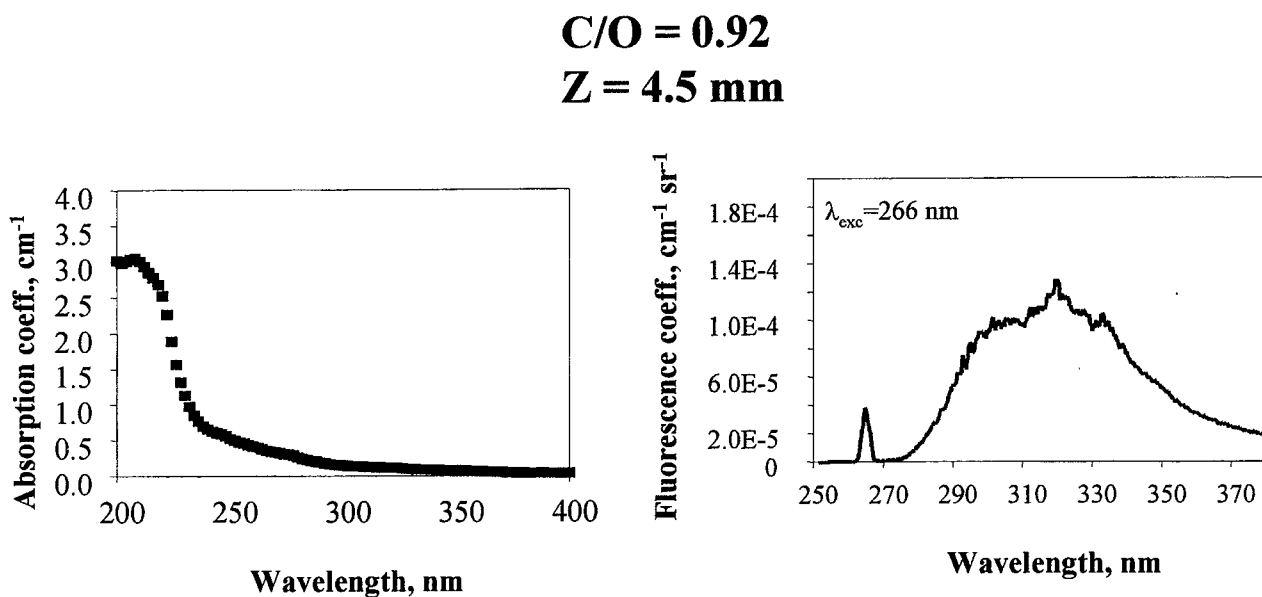


FIGURE 6: Light absorption and laser induced fluorescence spectra for the material sampled in the flame ethylene/air with C/O=0.92 at z=4.5 mm.

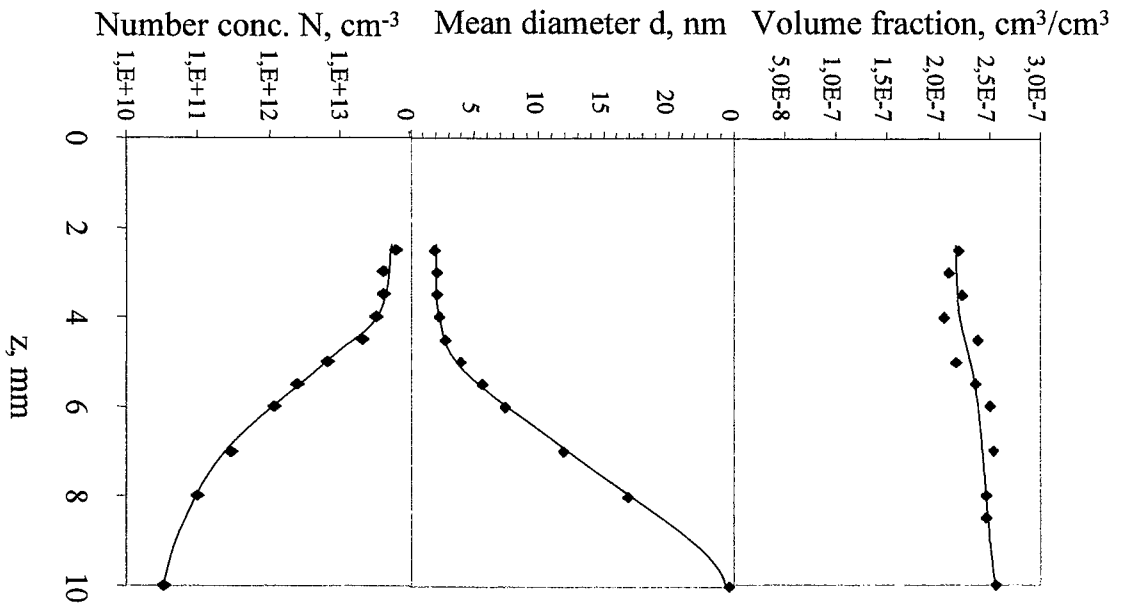


FIGURE 7: Particles volume fraction, mean diameters and number concentration versus the height above the burner for the flame ethylene/air with  $C/O=0.77$ .

## Coagulation rate

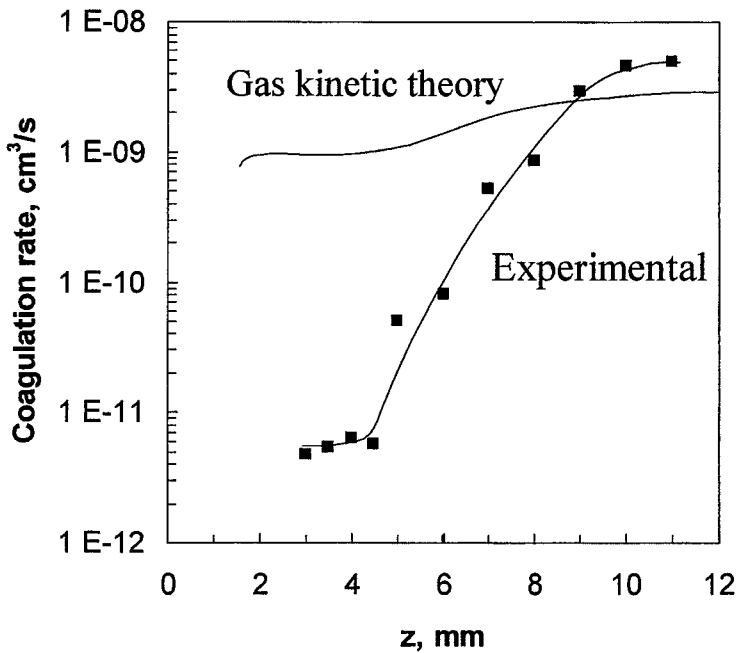


FIGURE 8: Coagulation rate versus the height above the burner for the particles produced in the ethylene/air flame with  $C/O=0.77$ . The values predicted by the Gas Kinetic theory are also reported.

# Coagulation rate versus the particles H/C atomic ratio

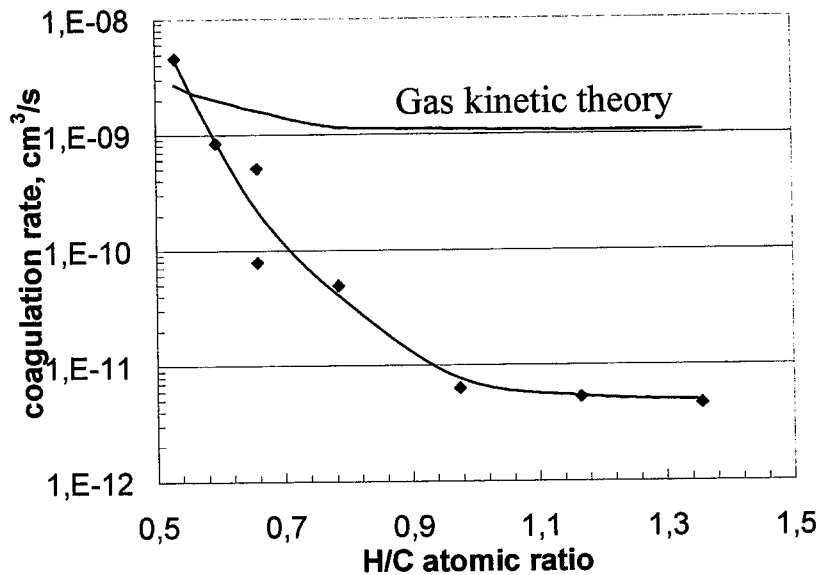


FIGURE 9: Experimental coagulation rate of the particles produced in the ethylene/air flame with C/O=0.77 and the values predicted by the Gas Kinetic theory plotted versus the H/C atomic ratio of the particles.

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