Optical properties of soot synthesized in pyrolysis of ethylene and acetylene in shock tube reactor

LABORATORY OF NONEQUILIBRIUM PROCESSES

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ABSTRACT

In this study, shock tube pyrolysis of 5% ethylene and 3% acetylene in argon was used to study the process of soot formation and properties of formed particles. LII measurements of soot optical properties were performed at the temperatures behind reflected shock waves 1800-2000 K, corresponding to a maximum soot yield . The reaction time of the soot yield 1.5 ms within operation time of the shock tube was chosen due to at this time soot volume fraction reaches the plateau. The absolute value of the refractive index function of soot E(m,1064) at a wavelength 1064 nm and the ratio of the refractive index functions at two wavelengths of 532 nm and 1064 nm were measured by laser induced incandescence. The E(m,1064) was found to be 0.44±0.05 for acetylene soot and 0.35±0.04 for ethylene soot by comparing the measured peak temperature of laser heated soot with the calculated peak temperature obtained using laser induced-incandescence model. The ratio E(m,1064)/E(m,532) was found to be 1.28±0.08 for acetylene and 0.8±0.05 for ethylene soot. The samples of soot nanoparticles were analyzed on a FEI Osiris high resolution transmission electron microscope (HR TEM) to determine the mean soot primary particle size and internal soot structure, namely the mean length of the graphene planes of soot crystallites, planes tortuosity and mean interlayer distance between neighboring graphene planes. The investigated optical and structural properties of shock tube pyrolysis soot were compared with the properties of acetylene and ethylene flame soot at corresponding mean soot particle sizes. A good correlation between the properties of pyrolysis and flame soot was obtained.

MOTIVATION

Problem

Soot optical properties correlation with internal structure.

Previous studies

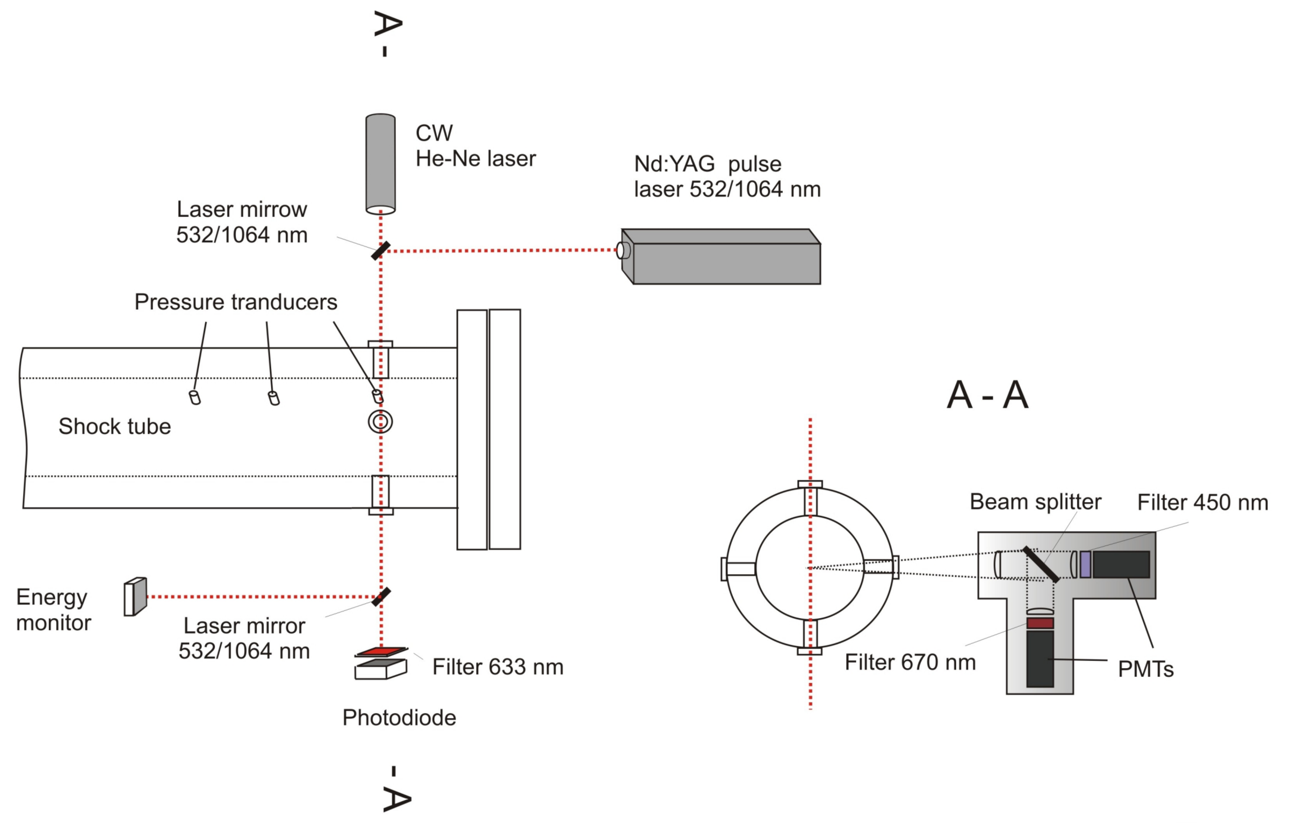
Soot optical properties and structure investigation in ethylene/air and acetylene/air flames [1],[2].

Goals of this study

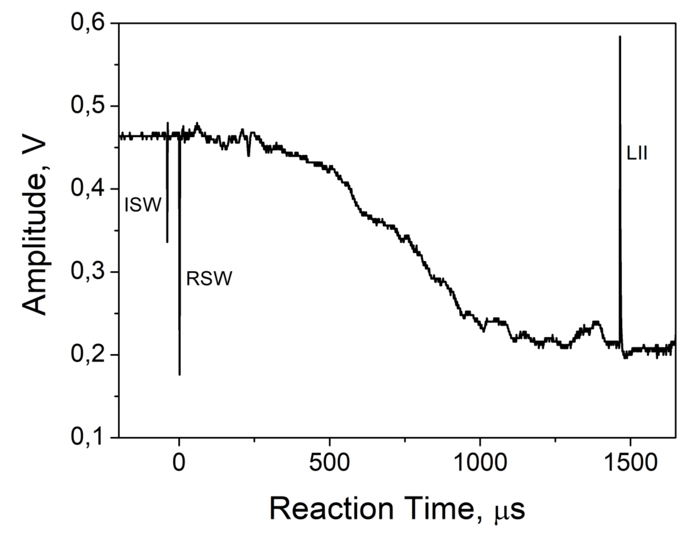
1. Measurements of refractive index function *E(m)* and *E(m)* ratio at two laser wavelengths 532 and 1064 nm for soot synthesized in ethylene and acetylene pyrolysis behind shock waves.
2. The determination of structure parameters of soot.

[1] *A.V. Eremin, E. V. Gurentsov, R.N. Kolotushkin* The change of soot refractive index function along the height of premixed ethylene/air flame and its correlation with soot structure. Appl. Phys. B 126 (2020).
[2] *A.V. Drakon, A.V. Eremin, E. V. Gurentsov, E. Yu. Mikheyeva, R.N. Kolotushkin* Optical properties and structure of acetylene flame soot. Appl. Phys. B (2021) to be published.

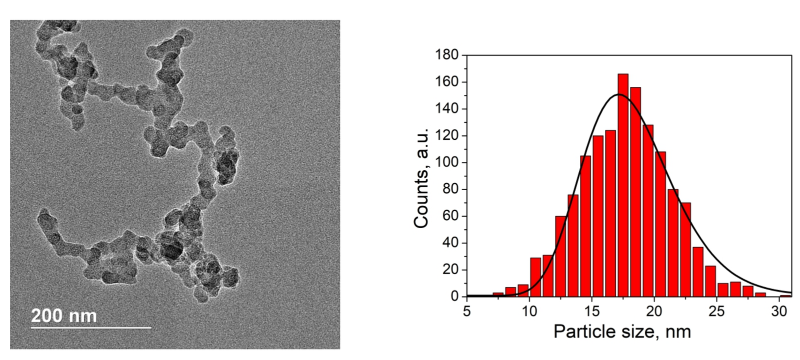
SOOT SYNTHESIS IN THE SHOCK TUBE



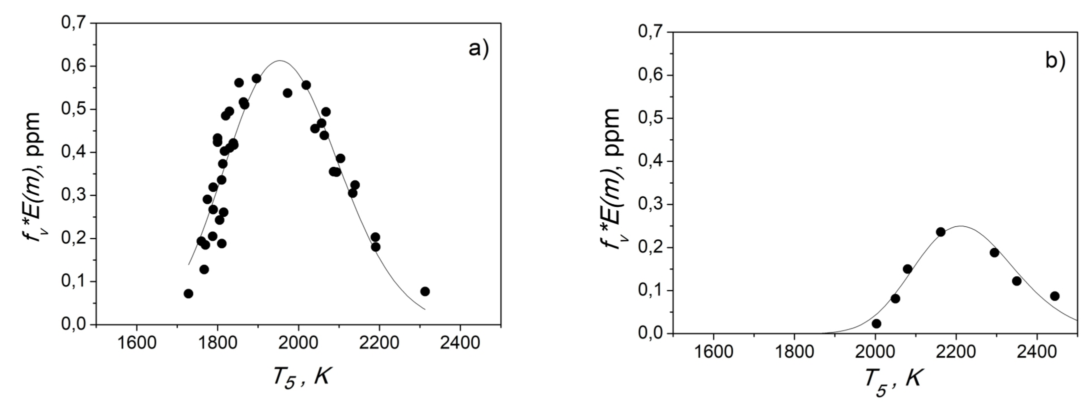
Extinction measurements of soot growth behind reflected shock waves



TEM particle sizing



Temperature dependence of soot volume fraction in pyrolysis



E(m) determination at 1064 nm

Refractive index

$$m = n - ik$$

Refractive index function

$$E(m) = \mathrm{Im}\left(\frac{m^2-1}{m^2+1}\right) = \frac{6nk}{(n^2-k^2+2)^2+4n^2k^2}$$

The maximum nanopartical heat temperature T_p^0 could be obtained theoretically by integration of energy balance equation as:

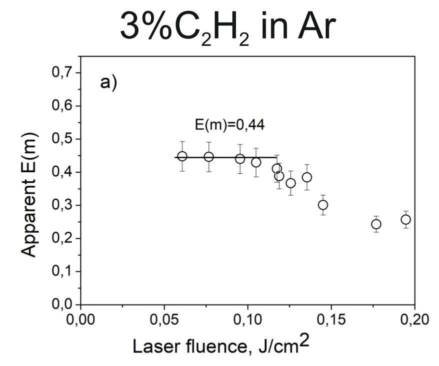
$$T_p^0 = T_g + \frac{6p \cdot R_0 \cdot E(m)}{r_p \cdot c_p \cdot l_{laser}} \qquad (1)$$

From the other side a two-color pyrometry of incandescence has been applied for determined T_p^0 in experiment:

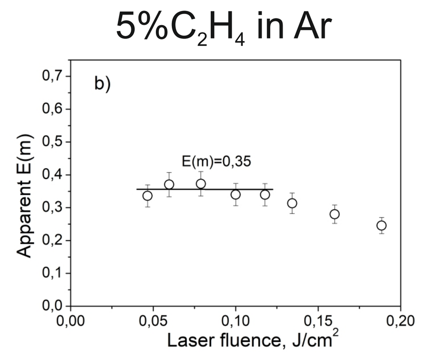
$$T_p^0 = \frac{hc}{k_B}\frac{\left(\frac{1}{\lambda_2}-\frac{1}{\lambda_1}\right)}{\ln\left[\frac{I_1}{I_2}\frac{I_{TL_2}}{I_{TL_1}}\frac{\varepsilon_T(\lambda_1)E(m)(\lambda_2)\lambda_1}{\varepsilon_T(\lambda_2)E(m)(\lambda_1)\lambda_2}\right]+\frac{hc}{k_B T_{TL}}\left(\frac{1}{\lambda_2}-\frac{1}{\lambda_1}\right)} \qquad (2)$$

The spectral variation of E(m) of soot nanoparticles was taken for account using the linear *E(m)* wavelength dependence at selected reaction time. Finally, the value of *E(m)* was determined by T_p equating using equations (1) and (2) by variation of E(m).

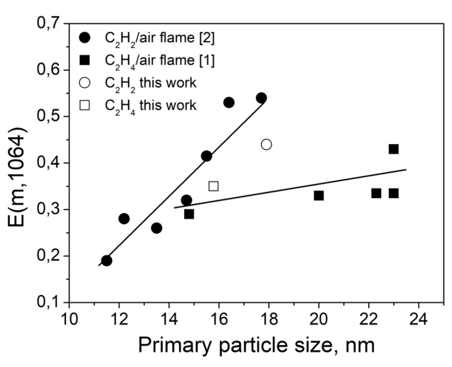
3%C_2H_2 in Ar



5%C_2H_4 in Ar



Comparison with flame data



E(m, 1064)/E(m, 532)

A soot particle illuminated by two wavelength to radiate the same incandescence intensity.

$$LII_{1064} = LII_{532}$$

The absorbed power is balanced by the thermal radiation and heat conduction to the surrounding gas.

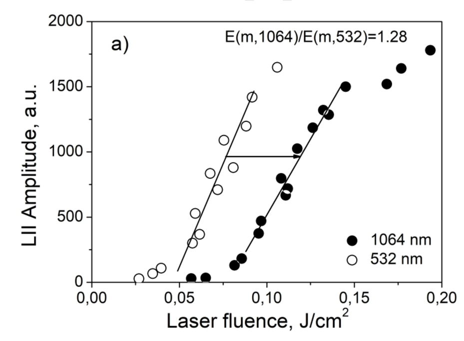
$$\exp\left(\frac{hc}{\lambda_{532}k_BT}\right) = \exp\left(\frac{hc}{\lambda_{1064}k_BT}\right)$$

Assuming the same spatial distribution of the laser irradiance and by adjusting the laser energies at 1064 and 532 nm the ratio of refractive index functions resulted in *E(m)* ratio:

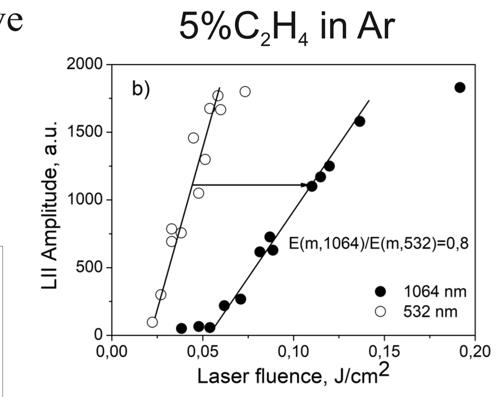
$$\frac{E(m,1064)}{E(m,532)} = 2\frac{E_{Laser}(532)}{E_{Laser}(1064)}$$

Therssen E, Bouvier Y, Schoemaecker-Moreau C, Mercier X, Desgroux P, Ziskind M, Focsa C. Determination of the ratio of soot refractive index function E(m) at the two wavelengths 532 and 1064 nm by laser induced incandescence. *Appl. Phys. B* 2007, 89, 41727.

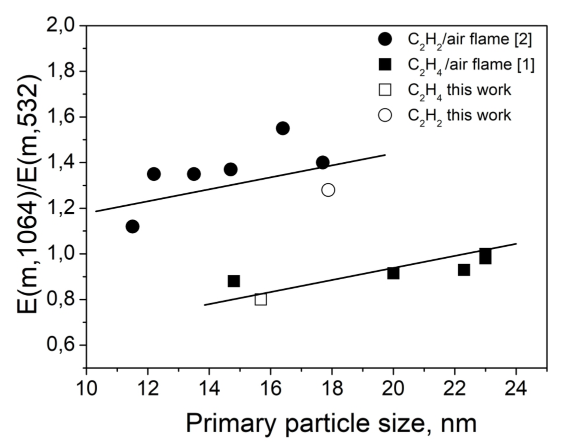
3%C_2H_2 in Ar



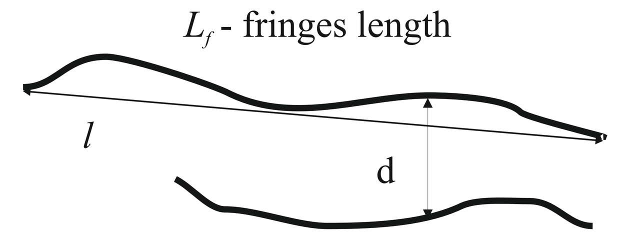
5%C_2H_4 in Ar

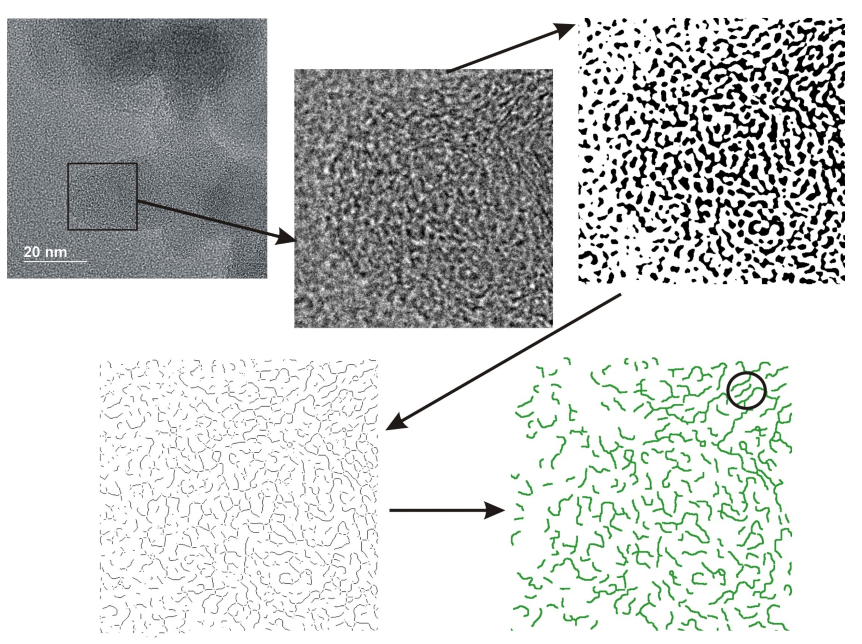


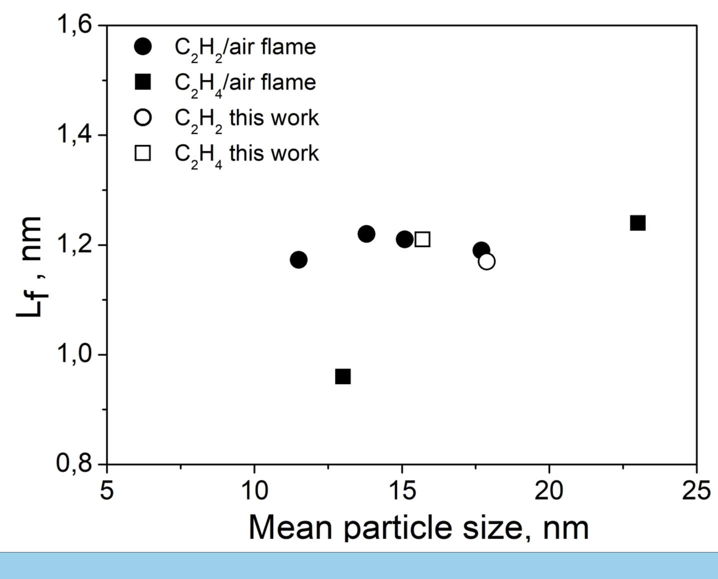
Comparison with flame data

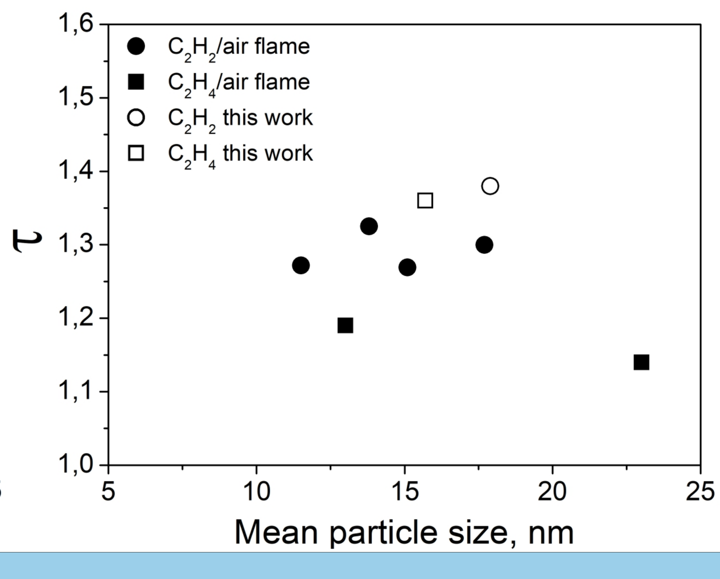


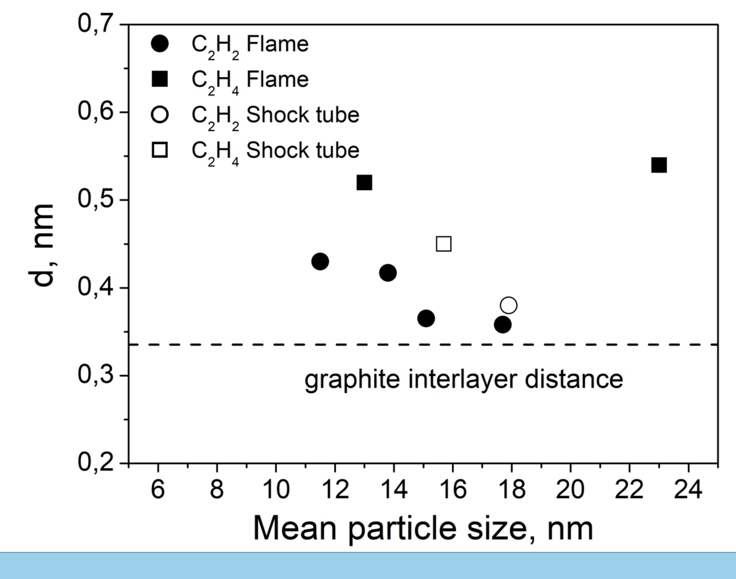
HR TEM soot structure analysis











CONCLUSIONS

The optical properties of soot particles synthesized in shock tube pyrolysis of acetylene and ethylene were investigated. The absolute values of E(m) at a wavelength of 1064 nm were found to be 0.44±0.05 and 0.35±0.04 for acetylene and ethylene soot correspondingly. The refractive index function ratio at wavelengths of 532 and 1064 nm was determined by recording the amplitude of LII signals and measuring the laser fluence. The ratio E(m,1064)/E(m,532) for acetylene soot was found to be 1.28±0.08 and 0.8±0.05 for ethylene soot. These data are in a good agreement to that, obtained in premixed ethylene/air and acetylene/air flames when analyzing the optical properties in dependence on soot particle size.

The variation in the optical properties of acetylene and ethylene soot was attributed to the variation of the soot internal structure depended on the type of hydrocarbon and primary soot particle size. The main reason for the optical properties variation of acetylene and ethylene soot can be a difference in mean distance between graphene planes in soot crystalline from 0.38 nm for ethylene soot to 0.45 nm for ethylene soot. These changes resulted in higher acetylene soot graphitization, optical band gap decreases and the increase of laser light absorption by acetylene soot particles at a longer wavelength.

ACKNOWLEDGEMENTS

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