

Soot Formation by Pyrolysis in a Shock Tube

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Introduction

Our aim is to study carbon nanoparticles formation in diesel engine conditions. For that, four different hydrocarbons were chosen in order to represent the major families of diesel fuel, mainly a monoaromatic (n-heptylbenzene), a diaromatic (1-methylnaphtalene), a linear (n-hexadecane) and a naphtene (decahydronaphtalene). These results were compared to those obtained from toluene pyrolysis. The originality of this study is to use a shock tube to produce the diesel combustion conditions, i.e. the encountered level of temperature and pressure in this type of engine. The pyrolysis and oxidation of the different hydrocarbons have been studied behind reflected shock waves at temperatures between 1300 and 2700K and pressures between 0.2 and 1.8 MPa [1, 2]. This method permits to follow directly soot induction delay times as well as soot growth. The so-obtained soot can then be collected and their multiscale organisation characterized by High Resolution Transmission Electron Microscopy (HRTEM). An image analysis procedure was developed to obtain quantitative structural and microtextural data. The evolution of these data was studied in relation with the experimental conditions.

Experimental setup

The soot formation from heavy hydrocarbons was conducted using a stainless steel shock tube of 7.15 m long and 52.5 mm internal diameter for the low pressure part. The shock tube is mainly constituted of 2 parts, the high pressure section in which an inert gas (He for instance) and a low pressure section filled with the studied mixture. The two parts are separated by a double diaphragm (Figure 1). Its sudden burst induces the high pressure gas flow in the low pressure section and hence gives birth to the incident shock wave. The

supersonic shock wave travels downward and produces an increase of the temperature and pressure of the studied mixture. The incident shock wave reflects at the flat end plate of the shock tube and travels backward inducing a second increase of the pressure and temperature. The pressure and temperature behind the reflected shock wave is maintained constant until the reflected shock wave reaches the contact surface. This time is known as the observation time and it is fixed by the tube characteristics as well as the gases which are used. For these experiments it is around 3ms. The operating conditions are chosen to produce, behind the reflected shock wave, the pressure and temperature encountered in engines.

Soot formation conditions are determined at the gas temperature and pressure obtained behind the reflected shock wave labeled T_5 and P_5 respectively. The last part of the shock tube is equipped with 4 piezo-electric pressure transducers, mounted flush with the inner surface, to detect the pressure jumps induced by the shock waves. In our conditions, the shock wave velocity is deduced from the pressure jump at the shock wave passage. Then the pressure and the temperature of the shocked gas are calculated by applying the conservation equations, the thermodynamic properties and the initial conditions (pressure temperature and composition) being known [1]. The main characteristics of soot formation (soot induction delay times (τ_{ind}) as well as soot growth constant and soot yield) are derived from a laser beam attenuation technique. A He-Ne laser beam (632.8 nm) passes through two silica windows and arrives at the front of an HAMAMATSU photomultiplier tube (R928) equipped with an interferential filter (633 \pm 2 nm). The two silica windows are located at the same axis as the last pressure transducer and 15 mm from the end-plate of the shock tube (Figure 2).

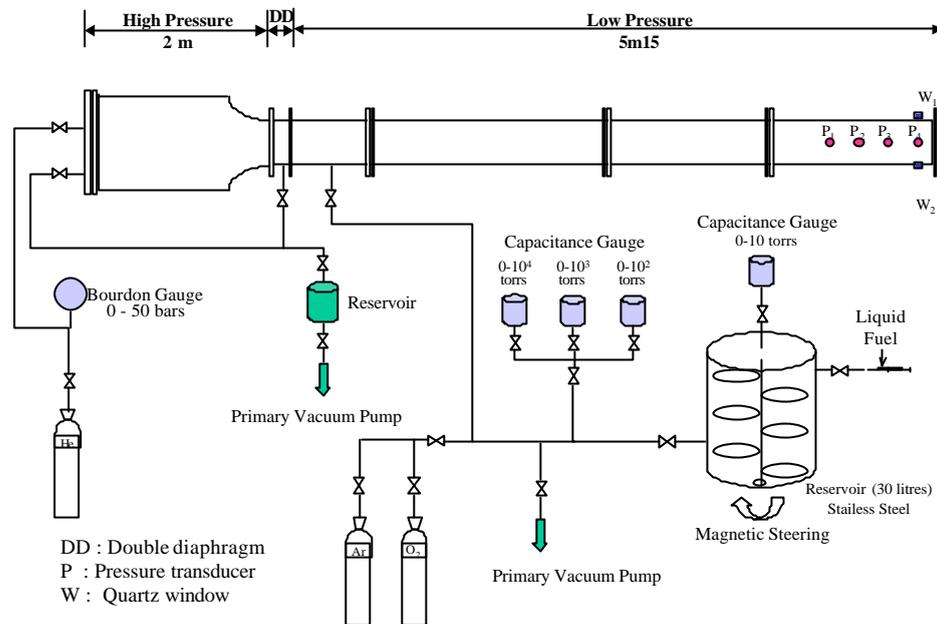


Figure 1. Experimental setup layout.

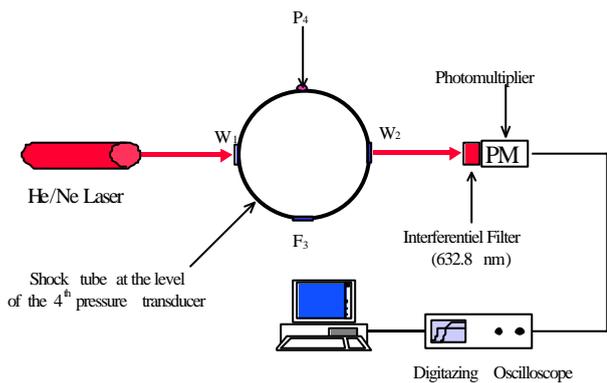


Figure 2. Optical and pressure measurements.

Soot behind reflected shock waves have only a limited time to be formed and around 3 milliseconds. Soot inception is characterized by an induction time which is required for the formation of the soot nuclei. This period is followed by a growth one where the soot spheres increase in size by surface growth mainly. If one considers only surface growth, and that coagulation is negligible, then this phase is characterized by a surface growth constant (assuming a first order law). The soot volume fraction tends towards a constant value after the growth period. This value is used to obtain the soot yield. Each phase of this process is experimentally characterized through the recording of the laser light absorption profile versus time (Figure 3).

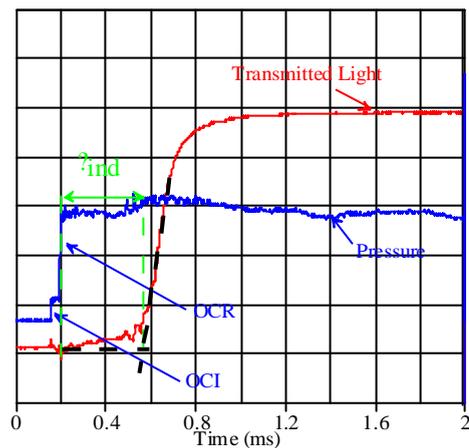


Figure 3. Example of signals recorded on a digitizing oscilloscope (OCI : incident wave; OCR :reflected wave).

The experiments were conducted for highly diluted mixtures of hydrocarbons in 99 to 99.8% argon. These mixtures were heated between 1300 and 2700 K, in presence of different amounts of oxygen (O_2 /hydrocarbon ratio between 0 and 2). The pressure was ranging between 0.2 and 1.8MPa. Toluene was used as a reference fuel since a lot of work has been done using shock tubes to study soot formation from it. And these results are compared to those obtained for a monoaromatic (n-heptylbenzene), a diaromatic (1-methylnaphtalene), a linear (n-hexadecane) and a naphtene (decahydronaphtalene).

HRTEM characterization of soot organisation

After each shot, the soot particles deposit all over the internal surface of the shock tube. Once the experiment is performed, the end-plate of the shock tube is dismantled carefully since the soot particles deposit on its surface. Sample of soot particles formed were collected by plunging this end-plate in a glass of anhydrous ethanol and undergoes a 5 min cycle of ultrasonic waves. A droplet of the mixture soot – anhydrous ethanol is deposited on a 3 mm diameter grid for the MET analysis. They were analyzed using HRTEM. A classical image analysis (Visilog 5.0) was used to determine the soot spherule diameter. A home made image analysis procedure permits the quantification of the soot structure [3].

The so-obtained soots are characterized by a multiscale organization (texture, microtexture and structure). They are usually made of more or less ramified chains of nanometric spheres with a concentric microtexture and a turbostratic structure.

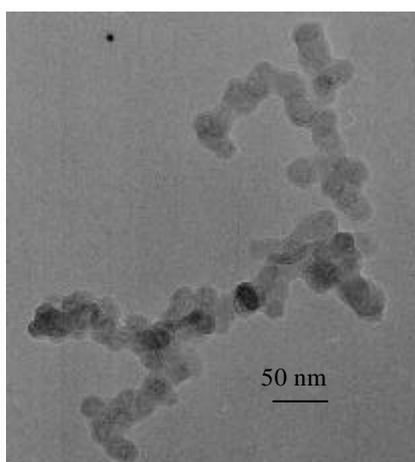
From the micrographs and using an image analysis process, the organization was quantified over about three orders of magnitude (0.3 to 200 nm). The sphere size distribution was determined from classical image processing procedure (VISILOG device) performed on medium magnification images (50,000X, see Figures 4 and 5). After skeletonization of high resolution images obtained at 310,000X (see Figure 9), an original home-made software allows the extraction of structural and microtextural data [3]. For instance, the distributions of the aromatic layer diameters L and of the interlayer spacings d_{002} can be determined. The errors on L and d_{002}

are respectively about 0.5 % (+/- 0.025 Å) and about 0.5 (+/- 0.02 Å). These parameters allow a pertinent study of the evolution of the soot organisation according to the experimental conditions (temperature, pressure, equivalence ratio of the gas mixture, and the fuel nature).

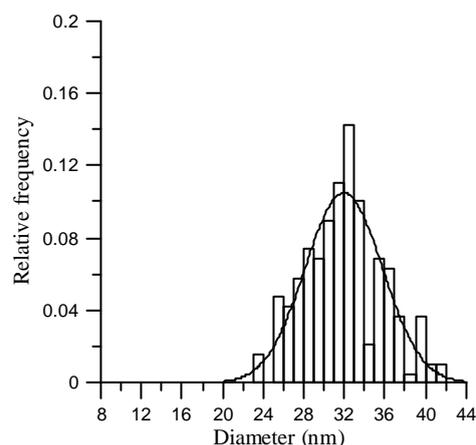
Influence of the initial temperature on the sphere size

At low magnification (50,000x), one could see the texture resulting of the arrangement of chains of spheres. In the case of toluene, when the temperature is increased from 1530 K (Figure 4) to 1965 K (Figure 5), the mean diameter decreases from 32 nm to 17.8 nm, and the distribution of size is narrower and narrower. An eventual effect of the precursor nature was studied. At 1718 K, the mean diameter is 26 nm with the toluene. It is almost the same for n-hexadecane (24 nm at 1777 K) and for decahydronaphtalene (26 nm at 1625 K). For n-heptylbenzene it seems to be slightly lower since it is 20 nm at 1742 K. At higher temperature the mean spheres have the same diameter, 17 nm for toluene and n-heptylbenzene (1965 K and 1901 K respectively). The temperature effect is the same for n-heptylbenzene (20 nm at 1742 K and 16 nm at 1901 K).

In conclusion, for a same temperature of pyrolysis, the sphere size does not depend significantly on the nature of the precursor (linear, monoaromatic, diaromatic). As the temperature increased from 1700 K to 2000 K, the sphere size decreases (Figure 6) and the distribution of size becomes narrower. Moreover, the chains are more ramified indicating a higher fractal dimension (compare Figures 4 and 5). The diameter decrease with the temperature could be in relation with the release of heteroatoms and the decrease of d_{002} , the mean interlayer spacing.

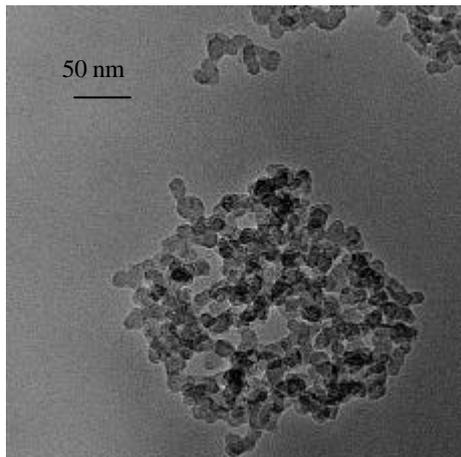


0,5% Toluene + 99,5% Argon
 $T_5 = 1530 \text{ K}$, $P_5 = 1310 \text{ kPa}$

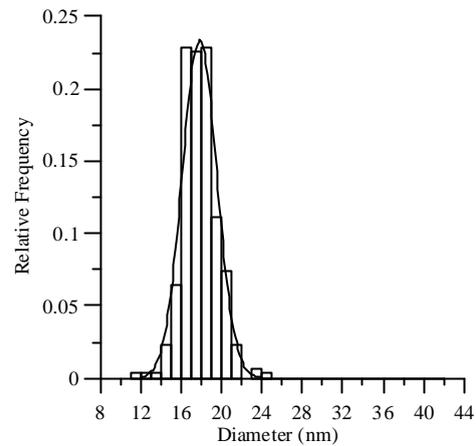


Number of measurements = 190
Mean Diameter = 32 nm

Figure 4. Sphere size distribution for toluene/argon mixture ($T_5 = 1530 \text{ K}$, $P_5 = 1310 \text{ kPa}$).



1% toluene + 99% argon
 $T_5 = 1965 \text{ K}$, $P_5 = 1396 \text{ kPa}$



Number of measurements = 297
 Mean Diameter = 18 nm

Figure 5. Sphere size distribution for toluene/argon mixture ($T_5 = 1965 \text{ K}$, $P_5 = 1396 \text{ kPa}$).

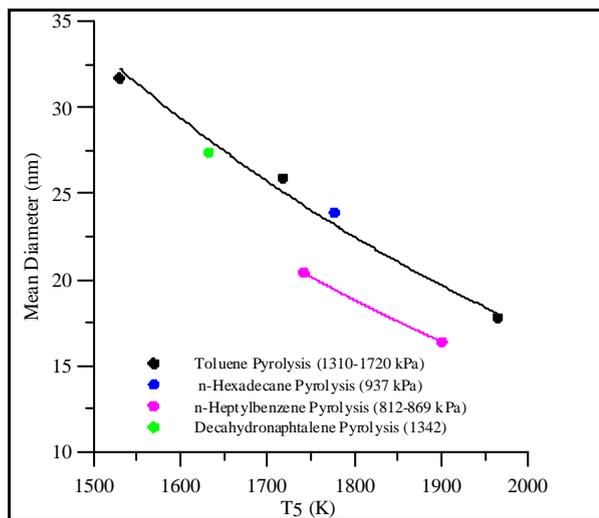


Figure 6. Mean diameter of the spheres, in function of the temperature for different hydrocarbons.

Influence of the initial temperature and oxygen ratio on the sphere size

The temperature effect is more pronounced when the oxygen is added to the mixture. The mean diameter of the spheres varied with the temperature as well as with the equivalence ratio. For O_2 /toluene ratio of 0.5, the mean diameter is 26 nm at 1700 K and drops to 13 nm at 2000 K. For a ratio of 1.8 and at 2000 K, the aggregates were more compact and the spheres are smaller : 18 nm at 1639 K (Figure 7).

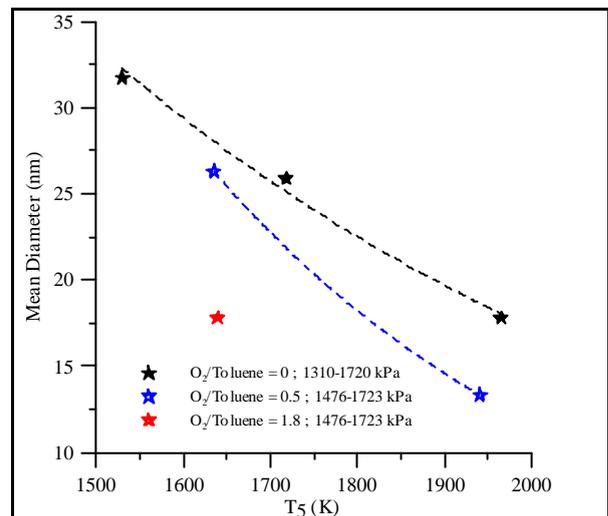


Figure 7. Mean diameter of the spheres, in function of the temperature for toluene at different O_2 /toluene ratios.

The oxidation could be responsible for a burn-off of the external part of the spheres. The other precursors seem to be less sensitive to the oxidation effect.

Influence of the initial temperature on the sphere structure

At higher magnification (310,000x), one could study the sphere microtexture and structure (Figures 8 & 9). The soot organization is usually due to a concentric arrangement of polyaromatic planes of nanometric size. These planes are frequently stacked by 2 or 3 to form Basic Structural Units (BSU). Globally, their

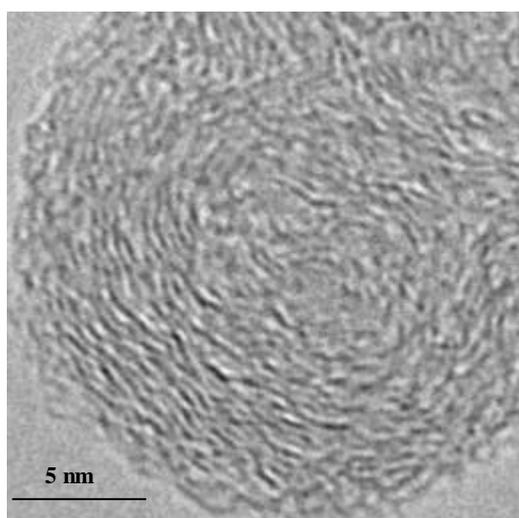
mean size L tends to increase with the temperature, whereas d_{002} decreases [1,2]. During the pyrolysis as during oxidation, the spheres present the same onion-like microtexture, i.e. a concentric arrangement of the BSU, and the order remains turbostratic as shown by the electron diffraction patterns. Such organization is similar to the one described for the carbon black particles [4]. The mean size L of the layer is 0.58 nm, whereas the largest size is more than 5 nm. A more detailed observation shows that the spheres are frequently constituted of 2 concentric zones. The inner core in which the BSU comprised no more than 2 stacked layers with a larger d_{002} . In the outer shell, the BSU were constituted of several layers (more than 3) and d_{002} is smaller. This spacing decreased as the number of the layers in the stack increased. At higher reflected shock temperature (1965 K), the mean length of the planes do not significantly change (about 0.6 nm), whereas d_{002} decreased from 0.43 nm to 0.39 nm in the inner zone and remains constant (0.39 nm) in the outer shell. As the temperature increases, the samples become relatively heterogeneous. At the highest temperature here studied (2599 K), the sample is highly heterogeneous, structurally and microtexturally. A quasi-amorphous phase (Figure 10a) coexists with a partially graphitized concentric carbon phase (Figure 10b), very similar to graphitized black carbons [5]. Such phases appear very similar to the ones obtained during the fullerene and nanotubes synthesis in an electric arc device [6] where the temperature are assumed to be above 2000°C.

As far as the nature of the precursor is concerned, only small differences were observed according to the toluene-based soots. The mean interlayer spacings d_{002} are always equivalent (0.39 nm). At about 1700K, with the n-heptylbenzene, and especially the n-hexadecane, the mean size of the layers L and the largest layer L_{max} are smaller. They are respectively 0.52 and 4.4 nm for the n-heptylbenzene, and respectively 0.50 and 2.0 nm for the n-hexadecane to be compared with the toluene values ($L = 0.58$ nm and $L_{max} = 5.7$ nm). The small sizes observed for the n-hexadecane precursor could be due the linear structure of the molecule.

Pyrolysis in presence of oxygen

With an O_2 /toluene ratio of 0.5 and at 1685 K, d_{002} is about 0.45 nm in the inner zone, i.e. slightly larger than for the pure pyrolysis. This could be due to the oxygen atoms grafted on the layer boundaries. d_{002} decreases to 0.39 nm as temperature is raised to 2000 K. In the outer shell, d_{002} does not vary with the temperature and remains at 0.39 nm.

Whatever the equivalence ratio is, the mean layer extent L and the largest layer L_{max} tend to increase with the temperature (compare Figures 8 & 9). Between 1700 and 2000K, this phenomenon appears slightly more pronounced than in absence of oxygen (pure pyrolysis). By reference to a similar increase of the layers of active carbons submitted to CO_2 activation [7], such an effect could be due to a preferential burn off of the shortest and more distorted layers.



0,66% toluene + 0,34% O_2 + 99% argon
 $T_5 = 1635$ K, $P_5 = 1723$ kPa

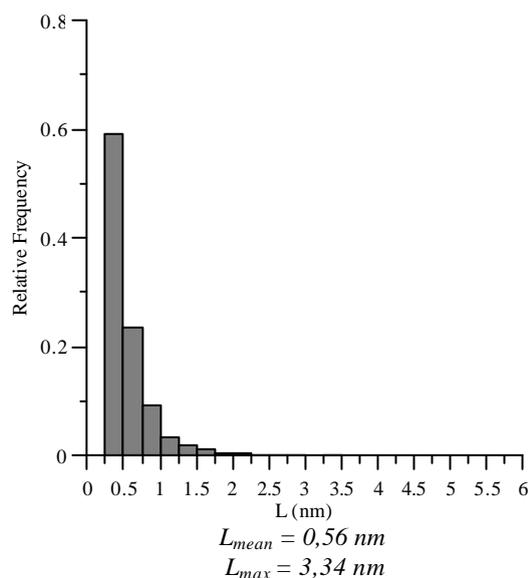


Figure 8. High Resolution TEM Micrograph and mean layer diameter distribution for toluene / O_2 / Argon mixture (O_2 /toluene = 0.5); $T_5 = 1635$ K, $P_5 = 1723$ kPa.

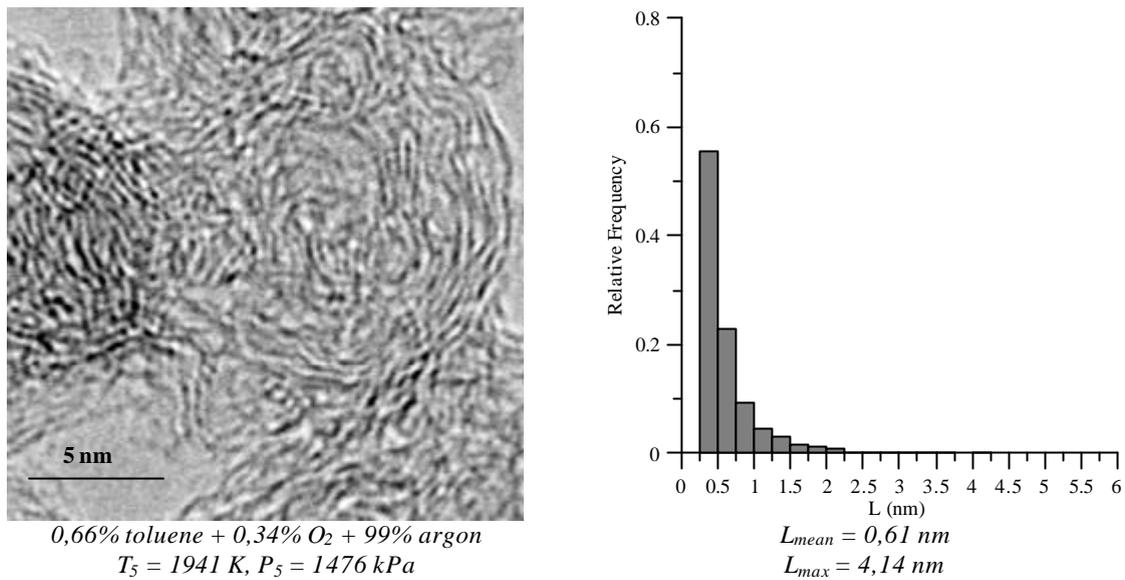


Figure 9. High Resolution TEM Micrograph and mean layer diameter distribution for toluene / O₂ / Argon mixture (O₂/toluene = 0.5); $T_5 = 1941 \text{ K}$, $P_5 = 1476 \text{ kPa}$.

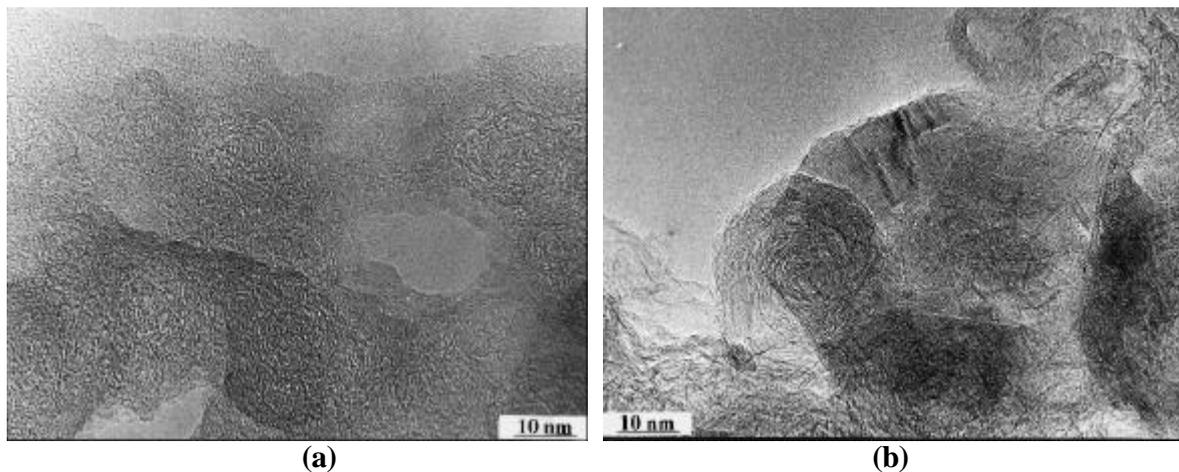


Figure 10. High Resolution TEM Micrograph of a soot obtained from 1% toluene + 99% Argon mixture at $T_5 = 2599 \text{ K}$ and $P_5 = 1817 \text{ kPa}$; visualisation of the soot heterogeneity : a quasi-amorphous phase (a) coexists with a highly organised phase (b).

Conclusion

The study of the soots synthesized in a shock tube give new information on the formation and growth of carbon nanoparticles occurring at high temperatures (up to 2600K) and in an oxidizing atmosphere. By using an in-home made analysis procedure of the TEM images, the multiscale organization (texture, microtexture and structure) can be now quantified in

detail. The effects of the presence of oxygen was also specified: oxygen atoms could limit the layer extent and oxidation reduce the spheres size. An increase of the temperature reduces also the mean sphere size and affects the fractal dimension. Such shock tube experiments have to be developed in order to acquire pertinent data required for a better understanding of the soot formation in the diesel engine. The better knowledge of the multiscale organisation of the soot

could allow a better expectation of their optical properties, as well as their density. One has to remember that many parameters (soot yield, growth rate for instance) are here deduced from a laser light absorption technique. Up to now, all the studies make the assumption that the soot are the same no matter what the precursor is or the temperature at which the soot are formed. A refinement of the value of the complex refractive index according to the soot nature could lead to a better precision in the determination of the main characteristics of the soot formation by the shock tube techniques.

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