

## High-temperature ultrafine aerosol formation burning low quality fuels

Francesco Carbone, Federico Beretta, and Andra D'Anna  
Istituto di Ricerche sulla Combustione – Consiglio Nazionale delle Ricerche  
Piazzale Vincenzo Tecchio 80, 80125 Napoli, Italy

An experimental study of the mechanisms of ultrafine particle formation from low quality fuel combustion is reported. Many residual products of petrochemical industry are enriched in heavy carbonaceous species and/or ashes. They are commonly considered wastes, even if their energy content is yet significant. Energy recovery and waste amount reduction from such low quality fuels may be performed through high temperature oxidation of their combustible fraction provided the control of their emissions including particulate matter and hazardous pollutants. In this paper, liquid and solid low quality fuels are oxidized in an atmospheric pressure entrained flow reactor. An oxygen rich, laminar premixed flame provides the hot gases flow where fuels are homogeneously added and burned. Generated aerosol are sampled downstream the reactor to perform on-line analyses. The size distribution function of ultrafine particles (1nm-150nm) was measured by the Differential Mobility Analysis technique coupled to a rapid dilution probe sampling. Experimental results show that ultrafine particles have a multimodal size distribution function in all investigated cases. Carbonaceous nanoparticles directly generated from carbonaceous fraction oxidation have size smaller than 10nm whereas ashes nucleate with larger sizes. Coagulation and condensation of volatile components seem to be the controlling mechanisms for the observed multimodal behavior of the ultrafine particle size distribution function.

### 1. Introduction

Fuel oils as well as heavy hydrocarbon/ash containing substances are largely used to produce heat or electrical power (Beer, 2000). Such fuels are both mineral and petrochemical industry products. Such products are both desired components, i.e. pyrolysis oils from biomasses, or waste components to be disposed preferentially recovering their energy content.

The most important drawbacks of low quality fuel combustion are related to the formation and emission of particulate matter significantly contributing to atmospheric pollution. Such particles can be generated via hydrocarbon pyrolysis both in vapor (Heines and Wagner, 1981) and liquid (Nettleton, 1979) phases, and because of the not combustible/ash fraction of the fuels. Particles are both carbonaceous and inorganic and might have sizes ranging from few nanometers to several hundred of microns (Lighty et al., 2000). Among the combustion generated aerosol the ultrafine fraction ( $D < 100\text{nm}$ )

has the strongest human health effects (Oberdorster et al., 2005). Nanosized particles ( $D < 10\text{nm}$ ), deeply penetrating in human body, are also of concern because of their huge number even for small mass concentration (Carbone, 2010a). Recent results show that nanoparticles are generated in not negligible amounts also from pulverized coal combustion and they can have several origins (Carbone et al., 2010b-c). This paper extends previous studies on coal combustion to the combustion of heavy oils in a laboratory scale flow reactor with particular emphasis to the determination of ultrafine particle distribution function in different operating conditions.

## 2. Experimental

A fuel lean flat laminar premixed flame operated at atmospheric pressure is used as the flame environment in which droplets of fuel oils are injected. The flame is sustained by vaporized n-heptane and it is homogeneously doped with droplets of fuel oils dissolved in n-heptane. The droplets are monodisperse in size (about  $70\mu\text{m}$ ). The fuel oil droplets only slightly modify the flame stoichiometry.

Two low sulfur n.5 fuel oils whose main properties are reported in Table 1 have been used. They differ for the ash content which is very low for the Pavia oil whereas it is about 0.29%wt for the CSZ oil. The oils are previously heated and subsequently dissolved in n-heptane with 5%wt concentration.

A Berglund-Liu-type Vibrating Orifice Aerosol Generator (VOAG model 3450, TSI), is used to feed the flame. It supplies a constant flow of  $235\mu\text{l}/\text{min}$  through a  $30\mu\text{m}$  orifice oscillating at a frequency of 20KHz. The VOAG syringe pump is immersed into an ultrasonic thermostatic bath at  $55^\circ\text{C}$ , to prevent fuel oil droplet growth and viscosity increase involving the orifice clogging. The fuel oil flow rate is of about  $7.5\text{ mg}/\text{min}$ . The droplets are dispersed and diluted in air with a flow rate of  $2.4\text{ l}/\text{min}$  (STP), preventing their coalescence. The resulting gas/droplet mixture is fed to the burner.

The burner consists of two coaxial stainless steel tubes and it is similar to that used in previous works (Carbone et al. 2010b-c). The inner tube ( $18\text{ mm ID}$ ) is used to carry the reacting mixture and one inch long Silicon Carbide honeycomb (300 CPSI, CTI s.a.) is placed on its top. Inner tube wall temperature was kept constant at  $120^\circ\text{C}$  to prevent n-heptane condensation. The outer ring ( $24\text{ mm ID}$  and  $34\text{ mm OD}$ ) is fed with  $9.0\text{ l}/\text{min}$  (STP) of sheath argon to minimize surrounding air entrainment/perturbation and reduce flame flicker. A flat plate is also placed at  $90\text{ mm}$  from the burner mouth.

The n-heptane completely evaporates through the honeycomb and the vapor burns stabilizing a flat premixed flame on the honeycomb mouth (cold gas velocity is  $16\text{cm}/\text{s}$ ). The flame equivalence ratio is 0.75 and the composition of the exhaust gases results in 5% of  $\text{O}_2$ , 9.5% of  $\text{CO}_2$  and 11% of  $\text{H}_2\text{O}$  in nitrogen.

*Table 1 Main properties of the used Pavia and CSZ fuel oils.*

Property	Pavia	CSZ
Density at $15^\circ\text{C}$ , $\text{Kg}/\text{m}^3$	995.80	991.60
Viscosity at $50^\circ\text{C}$ , cSt	180	120
HHV, kcal/kg	10.59	9.98
Ash, ppm wt	<100	29000
Sulfur, %wt	0.83	0.31

Fuel oil droplets survive after n-heptane evaporation and they are homogeneously carried in the flame where they devolatilize, ignite and oxidize downstream of the flame front. Temperature along the reactor axis has been measured and corrected for radiative losses, using a 250 $\mu$ m Pt/Pt-13%Rh thermocouple (Type R, Omega Engineering). Pure n-heptane is used during temperature measurements. Particle residence time in the reactor has been estimated assuming that particle velocity equals that of the hot gases.

### 2.1 Particle size distribution function (PSDF) measurement technique

PSDFs are on-line measured using a horizontal rapid dilution probe (8mm ID, 9mm OD) delivering the aerosol to a TapCon 3/150 Differential Mobility Analyzer (DMA). The aerosol is drawn through a pinhole, drilled on the probe wall, as effect of a slight underpressure into the tube where particle free nitrogen steadily flows (29.5l /min) (Kasper et al., 1997). Three probes with 0.3mm, 0.9mm and 1.5mm sampling pinhole diameters were used to perform dilution ratios ranging from  $1 \cdot 10^3$  to 30. The diluted aerosol temperature does not exceed 45°C while cooling rate is of order of  $10^5$ - $10^6$ Ks<sup>-1</sup>. Dilution is required to control coagulation during sampling and to reduce particle concentration within the electrometer detection range (Carbone, 2010b-c). The DMA was operated in three modalities, selected changing the maximum voltage applied to the electrostatic classifier and the sheath air flow rate. The measurements allow to reconstruct a PSDF in the size range from 1 to 150nm merging results obtained applying the several dilutions. All measurements were performed positioning the sampling pinhole on axis at a height above the burner (HAB) of 50mm that corresponds to a residence time in the reactor of about 55ms. The measured number PSDFs are averaged on more than 10 scans and corrected for dilution. Volume PSDFs are obtained by multiplying each point of the number PSDFs by the corresponding particle volume, calculated with the approximation of spherical particles. Such diameter are smaller of  $D_0=0.5$ nm than the mobility diameter (Fernandez de La Mora et al., 2003). PSDFs are subsequently fitted adding several lognormal distributions whose parameters  $N_i$ ,  $\langle D \rangle_i$  and  $\sigma_i$  are the number concentration, median diameter and width, respectively:

$$\frac{dFv}{d \ln D}(D) = \frac{\pi}{6} [D - D_0]^3 \cdot \frac{dN}{d \ln D}(D) = \frac{\pi}{6} [D - D_0]^3 \cdot \sum_i \frac{N_i}{\ln(\sigma_i) \sqrt{2\pi}} \exp \left\{ -\frac{1}{2} \left[ \frac{\ln D / MD_i}{\ln(\sigma_i)} \right]^2 \right\} \quad (1).$$

## 3. Results and discussion

Visual flame observation shows that a premixed flame zone, evidenced by a blue light emission, is stabilized close to the burner mouth. Temperature in this flame region reaches values of the order of 1700K thereafter it decreases to values as low as 1300K at increasing heights above the burner. At 50mm above the burner, i.e. the location in the reactor where sampling is performed, temperature is of the order of 1350K. The ignition of the droplets occurs immediately downstream of the flame front (residence time of about 1ms) whereas the endpoint of the luminous strikes, corresponding to burning quenching, occurs at about 45mm (residence time of about 35ms). A diffused orange luminosity is observed up to about 30mm. It is probably due to the radiation due to pyrolysis products formed during fuel oil oxidation in the post-flame zone.

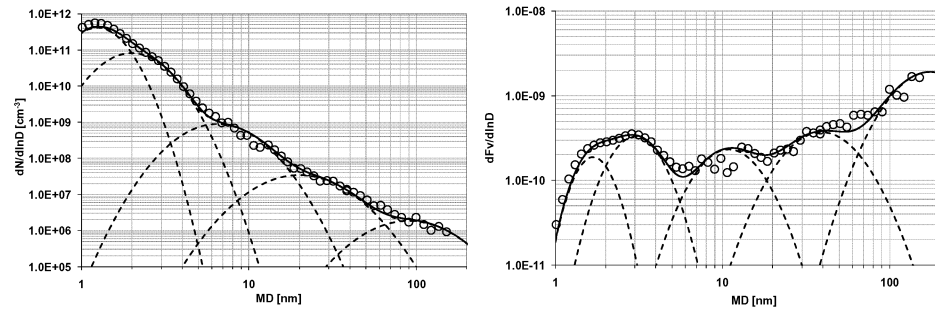


Figure 1 Size distribution functions of ultrafine particle generated using the Pavia oil. On the left column, number PSDFs measured for the Pavia oil, corrected for the dilution ratio. On the right, reconstructed volume PSDF. Solid lines show data fitting performed using five lognormal modes (dashed lines).

Table 2 Parameters used to reproduce the experimental data with a sum of modes (lognormal distribution functions)

Mode	Pavia			CSZ			CB	
	$N, \text{cm}^{-3}$	$MD, \text{nm}$	$\sigma$	$N, \text{cm}^{-3}$	$MD, \text{nm}$	$\sigma$	$MD, \text{nm}$	$\sigma$
I	2.7E11	1.25	1.3	2.3E11	1.3	1.35	1.6	1.35
II	7.0E10	2.0	1.4	7.0E10	2.2	1.5	-	-
III	9.0E8	6.5	1.5	8.0E8	6.5	1.5	-	-
IV	4.0E7	20	1.6	5.0E7	20	1.6	-	-
V	2.2E6	90	1.6	6.0E6	90	1.6	-	-

Measurements of particle sizes performed at the end of the reactor show a high number concentration for  $D < 2$  nm particles. Background measurements were performed on oil-free flame, pure nitrogen, and ambient air, to assess the influence of artifacts in the sampling and measurement procedure. Background signals are significantly smaller of that obtained in the flame for  $D > 1$  nm.

Figure 1 reports on the left column the PSDF in number, measured on the axis at  $HAB = 50$  mm using the Pavia oil. The PSD function is firstly measured at the highest DR to prevent particles coagulation in the probe. It shows a very large number of particles with sizes between 1 nm and 2 nm while particle number concentration falls by orders of magnitude with increasing sizes.

The entire ultrafine PSDF is obtained by merging measurements at the highest dilution for  $D < 10$  nm with that at intermediate dilution for  $D$  from 10 nm to 20 nm and that at the lowest dilution for larger sizes. The particle number is huge because of smallest particles whereas it falls by six orders of magnitude with increasing sizes. Data fitting has been performed adding five lognormal distributions and it is also plotted in Fig. 1. The modes of the PSDF are more clearly identified in the volume PSDF that shows concentration ranging from tenth of ppb to a ppb depending on  $D$ .

The same experimental and fitting procedures described for the Pavia oil, have been used for the analysis of results obtained using the CSZ oil. The PSDF obtained from the oxidation of carbon black (CB) in a similar reactor have been adapted from Carbone et

al. (2010c) and fitted too. The value of the parameters to reproduce all the experimental data are reported in Table 2. The PSDFs are converted in number and volume yields of ultrafine particles on oil mass basis, and reported in Fig.2. The number yields is huge and it range from  $10^6$  to  $10^{12}$  particles per microgram of fuel to be burn. The volume yield range from some tenths up to several cubic millimeter per coal gram. This implies that ultrafine particles, assumed to have unit density, are from  $\sim 0.01\%$  for the CB to  $\sim 0.6\%$  for the Pavia oil and  $\sim 0.8\%$  for the CSZ oil, of the fuel mass.

The PSDFs obtained using the two oils are almost identical in the size range between 10nm and 50nm where the contribution of particles generated from carbon black is completely negligible.

Comparison of PSDF obtained during oil combustion with that obtained with a pure carbonaceous compound such as Carbon Black particles shows that particles smaller than 10nm produced during oil combustion can be carbonaceous particles. Their yield is almost unaffected by the fuel type and it of the order of 0.1% as shown in Fig.3 where the yields of the different modes of the PSDFs evaluated for the three fuels are reported. Larger size modes are not present in carbon black combustion whereas they are significant for the other two fuel oils. Moreover significant larger yields are obtained from the CSZ oil having the highest ash content. Ashes seem to preferentially nucleate with sizes larger than 20nm and for the fuels having larger ash contents.

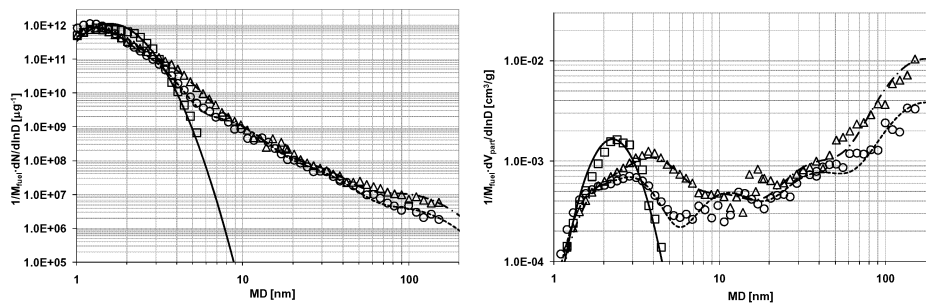


Figure 2. Number (left) and volume (right) yields on oil mass basis of ultrafine particles. Lines are the best fit of results:  $\circ$  Pavia oil;  $\Delta$  CSZ oil;  $\square$  Carbon Black.

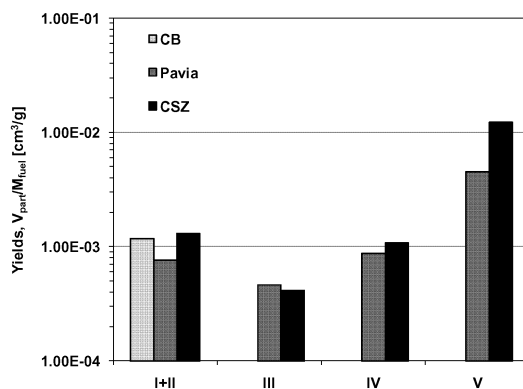


Figure 3. Yields of the different modes of the PSDFs evaluated for the three fuels: light grey Carbon Black; heavy grey Pavia oil; black CSZ oil.

#### 4. Conclusion

PSDFs obtained from fuel oil combustion in laboratory reactor have been measured from 1nm to 150nm and compared to that obtained from carbon black oxidation in similar conditions. Ultrafine PSDFs are multimodal for all investigated low quality fuels and they are satisfactorily reproduced by the sum of five lognormal modes. The modes are roughly centered at 1.5, 3.5, 10, 40, 150nm, respectively. Results reported in this paper clearly show that ultrafine ( $D < 150\text{nm}$ ) and nano ( $D < 10\text{nm}$ ) particles have a very high number concentration so that they cannot be neglected. Comparison of the results from different fuels allowed to get information on the origin of each mode of the PSDF. The smallest modes are attributed to carbonaceous particles from carbonaceous fraction oxidation. Ash nucleation seems to be the principal formation mechanism of particles in the larger size modes.

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