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A Study on the Structural Properties of Aerosols from Biomass Combustion for Domestic Heating

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Biomass combustion leads to the release of huge amounts of toxic contaminants that disturb the atmospheric ambient interfering on climate and creating appalling health effects. However, there is still a lack of information on the physicochemical properties of the emitted products, in special with regard of the particulate phase.
The main goal of this study was the characterization of size and morphology of particles emitted from combustion of wood from three common Iberian trees (oak -*Quercus pyrenaica*-, beech -*Fagus sylvatica*- and poplar -*Populus nigra*-), in a woodstove. The size of the monomers and the morphological descriptors of the carbon aerosol aggregates were studied by Scanning Electron Microscope (SEM) and Digital Image (DIA) techniques.
The morphological characterization, by parameters such as elongation, concavity and sphericity, allowed to directly link the carbon emission factors (organic carbon vs. elemental carbon, determined by a thermo--optical method), and thus the combustion efficiency rather than with the type of wood, with the recently emitted fresh carbon aggregate structure. A major compactness on the fresh structure will be directly favor the adsorption of readily available atmospheric compounds, directly related to a quicker and higher degree of photochemical oxidation in the atmosphere and severe climate and environmental effects.

1. Introduction

During the last years, the use of biomass burning as energy source has been encouraged in the developed countries in order to reduce the consumption of fossil fuels and the and thus reduce the CO_2 emissions related. However, the atmospheric brown cloud phenomena characterized by a high content of soot that especially affects the tropical Indian Ocean has been directly associated with inefficient biomass burning activities and it is considered as the second major agent that contributes to global warming (RamanathanandCarmichael, 2008). The scientific community is on alert and the debate is on the table. Whether an increase on the use of wood burning in the mix of fuels for energy production might be favorable in terms of pollution and climatic effects might be attached to the type and form of fuel and combustion type and efficiency. Thus, more specific information on the emitted products, optical and hygroscopic properties and subsequent atmospheric reactions from this type of combustions are urgently needed, especially in terms of deciding a proper use and abatement strategies.
Biomass combustion as source of thermal energy in domestic environments is not only typical from the Indian subcontinent. The use of woodstoves for heating is quite common in the Central and Northern European regions, where biomass combustion can contribute up to 70 % of particulate organic matter in rural regions of Europe during winter time (Puxbaum et al., 2007). But the use of wood as fuel for domestic heating increased in the Mediterranean countries during the last years. Only in Portugal, it has been estimated an annual of consumption of 1.950 kt (Gonçalves et al., 2012).

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Particles emitted by the combustion of the biomass products are frequently associated to high OC/EC, mainly due to the production of high contents of Primary Organic Aerosols (POA) that enhance the production of initial Organic Aerosol mass (Puxbaum et al., 2007). These higher OA contents right after formation lead to a more complex state of mixture in the initial microstructure. Recent studies suggest that this initial high OA production does not necessarily imply a subsequent high formation of secondary products, since they found much lower Total OA to POA ratios than those observed for urban environments (Ortega et al., 2013).
This type of combustion generates a carbonaceous aggregate forming a complex structural unit of assembled monomers several nanometers in size, also including metallic nanoinclusions and coated by a variety of chemical compounds. Determining whether those monomers are a chain-like construction or collapsed porous structures, as well as the nature/thickness of the coating layers, are crucial to accurately determine their climate change implications (Adachi et al., 2010; CozandLeck, 2011; Shiraiwa et al., 2010).
The purpose of this study was to obtain specific information about the difference in structure from the particles emitted in a set of different controlled tests involving the combustion of three typical Iberian wood species in a woodstove.

2. Methodology

2.1 Fuel characteristics

Wood from three typical Iberian tree species, oak -*Quercus pyrenaica*-, beech -*Fagus sylvatica*- and poplar -*Populus nigra*-, was used as fuel**.** The wood was cut into logs of 0.3 to 0.4 m in length (Figure 1a) with a total biomass burned during each cycle of around 1.7 to 2.0 kg. The combustion of a batch of fuel lasted between 45 and 60 min, depending on the physical-chemical characteristics of the biomass fuel and on the mass of the fuel batch used. Between three and five burnings of each wood type were carried out.

2.2 Experimental set up

The biomass combustion experiments were carried out with a typical Portuguese wood stove (Solzaima, model Sahara) commonly used in Portugal for domestic heating (Figure 1b). Made in stainless steel, with the front panel and grate made in cast iron, it is characterized by a 0.093 m^3 combustion chamber of 0.44 m height, 0.59 m width and 0.36 m depth in dimensions. It was equipped with a vertical chimney with 0.2 m internal diameter and 3.3 m height. The combustion air entered the combustion chamber below the stove grate by natural convection, and flowed throughout the grate and the fixed bed of burning biomass. The combustion flue gas composition was continuously monitored at the exit of the chimney (at 2.8 m above the exit of the stove combustion chamber), namely for total volatile hydrocarbons (THC), O_2, CO_2 and CO. Temperature was monitored continuously using several K-type thermocouples at different locations. The weight of fuel at the grate of the stove and of the airflow rate entering the combustion chamber were continuously monitored by a weight sensor (load cell DSEUROPE Model 535QD-A5) and a mass flow meter (Kurz, Model: 500-2.0-P 40), respectively.

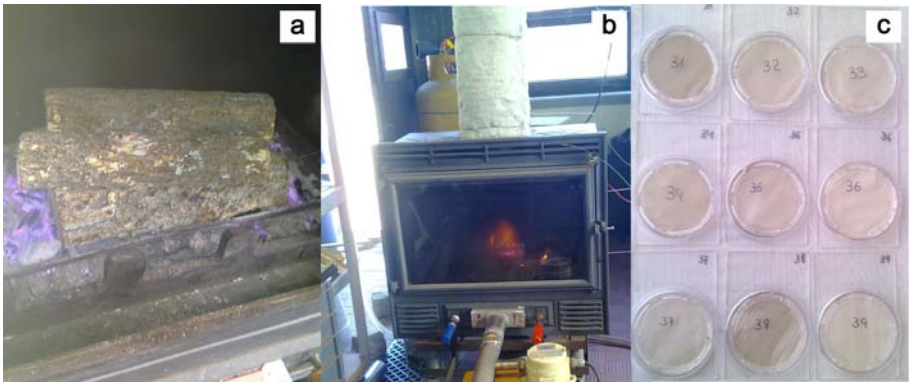

Figure 1: (a) detail of the wood logs in the combustion chamber, (b) view of the stove during combustion, and (c) filters for subsequent microscopy analysis

2.3 Sample collection and preparation

For particle sampling, two different dilution steps were carried out: i) a first dilution tunnel was installed downstream of the chimney in order to dilute the combustion flue gas exiting the chimney. This dilution tunnel consists of a tube of circular section with 11 m length and 0.20 m internal diameter. The gas velocity

in the cross section of the dilution tunnel was determined using a Pitot tube, a pressure sensor and a K-type thermocouple; this allowed the calculation of the volumetric gas flow rate throughout the tunnel, and respective combustion gas dilution ratio. ii) In order to reduce the particle concentration before sampling, another dilution step was needed. A Venturi system was used in order to take a sample from the dilution tunnel. Around 60 L/min of filtered dry compressed air were used in order to take ~ 10 L/min of sample from the dilution tunnel under isokinetic conditions. This flow was conducted through a second tunnel of ~1.13 m length and 0.07 m internal diameter, where it was diluted again with ~ 350 L/min of filtered dry compressed air. More details of the experimental setup can be found in Tarelho et al. (2011) and Calvo et al. (2011). The sample collection for microscopy study was conducted with a Gent PM_{10} stacked filter unit sampler using polycarbonate filters (0.2 μm pore size). The Gent was placed at the end of the second dilution tunnel. The samples were stored in sealed Petri dishes and stored at low temperature (<10ºC) to minimize losses (Figure 1c). A circle of 12 mm of diameter in each filter was cut and pasted onto a brass stub with double sided carbon conducted stickers. The samples were Au-Pd coated during 60 s to favor conductivity and avoid charges during imaging in the electron microscope. A total of 8 samples were analyzed at different burning phases: Beech (at initial and intermediate burning phase), Oak (at initial and final burning phase), and Poplar (at intermediate and final burning phase), see Table 1.

2.4 Scanning Electron Microscopy

A Jeol JSM 6335F equipped with an Energy-Dispersive X-ray Spectrometer (Oxford Instruments, X-Max model) was used for imaging the aggregates in the samples. Images from 25,000-100,000 times in magnification were acquired to guarantee errors smaller than 10% on the image measurement in more than 12,000 particles. The size of the individual spherules contained in the aggregates and shape parameters from the particles were measured by image processing. The size of the spherules were determined by following the method in Xiong and Friedlander (2001). Three different morphological parameters were measured onto the aggregates:

(a) Circularity = $4 \cdot \pi \cdot \text{Area}/\text{Perimeter}^2$. This shape parameter compares the surface of the particle surface with a circle of the same perimeter. The circularity is generally sensitive to the departure from roundness exhibited by the particle and needs to be interpreted with caution. In theory, it is circularity reaches the value of 1 for perfect spheres and decreases with as the particle becomes more irregular or elongated.

(b) Elongation = $(D_{max}-D_{min})/(D_{max}+D_{min})$. This parameter measures the level of *anisometry* of the particle and is estimated from the particle minimum and maximum diameters (D_{min}, D_{max}) of a regular equivalent ellipse, where D_{max} is the longest projection of the aggregate and D_{min} is the shortest projection of the estimated ellipse. Elongation is close to zero for compact aggregates increasing with the aggregate's ramification.

(c) Convexity = $\text{Area}/\text{Area}_{convex}$. It is calculated as the ratio between the area of the particle (Area) and the area of a polygon of n sides in which the particle is inscribed (Area_{convex}). The convexity is close to 1 when the aggregate is compact and decreases as aggregate ramification increases (CozandLeck, 2011).

Table 1: Tests, type of fuel, phase of combustion during sampling, mean and standard deviation values of the morphological parameters and OC/EC and EC/$PM_{2.5}$ ratios during combustion

Test	Fuel	Phase	Elongation	Convexity	Circularity	OC/EC	% EC/$PM_{2.5}$
Q3	Beech	Initial	0.38±0.23	0.89±0.11	0.86±0.2	3.77	16.45%
Q6-A	Beech	Initial	0.38±0.22	0.89±0.14	0.86±0.21	**11.31**	**6.11%**
Q6-B	Beech	Middle	0.42±0.23	0.86±0.13	0.77±0.26		
Q7	Poplar	Final	0.42±0.22	0.87±0.13	0.81±0.26	8.01	8.58%
Q9	Poplar	Initial	0.37±0.23	0.89±0.12	0.83±0.25	4.22	16.14%
Q10	Oak	Middle	0.44±0.23	0.87±0.12	0.8±0.25	3.36	19.71%
Q11-A	Oak	Middle	**0.46±0.22**	**0.78±0.13**	**0.61**±0.28	**2.07**	**28.23%**
Q11-B	Oak	Final	**0.53±0.24**	**0.73±0.15**	**0.46**±0.29		

3. Results

3.1 Size of the monomers

For the biomass combustion experiments, the size distribution of the primary particles or monomers comprising the aggregates fitted a lognormal distribution with only one mode in a range from 20 to 80 nm and peaks between 30 and 47 nm depending on the type of wood (Figure 2), with larger sizes for the oak aggregates and smaller for the aggregates resulting from beech combustion. Median diameters between 39 and 47 nm have been previously found in aggregates resulting from combustion of different types of biomass fuels (Chakrabarty et al., 2006). Mean values of 38 ± 12 nm are presented by Sachdeva and Attri (2008) for this type of small-scale combustion. These sizes are larger than that of monomers emitted from diesel engines, which generally have mean diameters closer to 20 nm (XiongandFriedlander, 2001).

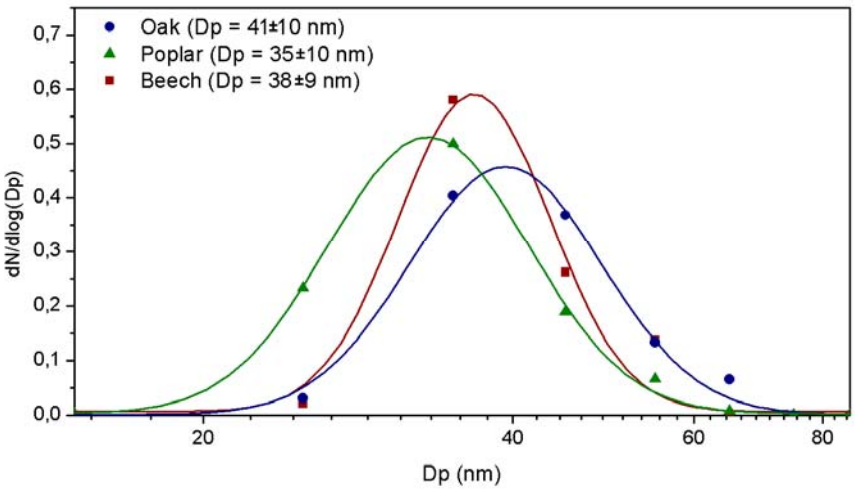

Figure 2: Lognormal curves of the size distributions of the monomers resulting from combustion of oak, poplar and beech experiments, respectively

One interesting finding is the lack of a second mode in the size distribution of the monomers, typical from biomass combustion, that corresponds to the formation of a very specific type of carbonaceous particle known as “tar ball” (Figure 3), which peaks generally fall in larger sizes than 100 nm (Chakrabarty et al., 2006). These “tar balls’’ were defined by Pósfai et al. (2004) as amorphous, carbonaceous spherules that occur in the tropospheric aerosol as a result of biomass and biofuel combustion. They are particularly abundant in slightly aged (minutes to hours old) biomass combustion flue gas, indicating that they likely result from gas-to-particle conversion within smoke plumes (Pósfai et al., 2004), and this is a possible reason why they were not that representative in the set of experiments in this work.

Tar balls are readily identifiable by electron microscopy by their lack of ordered microstructure, what also makes them easily distinguishable from the soot spherules. The absence of crystallization can be associated with the low content of elemental carbon (EC). Brown carbon, a class of light absorbing organic carbon, with an effective resonance wavelength in the ultraviolet (UV) spectral region, has been found to be an important component of tar balls (Chakrabarty et al., 2010). During our set of experiments, a large variability has been found in the relationship between the absorption on the UV wavelength and the rest of the wavelengths used in the aethalometer model (Harrison et al., 2013). This is a method that has been increasingly used to distinguishing biomass from fossil fuel sources by the estimation of the Angstrom coefficient –α–. Further study will be needed to investigate whether these variations could be associated with a higher/lower tar ball concentration in the aerosol samples.

3.2 Morphological properties of the aggregates

The results of the morphological parameters are shown in Table 1. Mean elongation, convexity and circularity ranges of 0.37-0.53, 0.73-.89 and 0.46-0.86 have been recorded respectively, all of them with similar standard deviation in each of the three cases. These values correspond to an intermediate stage between open branched aggregates and highly compacted ones, which already differs from the general association of fresh combustion aggregates to a high degree of ramification. The values from the particles in experiments Q3, Q6, Q7, Q9 and Q10 are more compact right after formation with similar morphological values to those from the Indian Subcontinent (CozandLeck, 2011). This region is known for the presence of the atmospheric brown clouds mainly derived from the high “brown carbon” content (mentioned earlier)

in the abundant wood-combustion emissions characterized by a high light absorption. The results suggest that aggregates from biomass combustion can be associated from an intermediate to a high degree of compactness already right after formation and thus, compactness would not only come from atmospheric processing for them. On the other hand, the results from the experiment Q11 correspond to aggregates linked to a higher degree of ramification than the rest, more similar to what is generally associated with recently emitted ones (CozandLeck, 2011). This might be related to the combustion parameters during the combustion, in which the maximum temperature at the chamber is reached earlier than for the rest of the experiments and had smaller OC/EC ratio and a quite high EC/$PM_{2.5}$ concentration (Table 1). It is already known that the presence of organic coatings favour the collapse of the structure forming more compacted features. And so, a low organic content might help to preserve the fresh-like morphology in particles from experiment Q11.

One surprising result that the morphological parameters in the study have not been able to identify is a thick organic coating layer in the aggregates from experiment Q6 samples (Table 1) that made impossible the sizing of the monomers in these samples. This is probably related to the high OC/EC ratio during the experiment as consequence of a lower temperature during the combustion (the wood was slightly humid). The experiments had a maximum combustion chamber temperature in the range 600-650 ºC, excepting Q6 experiment where the maximum temperature reached in the combustion chamber was in range 400-460º. The introduction that better mathematically describes this behaviour will need to be investigated.

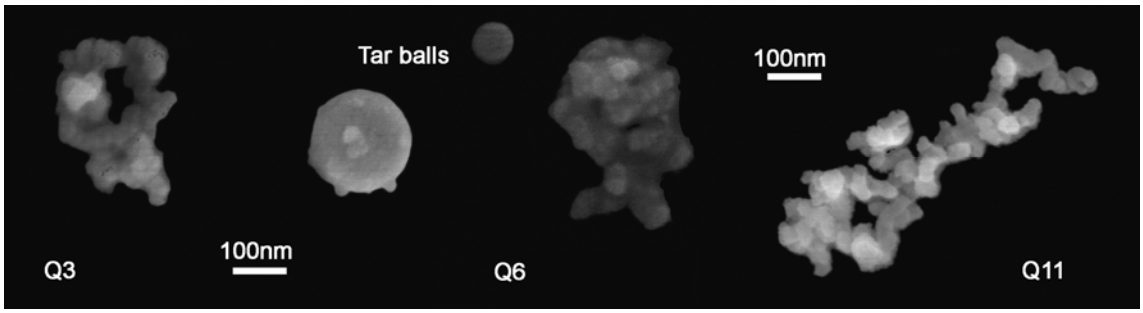

Figure 3: Examples of aggregates and tar balls in the samples from combustion experiments Q3, Q6 and Q11, respectively

This finding is especially interesting in terms of climate effects since it has been already demonstrated that particles from one or other type of morphology are associated with very different optical properties, as well as the thickness of the organic coating. Open, chainlike shapes absorbs sunlight less efficiently than if compact (Adachi et al., 2010). Organic coatings enhance the light absorption especially when the aggregate center is located within the coating layer but also alter the hygroscopic properties of the soot particles. Thus, the morphological results suggest that the particles are very probably associated with high a light absorption, and experiments Q3-Q10 are associated with higher light absorption coefficients than those in Q11 experiment. However, the results from the aethalometer in Harrison et al. (2013) show a high variability on the absorption response. A potential relationship between the particle morphology and this variability will be further investigated.

4. Conclusions

The structural characteristics of particles emitted in a set of controlled combustion experiments of three distinct Iberian wood species (oak -*Quercus pyrenaica*-, beech -*Fagus sylvatica*- and poplar -*Populus nigra*-) in a stove used for domestic heating have been studied. Similar results to existing published information have been found for the size of the soot monomers, whose mean diameters varied from 35 to 47 nm depending on the wood type. The size distribution of the monomers fitted a lognormal curve with a single mode. A second larger mode, generally associated with a high presence of tar balls was not observed, suggesting a relative low concentration of these tars in most samples, excepting for the combustion experiment Q6. The aggregates resulting from this combustion experiment were associated with a thick organic coating, probably linked to its OC/EC ratio, and thus, monomers and tar balls were nearly indiscernible within the structure.

The measured morphological parameters had mean values of 0.37-0.44 for the elongation, 0.87-89 for the convexity and 0.77-0.86 for the circularity for all the combustion experiment, excepting Q11. These values indicate an intermediate to high degree of compactness, being close to those found in atmospheric studies

in locations where wood-combustion emissions are predominant. This will imply that for these type of combustion aggregates can be already compacted readily after formation rather than by subsequent atmospheric processing. The aggregates from experiment Q11 had quite different mean values of 0.46-0.53 for elongation, 0.73-0.78 for convexity, and 0.46-0.61 for circularity. These values indicate a higher degree of ramification, being closer to the morphologies generally associated to fresh aggregates, especially those from fossil fuel combustion. This is probably related to the high concentration of EC in the samples, which is closer to that resulting from fossil fuels combustion.

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