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Atmospheric tar balls: aged primary droplets from biomass burning?

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Abstract

Atmospheric tar balls are particles of special morphology and composition that are abundant in the plumes of biomass smoke. These particles form a specific subset of brown carbon (BrC) which has been shown to play a significant role in atmospheric shortwave absorption and thus climate forcing. Formerly tar balls were hypothesized to be formed in secondary processes in the atmosphere from lignin pyrolysis products. Based on their typical size distributions, morphology, chemical characteristics and other features we now suggest that tar balls are initially produced by the emission of primary tar droplets upon biomass burning. To verify our hypothesis tar balls were produced under laboratory conditions with the total exclusion of flame processes. An all-glass apparatus was designed and tar ball particles were generated from liquid tar obtained previously by dry distillation of wood. The size range, morphology and the chemical composition of the laboratory-generated tar ball particles were similar to those observed in biomass smoke plumes or elsewhere in the atmosphere. Based on our results and the chemical and physical characteristics of tar we suggest that tar balls can be formed by the chemical transformation of emitted primary tar droplets.

1 Introduction

Light absorption by anthropogenic aerosol is getting increasingly important as carbonaceous particulates including soot (black carbon, BC) become more predominant in the chemical composition of tropospheric aerosol. Recent studies indicate that BC has become the second most potent climate forcing agent, now accounting for as much as 60 % of the energy attributed to the greenhouse absorption of excess carbon dioxide (Ramanathan and Carmichael, 2008). It should be noted, however, that unlike CO_2 that absorbs only in the infrared spectral range, atmospheric BC directly absorbs sunlight (both incoming and reflected) with an exceptionally high efficiency. On a per mass basis BC is 360 000–840 000 times more efficient in terms of instantaneous energy absorption than carbon dioxide (Jacobson, 2002), and its 100 yr global warming potential (GWP) is a factor of 700 higher than that of CO_2 (Bond and Sun, 2005). Contrary to the greenhouse gases, the mass concentrations of BC exhibit a very inhomogeneous spatio-temporal distribution in the lower troposphere due to BC's short atmospheric residence time as well as the distribution and variability of its emission sources. In addition, unlike greenhouse gases, BC is not a single chemical species of standard size, morphology, chemical and phase composition, and optical properties, but a sort of collective term for widely different light-absorbing particulates (Andreae and Gelencsér, 2006; Buseck et al., 2012). Furthermore, no single method exists for the atmospheric determination of BC, but an array of instrumental techniques based on fundamentally different principles (ibid.). As a result, any assessment of the global forcing of BC is loaded with very high uncertainty, at least a factor of 3 (Forster et al., 2007). Quite recently it has been established that a substantial part of the carbonaceous continuum (brown carbon, BrC) between pure graphite and non-absorbing organic aerosol contribute significantly to atmospheric light absorption globally (Chung et al., 2012). In spite of the fact that most climate models have so far ignored the absorption of BrC it may contribute by as much as 20 % to the total absorption at 530 nm. This high contribution of BrC absorption may result in a change of sign in the net TOA forcing of aerosols (from being reflective to slightly absorbing) over vast regions impacted by biomass smoke (idem). A specific group of atmospheric particles that likely belongs to BrC regarding its optical properties are tar balls which were first described in biomass smoke plumes with a contribution to particle number as high as 90 % e.g. in aged smoke from smoldering fire or during an active fire season in the western United States (Pósfai et al., 2003, 2004; Hand et al., 2005).

Tar balls can be easily recognized using transmission electron microscopy (TEM) by their relatively narrow size range, almost perfectly spherical shape, the lack of an internal core and their chemical composition. In contrast to other spherical aerosol types such as sulphates, the amorphous tar ball spheres are refractory and do not volatilize under the electron beam. These particles distinctly differ from Diesel soot particles as they have much larger geometric size, they occur externally mixed (i.e. without being coagulated with one another or other particles, including soot), and they do not have the internal fine structure of concentrically wrapped, curved graphene-like layers that are typical for soot.

According to electron energy-loss elemental mapping of individual particles, tar balls consist mostly of carbon and oxygen and only traces of sulphur, potassium, chlorine and silicon. These elements are homogeneously distributed over the entire volume of a relatively fresh tar ball particle. In the literature the C / O atomic ratio in atmospheric tar balls varies widely. Several studies established high C / O ratios (7–10) (Pósfai et al., 2003, 2004; Hand et al., 2005; Niemi et al., 2006; Adachi and Buseck, 2011), whereas others found some tar balls with significantly lower C / O ratios in the range of 1–2 (Tivanski et al., 2007; China et al., 2013).

It should be stressed that tar ball particles might undergo ageing processes in the atmosphere resulting in a significantly enhanced oxygen ratio in the outermost layer of the particles at a thickness of 30–40 nm (Hand et al., 2005; Tivanski et al., 2007; China et al., 2013). During their long range atmospheric transport tar ball particles occasionally form aggregates with up to 10 particles, including coagulation with dust particles (Hand et al., 2005; Deboudt et al., 2010).

It was hypothesized that tar ball particles form in secondary processes from pyrolysis products in the atmosphere (Pósfai et al., 2004). The authors assumed that the low volatility products of biomass pyrolysis undergo radical polymerisation with OH radical in multiphase reactions resulting in highly refractory carbonaceous particles. Based on the most characteristic features of the relatively fresh tar ball particles (spherical shape, large size, lack of coagulation, homogeneous composition, lack of internal core and graphene structures, high C / O atomic ratio) we now suggest a direct emission mechanism for the droplets which may then undergo transformation processes. Our hypothesis is that tar balls are ejected upon burning from the pores of plants as liquid tar droplets then undergo chemical transformations that increase their viscosity and solidify them into highly refractory particles, as observed in the atmosphere. Following this hypothesis the objective of our work was to generate pure tar ball particles from liquid tar-water emulsions in the laboratory, mimicking processes and conditions that may occur during biomass burning with one notable exception: with the total exclusion of contact with open flame. A secondary goal was to generate pure tar ball particles for experimentally determining their optical properties that are relevant in radiative transfer calculations.

2 Experimental

2.1 Particle generation and analysis

A closed all-glass apparatus (Fig. 1) was designed and constructed in which droplets were generated from tar-water emulsion (~ 1 : 1 volume ratio) by bubbling purified nitrogen (Messer, purity 99.5 %) through it. The bubbler was a 60 mL peptide synthesis fritted funnel of 10–20 µm porosity (Sigma-Aldrich Co.) which was held in a water bath at 99 °C. The generated droplets were passed through a glass tube of 200 mm long (12 mm internal diameter) heated directly with a Bunsen burner from outside. The temperature of the heated zone (30 mm long) varied between 560 and 630 °C, as measured with a thermometer (Testo 925 K-type thermocouple thermometer). Since the gas flow rate in the tube was $\sim 0.6\,\mathrm{L\,min^{-1}}$, the residence time in the heated zone was about 0.3 s. After the heated zone the nitrogen flow was mixed with dry air at a flow rate of $7.4\,\mathrm{L\,min^{-1}}$ then passed through a buffer volume of 10.75 L (residence time 1.2 min). At the outlet the particles were collected on TEM grids (lacey formvar/carbon TEM copper grid of 200 mesh, Ted Pella Inc., USA) fixed on 13.1 mm spots of quartz filters (Whatman QMA) placed into a filter holder (syringe-filter holder). The sampling time was 5 min in all cases.

Particles were also collected directly at the outlet of the bubbler (without heating) on TEM grids for analysis.

The morphology and elemental composition of the particles were studied using a Philips CM20 TEM operated at 200 kV accelerating voltage, equipped with an ultra-thin-window Noran Voyager energy-dispersive X-ray detector. Dolomite standard was analysed to obtain sensitivity factors (“k-factors”) for thin film analyses of C, O, (Mg, Ca).

2.2 Pyrolysis

Upon biomass burning pyrolysis occurs in the deeper zones of the pores of the plants in which the oxygen supply becomes limited and the temperature is between ∼ 200 and 500 °C (Ohlemiller, 1985; Mohan et al., 2006). We simulated this process by the dry distillation of wood. In our experiments we produced liquid tar by the dry distillation of dry chops of European Turkey oak (*Quercus cerris*) which is one of the most commonly used firewood in Hungary (Hungarian National Food Chain Safety Office, Forestry Directorate, 2013). The water content of the firewood was 7.1 wt%, the size of the wood chops was about 25 mm × 10 mm × 10 mm. Dry distillation was performed in a long-neck 100 mL Kjeldahl flask fixed in a slightly tilted position in order to collect the condensed pyrolysis products at the mouth of the flask. Although the flask was open during the distillation process, there was no contact with the gas flame since the experiment was conducted under a closed hood. The temperature inside the spherical part of the flask reached 530 °C as measured with a thermometer (Testo 925 K-type thermocouple thermometer). Distillation lasted about 20 min. Pyrolysis products were collected in 40 mL vials, separated into tar and water phases. It is well established that high water yield might cause phase separation (Oasmaa et al., 2010). Precipitation of solids was not observed.

3 Results

The experimental setup, including the dry distillation of wood was intended to simulate the series of processes that may take place during the burning of wood. Liquid tar and water emulsion may form inside the pores by pyrolysis upon burning (simulated by dry distillation) then ejected as small droplets (simulated by bubble bursting) by forces exerted by the evolving gaseous pyrolysis products and partial vaporisation of water from the pores. It was observed that free water can explosively vaporize upon fast pyrolysis (Mohan et al., 2006). It is also notable that the sizes of atmospheric tar ball particles are comparable with those of the internal pores of various woody species (Plötze and Niemz, 2011). The ejected droplets then pass through the glowing (or flaming) zone where they possibly suffer a heat shock (simulated by passing through the heated zone) before they are released into the atmosphere (simulated by the residence in the buffer flask). It should be noted that the produced liquid tar may also suffer an initial heat shock under the conditions of dry distillation. Heat shock may substantially accelerate chemical transformations of the tar and the release of volatile compounds. It should be emphasized that – unlike typical conditions in biomass fires – flame chemistry is totally excluded in the setup as direct contact with flames is completely avoided.

3.1 Morphology of the laboratory-generated particles

The morphology of the produced particles is similar to tar ball particles found in biomass smoke in both the non-heated and heated samples. In the samples collected directly at the outlet of the bubbler (without applying heat shock) both spherical and slightly deformed, egg-shaped particles were observed (Fig. 2a). These particles were present as both aggregates and individual particles. In some aggregates the interstitial void between the particles was filled with an apparently liquid phase which is presumably the aqueous phase of the emulsion (Fig. 2a).

The shape of the particles (deformed-spherical) indicated that that the majority of these particles originated from droplets which have not been exposed to heat shock. As expected, these droplets were emitted by bubble bursting (direct emission, in analogy with the ejection of droplets from pores). The optical diameter of these particles varied from ~ 90 nm to ~ 1200 nm, the average was about 300 nm. This size range largely overlaps with those of the atmospheric tar balls (30–500 nm) (Pósfai et al., 2003, 2004; Fu et al., 2012; Adachi and Buseck, 2011).

In contrast to the aerosol samples collected directly after the bubbler, almost only perfectly spherical particles were observed in the samples collected at the outlet of the apparatus. In other terms, particles undergoing a heat shock at ~ 600 °C solidified to the extent that they could withstand the impaction into the sample grid. The optical diameters of the spherical particles were basically the same as those of the "raw" particles and atmospheric tar balls (diameters between ~ 140 and ~ 800 nm, on average 300 nm), though only a limited number (15) of size measurements were available. Similarly to the atmospheric tar ball particles the laboratory-generated particles did not contain any internal core according to their homogeneous contrast in the bright field TEM image (Fig. 2d).

The observed phenomenon, the flash solidification of tar droplets may follow from the ultra-high reactivity of tar constituents which is well-known in tar (or bio-oil) chemistry. The tar (or bio-oil) is an unstable mixture of a plethora of different chemical compounds. The storage of the bio-oil obtained by dry distillation of biomass is always a great challenge since numerous chemical reactions take place resulting in a rapid increase of viscosity. During storage the aldehydes and ketones of the bio-oil can react via aldol condensation and form larger molecules even at room temperature (Mohan et al., 2006). The temperature plays a crucial role in this ageing process. According to Czernik and co-workers (1994), the viscosity of bio-oil can be doubled after ageing at 90 °C for 8 h. For the same viscosity increase more than 84 days were needed at 37 °C. In the overview by Lu et al. (2009) four stages of the ageing of bio-oil were distinguished, associated with fast increase in the viscosity: "thickening, phase separation, gummy formation from the pyrolytic lignins (around 140 °C), and char/coke formation from the gummy phase at higher temperatures". Ageing processes can thus be dramatically accelerated at elevated temperatures. In our experiments similar behaviour of the generated particles were observed. The “raw” particles collected without a heat shock were mostly droplets whereas those which underwent ageing (heat shock at 600 °C) were solidified. Pattanotai and co-workers (2013) demonstrated that beside gas formation the tar can polymerise and form char already inside the pores of the burning biomass at higher temperatures.

3.2 Chemical composition of laboratory-generated tar ball particles

Figure 3 shows a typical EDS spectrum of a tar ball particle produced from thermally aged tar droplets and the average carbon-to-oxygen atomic ratio of 15 particles. These particles contained other elements (K, S, Si) only in trace amounts. The carbon-to-oxygen ratio of the tar ball particles after thermal shocking varied between 6 and 18, the average being 9.8.

It should be noted that the chemical composition of tar ball particles might depend on many factors, including the type of the burned biomass and the conditions of burning. Furthermore, most methods used for the determination of elemental abundances in individual particles are semi-quantitative only, thus they involve significant uncertainties. Nevertheless, the EDS spectra of the tar balls generated in our experiments are very similar to those reported for atmospheric tar ball particles.

4 Conclusions

For the first time perfectly spherical carbonaceous particles very similar to atmospheric tar balls in all of their observed properties were produced in the laboratory with the total exclusion of flame. All the characteristic features (perfectly spherical shape, size range, lack of coagulation, lack of internal core, homogeneous composition, lack of graphene fine structure, high C / O atomic ratio) of laboratory-generated particles match those observed in atmospheric tar ball particles. Based on these findings and the initial assumptions it can be hypothesized that tar ball particles may indeed form by the ejection of liquid tar droplets (pyrolysis products of biomass burning) from the pores of the burning biomass, followed by rapid thermal transformation upon passing through the flame or glow zone of the fire. In the light of atmospheric observations of tar ball particles it can be added that multiphase chemical reactions in the smoke plume may also contribute to the ageing (solidification) of the ejected tar droplets. The experimental setup that was used in this study has the further advantage that pure tar ball particles can be generated for the direct experimental determination of atmospherically relevant optical properties of this important subset of light-absorbing carbonaceous (brown carbon) particles. However, in order to better understand the complex processes of tar ball formation further studies are clearly warranted.

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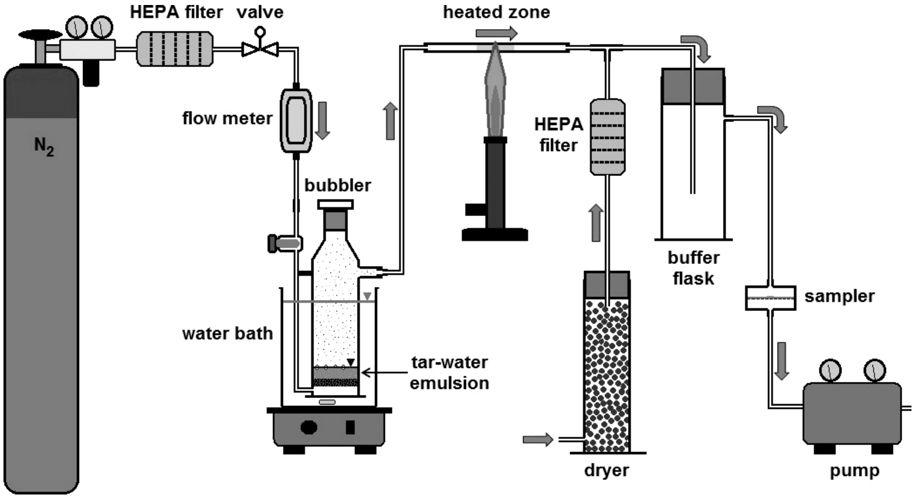


Fig. 1. All-glass apparatus for generation and collection of tar ball particles from liquid tar-water emulsions.

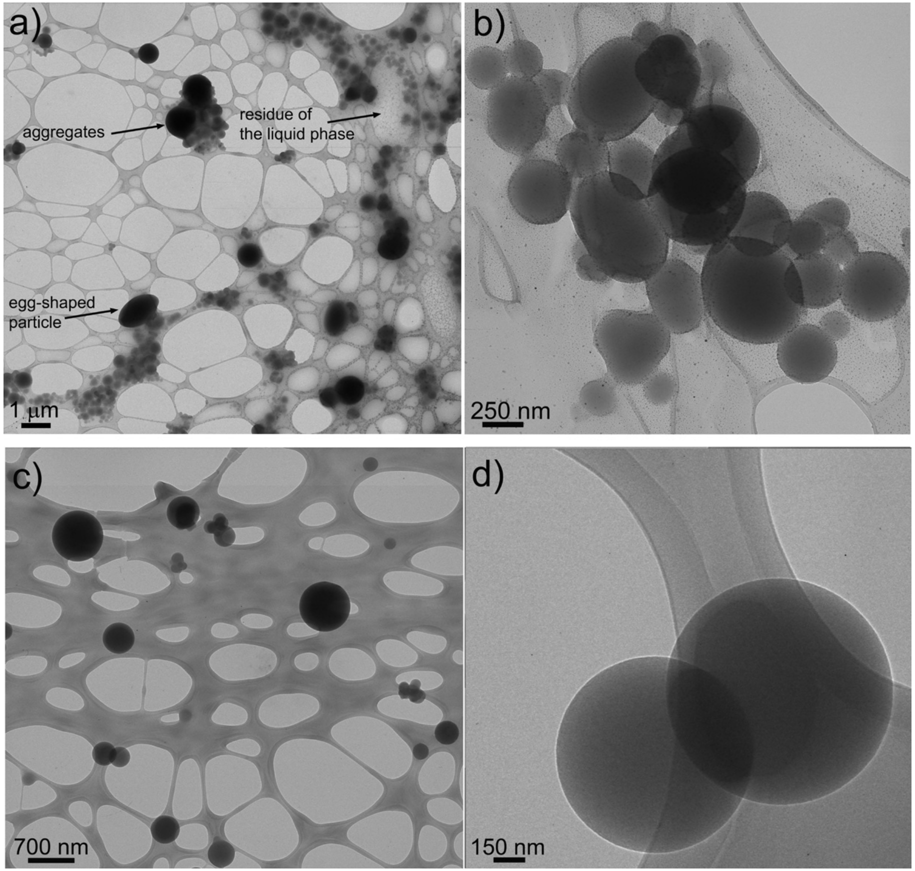
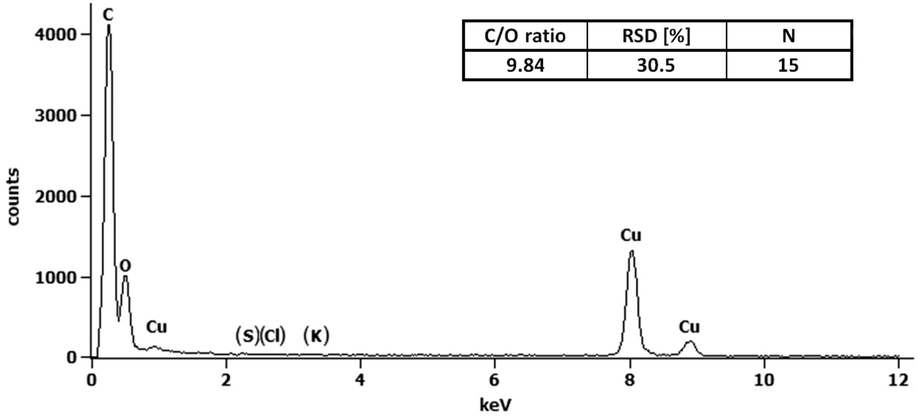


Fig. 2. Bright-field TEM images of particles collected after the bubbler (without heating) (**a** and **b**) and those collected at the outlet of the apparatus (after heat shock and ageing) (**c** and **d**).



C/O ratio	RSD [%]	N
9.84	30.5	15

Fig. 3. Typical EDS spectrum from a laboratory-generated tar ball particle and the average C/O molar ratio of 15 measured particles. (The copper peaks are artifacts that originate from the supporting grid.)

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