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Emissions of Tar Balls from Domestic Coal Burning Braziers

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On the central-plateau of the South African Highveld, domestic coal combustion is associated with the release of carbonaceous aerosols often produced as dendritic carbonaceous particles and tar balls. However, very few studies have been conducted to validate this contribution. Combustion of coal in low-income settlements is done using self-constructed devices (predominantly braziers) known as *imbaulas*. Combustion characteristics in these devices are influenced by fire ignition methods. The most common ignition method in South African Highveld areas is the bottom-lit updraft (BLUD) relative to the less favoured Top lit-updraft (TLUD) ignition technique. Aerosols samples were collected using Nucleopore filters combustion phases (ignition and pyrolysis). The JSM 5800LV SEM at the University of Pretoria and the Vega3 LM at the University of Johannesburg were used to observe particle morphologies from coal-burning fires. Both instruments were equipped with energy dispersive spectroscopy (EDS), which provides the possibility to analyse particle chemical compositions. Tar balls were identified in both ignition methods (BLUD and TLUD) and in pyrolysis (stage I and II). When sampling close to the fires (at ignition and pyrolysis stage I), the filter material rapidly clogged and a continuous layer of liquid/ tarry substance coalesced and covered the entire filter membrane, with some pores completely closed. At the 5 m exit point, micrographs showed distinct particles morphologies, including giant spherical organic particles that had condensed as the exhaust stream cooled. Perfectly spherical giant tar balls were observed in ageing smoke from smouldering combustion conditions typical of poorly ventilated BLUD fires. The spherical tar ball particles were found as individual spherical particles and as aggregates forming diffusion accretion chains. It is hypothesised that spherical organic particles may have been formed by the ejection of liquid tar droplets (pyrolysis stage I products of coal burning) from the pores of the burning coal, followed by rapid thermal transformation upon passing through the flame or glow zone of the fire.

Keywords: Coal, *imbaula*, combustion phase, particulate, carbonaceous aerosols

1 Introduction

Over three billion people of the global population rely on solid fuel as a primary source of energy, especially for cooking and space heating purposes (World Energy Outlook, 2015). Solid fuels such as coal and wood are widely used due to their inherent natural reliability characteristics and low-cost implications (Smith *et al*., 2012, Kimemia *et al*., 2010). Biomass is a sustainable and renewable energy source with the potential to replace or minimise reliance on fossil fuel for domestic activities (Boman *et al*., 2003). Residential solid fuel reliance is declining in developed countries. However, in developing nations over 50% of households still depend on coal, wood and animal dung to meet their daily energy requirements (Ludwig *et al*., 2003; Lim *et al*., 2013).

For the past decades, a strong emphasis has been placed on black carbon (BC) as a major potent climate forcing agent, accounting for as much as 60% of the greenhouse absorption of excess carbon dioxide (Bond *et al*., 2013; Ramanathan & Carmichael, 2008; Jacobson, 2002). Only quite recently has it been established that brown carbon (BrC) - a substantial part of the carbonaceous continuum between pure graphite and non-absorbing organic aerosol - contribute significantly to atmospheric light absorption globally (Tóth *et al*., 2014; Chung *et al.*, 2012). Most climate models have so far ignored the effect of BrC on climate forcing (China *et al*., 2014; Tóth *et al*., 2014). BrC is estimated to contribute by as much as 20% to the total absorption at 530nm (Liu *et al*., 2014; Chung *et al*., 2012).

Tar balls fall within this group of atmospheric particles referred to as BrC (Alexander *et al*., 2008). They were first described in biomass smoke plumes (Pósfai *et al*., 2003, 2004) with a contribution to particle number as high as 90%, especially in aged smoke from smouldering fires (Hand *et al*., 2005). According to Tóth *et al*. (2014), tar balls can be easily recognised using transmission electron microscopy (TEM) by their relatively narrow size range, almost perfectly spherical shape and their chemical composition.

In contrast to other spherical aerosol types such as sulphates, tar balls do not volatilize under the electron beam and are refractory. These particles are distinctly different from BC particles in that they have much larger geometric sizes than nanospheres of BC (Tóth *et al*., 2014). Again, these particles occur externally mixed (i.e. without being coagulated with one another or other particles), and unlike other BC particles, they do not have the internal microstructure of concentrically wrapped, curved graphene-like layers. According to electron energy-loss elemental mapping of individual particles and determination of elemental composition of these particles using EDS, tar balls consist mostly of carbon and oxygen and sometimes with traces of sulphur, potassium, chlorine and silicon. These elements are homogeneously distributed over the entire volume of a relatively fresh tar-ball particle (Tóth *et al*., 2014).

The burning of coal or wood is predicted to cause various forms of pollution indoors and outdoors (Smith *et al*., 2010). Nevertheless, it is suggested in the literature that with proper combustion technology modification an improved performance can be achieved (Kimemia & Annegarn, 2010). Therefore, it is essential to investigate further combustion parameters which can improve combustion condition in small scale coal burning (Frey, 2008).

In South Africa, more than 75% of electrified households use wood and coal for major domestic activities including cooking and space heating (Balmer, 2007; Makonese *et al*., 2014; Kimemia, 2010; Masekameni *et al*., 2014). In the central Highveld areas of South Africa coal is combusted using a variety of appliances ranging from commercial cast iron stoves to locally manufactured metal stoves and the most popular self-fabricated stoves using 20-25 L metal buckets, termed *Imbaula* (Makonese, 2015; Masekameni, 2015).

In South Africa, combustion of solid fuels in low-income households is done in self-fabricated and inefficient stoves, leading to increased emissions (Masekameni *et al*., 2014; Makonese, 2011; Kimemia & Annegarn, 2011). There is, therefore, need to evaluate the emission performance of existing small-scale coal-combustion devices in use. Information from this study will be useful for predicting emission formation in the design of energy production units to meet emission regulations and to assess the environmental effects of different alternatives (Sippula, 2010).

Coal used in domestic combustion technologies comprises of over 60% carbon, 20% volatile organic compounds, less than 10% moisture content and over 20% ash content. The amount of volatile matter in coal is relatively low compared to wood, which is above 70% (Frey, 2014; Tissari *et al*., 2007). Therefore, during ignition, coal requires a catalyst to burn; often wood kindling is used for ignition due to the inherent higher volatiles (McDonald *et al*., 2000; Sippula, 2010; Tissari *et al*., 2005).

The formation of particles is high at low-temperature conditions and during incomplete processes, where soot might be formed comprising of elementary carbon, black carbon and gas precursor to aerosols as PAHs (Sippula *et al*., 2009; Wang *et al*., 2009). Some of the aerosols present are influenced by the fly ash comprising of the inorganic compounds contained in the fuel. Previous studies reported emissions from small-scale combustion as average concentration of particles above 2.5 µm over the entire burn cycle, with little emphasis on varied combustion phases (Masekameni *et al*., 2014; Makonese, 2015). However, combustion in fixed bed varies at various phase (ignition, pyrolysis, coking and smouldering) (Masekameni *et al*., 2016). It is, therefore, essential to evaluate emission profiles at each combustion phase (Makonese *et al*., 2016).

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) are very powerful tools to study the shape and morphology of aerosol particles (Gwaze, 2007). Equipped with energy dispersive X-ray (EDX) or electron energy loss (ELL) spectroscopy they give information on the elemental composition of the particles of interest (Burtscher, 2001). While TEM allows a higher resolution down to the nano- and atomic scale, SEM usually has better contrast. For TEM, very thin grids (often copper) coated with a carbon film/ gold, are used. The quality of this film is extremely important to obtain a good resolution. If samples are used for quantitative analysis (e.g. of the size distribution) care has to be taken to have a well-defined size dependence of the sampling process (Burtscher, 2001).

Microscopy techniques have become the most 'sought after' and effective tools in coal combustion and atmospheric research, particularly the use of beam microscopes which include Scanning and Transmission Microscopes (Silva *et al*., 2011). Microscopy techniques can be useful in the study of a range of particle properties since important information on particles resides in the morphology and chemical composition of individual particles (Gwaze, 2007; Fletcher *et al*., 2001). High-Resolution Scanning Electron Microscope (HRSEM) has been used to a lesser extent in coal combustion research (Lu *et al*., 2009). In published and peer reviewed literature, there is limited information concerning characterising emissions from residential coal combustion processes in South Africa using an SEM except for the work of Wentzel *et al*. (1999) who characterised aerosols from the Soweto atmosphere and Gwaze (2007). Unfortunately, their work has not been followed up although it is vital to understand the modes of formation and transformation of conglomerates originating from low-temperature coal combustion.

In this study, we have evaluated carbonaceous tar balls generated during residential coal burning sequences at three combustion phases. The studied the morphology of carbonaceous tar ball including semi-quantities of elemental composition. The study further proposes the use of a high-resolution SEM for characterising and assessing the morphology and characteristics of coarse (>10 µm) and fine particles (< 2.5 µm).

2 Methodology

2.1 Fuel Preparation

Mostly used D grade bituminous Grade D (high ash) coal was purchased from Witbank Slater coal mining company. Coal samples were taken to the external laboratory for proximate (major elemental composition) analysis.

2.2 Coal analysis

The fuel samples were analysed on an air-dried basis. Experimental results presented in this paper are based on the proximate and ultimate analysis results for the D-grade coals used in making the fires as shown in Table 1.

Table 1: Fuel analysis specifications

Parameter (Air Dried Basis)	Standard Method	Slater Mine D-Grade Coal
Moisture content (%)	ISO 5925	3.5
Volatiles (%)	ISO 562	20.3
Ash (%)	ISO 1171	24.2
Fixed carbon (%)	By difference	52.0
Calorific value (MJ kg^{-1})	ISO 1928	23.4
Calorific value (Kcal kg^{-1})	ISO 1928	5590
Total sulphur (%)	ASTM D4239	0.63
Carbon (%)	ASTM D5373	62.6
Hydrogen (%)	ASTM D5373	2.76
Nitrogen (%)	ASTM D5373	1.
Oxygen (%)	By difference	5.0
Total silica as SiO_2 (%)	ASTM D4326	58.6
Aluminium as Al_2O_3 (%)	ASTM D4326	27.6
Total iron as Fe_2O_3 (%)	ASTM D4326	6.63
Titanium as TiO_2 (%)	ASTM D4326	0.82
Phosphorous as P_2O_5 (%)	ASTM D4326	0.55
Calcium as CaO (%)	ASTM D4326	2.30
Magnesium as MgO (%)	ASTM D4326	0.83
Sodium as Na_2O (%)	ASTM D4326	0.42
Potassium as K_2O (%)	ASTM D4326	0.79
Sulphur as SO_3 (%)	ASTM D4326	1.10
Manganese as MnO_2 (%)	ASTM D4326	0.12

2.3 Fire-ignition methods

Throughout the tests, care was given to the methods for both ignition technologies–the conventional bottom lit updraft (BLUD) and the less common top–lit updraft (TLUD) methods. The stove was set using ~35 g of paper, ~400 g of wood kindling and ~4 000 g of coal. The same mass of wood and paper was used for all tests for consistent operation and ease of comparison of results.

During the TLUD ignition method, the fuel ordering entailed placing 2 500 g of coal on the grate, followed by the paper (35 g), wood (400 g), and the remaining 1 500 g of coal on top. The entire stove was placed on a heat shield located on the platform of the mass balance.

In the BLUD ignition method, 35 g of paper was used to ignite 400 g of wood; after the wood fire had attained a sustainable flame, the 4 000 g of coal was fuelled in the stove.

Tests were conducted under controlled laboratory conditions, keeping parameters such as ignition method, coal particle size, coal grade, moisture content and ventilation rates constant.

2.4 Stove characterisation

Two varied ventilation field braziers used during the experiment are shown in Figure 1. The braziers have a fuel support grate, made of wire. Devices vary greatly regarding the number and sizes of the side holes (i.e. affecting ventilation rates), the presence of a grate and its position in the metal drum (Kimemia *et al*., 2011, Masekameni *et al*., 2014).

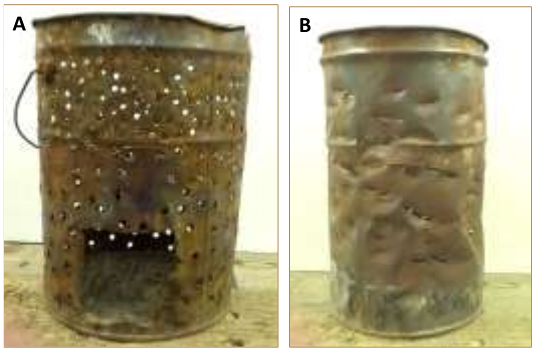

Figure 1: Illustration of imbaulas used in the experiment: (A) high ventilation case, (B) low ventilation case.

Ventilation rates affect the overall performance of the stove, and these rates differ significantly from one device to the other. There is a need to specify parameters such as ventilation rates, grate height and stove diameter to evaluate realistically and compare the morphology of various combustion phases in a brazier (Table 2).

Table 2: Stove description

Vent.	Heig (mm)	Diam. (mm)	Grate height.	Hole area below grate	Hole area above grate	Total hole area
High	370	290	185	248	159	407
Low	440	290	250	145	103	248

2.5 Electron microscopy technique

Electron microscopy techniques are widely used to image the shape and structure (i.e. morphology) of solid surfaces or particles (Boman, 2005). In the present study the JSM 5800LV SEM at the University of Pretoria, and the Vega3 LM at the University of Johannesburg were used to observe particle morphologies from coal-burning fires. Both instruments were equipped with energy dispersive spectroscopy (EDS), which provides the possibility to analyse particle chemical compositions. The samples from real-world uses of braziers were collected on quartz fibre filters; samples from laboratory tests were collected on polycarbonate membrane filters using suction sampling.

The three most common modes of operation in SEM analysis are (i) backscattered electron imaging (BSE), (ii) secondary electron imaging (SEI), and (iii) electron dispersive spectroscopy EDS (Kutchko & Kim, 2006). The SEM have its limitations; there is current evidence which suggests that the samples under observation in SEM are susceptible to mass loss of adsorbed water or volatiles due to the necessity of operating in a vacuum and possible damage to particles by electron beam or electrostatic disruption (Gwaze, 2007).

Therefore, only non-volatile particle components can be characterised using the SEM (Chakrabarty *et al*., 2006). The influence of the accelerating voltage of the electron beam on the shape on the aerosol particles was characterised by varying the accelerating voltages between 10 and 20 kV.

2.6 Determination of combustion phases

Emission rates of a two-ventilation field obtained *imbaulas* were measured for each of the two combustion phases of a typical combustion sequence. The first phase is termed ignition during which kindling and fire starter material combust, typically lasting five minutes. The following phase, pyrolysis (stage I), is the period as the coal heats up, releasing volatile and semi-volatile compounds; condensation of the semi-volatile material results in dense white to greyish smoke, (stage II) long flames as volatile matter burns in homogeneous gas phase combustion.

2.7 Quality control

Calibration of the SEM was done similarly to what is reported in Gwaze (2007). The calibration of the instrument was verified by measuring standard grids of alternating SiO2/Si surfaces with lateral (xy) dimensions between 0.9 and 15 µm, and polystyrene latex (PSL) spheres of diameters of 0.126 ± 0.001 µm and 0.600 ± 0.005 µm. Deviations between measured sizes of both the standard grids and PSL spheres and nominal specifications were below 7%. The X-ray detector was regularly calibrated with Cu standard sample.

3 Results

3.1 Stage II pyrolysis

Tar balls were emitted from domestic coal combustion processes. Figure 2 shows a micrograph of tar ball particles sampled and fractal aggregates (collected < 1 m from the brazier) from a BLUD fire during pyrolysis stage II. The size and shape of the spherules were dependent on the ventilation rates. In the high ventilation brazier, fewer spherical particles were observed compared to samples collected from the low ventilation brazier. Carbon and oxygen comprised the bulk of the elemental composition of these spherules. Pósfai *et al*. (2003) argues that particles of this type are carbonaceous and are formed in smouldering fires, and their abundance increases in the atmosphere with the age of the plume. The observed particles are similar to spherical C-rich particles collected from coal combustion processes in previous studies (Shi *et al*., 2003). However, since EDS analyses only gave qualitative elemental compositions, we had no direct evidence that the C element in these particles occurred only in organic compounds.

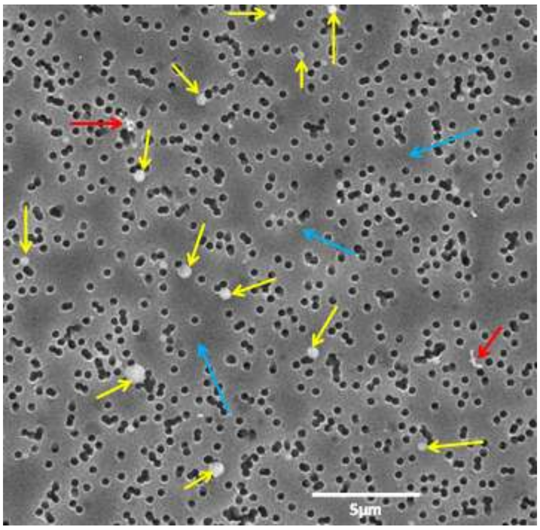

Figure 2: SEM image from BLUD low ventilation (pyrolization stage II)

The yellow arrows show spherical organic particles; the red arrows show fine mode soot particles and the blue arrows show dark halos indicating the presence of moisture in the sample. Similar to Tóth *et al*. (2014) and based on the most characteristic features of the relatively fresh tar balls (i.e. spherical shape, large size, homogeneous composition, and high C/O ratios); we suggest a direct emission mechanism for the spherules.

The spherical particles indicate that the droplets do not only occur on the filter but are already present in the exhaust or atmosphere where they are formed through a condensation process. These spherical particles are likely to be produced by the direct emission of liquid droplets followed by heat transformation upon coal burning.

We hypothesize that the spherules are ejected from the pores of coal particles as liquid organic carbon droplets then undergo chemical transformations that increase their viscosity, form aggregates, and solidify into highly refractory particles, as is observed in the atmosphere.

3.2 Ageing of tar ball particles

To investigate the effect of ageing (on the scale of a few seconds) on condensed matter emissions and to note how commonly these conglomerates and spherical organic particles occur in different fires and ventilation rates we collected ~5 m above the brim of the burning brazier through a 4 m long exhaust duct. Results are presented for the BLUD and TLUD ignition methods in both the high and low ventilation braziers, during the pyrolization (stage I and or stage II).

3.3 Stage I pyrolysis

Results show that when sampling particles ~5 m above the combustion devices, spherical tar balls are dominant for both fire-ignition methods. TLUD fires emitted spherical organic particles with smaller mode diameter compared to BLUD fires. The spherical particles form diffusion accretion chains in TLUD fires, whereas BLUD fires show numerous condensation spherules (Figure 3a & b). This suggests that the particle mass concentration and particle mean diameters are influenced by the ignition method employed, and the subsequent evolution of particles and gases through and above the fuel bed.

For the low ventilation rates, the spherical organic particles observed are two to three times larger compared to those observed for the high ventilation rate. Also, note the presence of a thick film of carbonaceous material on samples collected from the low ventilation brazier (Figure 3a).

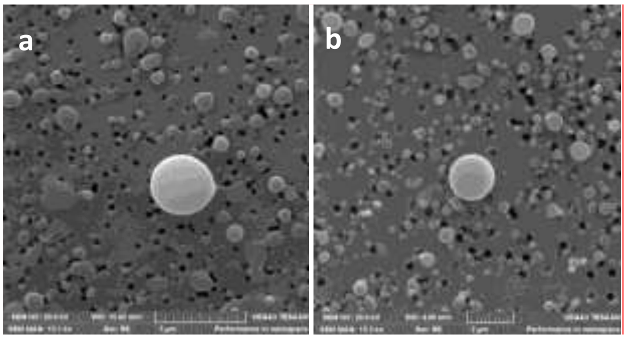

Figure 3: Tar ball particles sampled during pyrolysis stage I from BLUD fires: a) a low ventilation brazier, and b) a high ventilation brazier

Figure 4 shows an electron micrograph of a typical 'giant' tar ball particle collected from the low ventilation BLUD during the coal pyrolization stage I. These particles are three-fold larger compared to particles from the corresponding high ventilation BLUD brazier.

This suggests that ventilation rates may influence the particle mode diameter of the spherical particles in BLUD fires. However, it should be noted that this is a qualitative observation based on visual inspection of the micrographs¬–automated particle recognition and counting facilities were not available on the SEM instrument used. There is a need for future studies to use commercial particle sizers (e.g. differential mobility particle sizers–DMPS, and scanning mobility particle sizer–SMPS) to analyse the specific mode diameter.

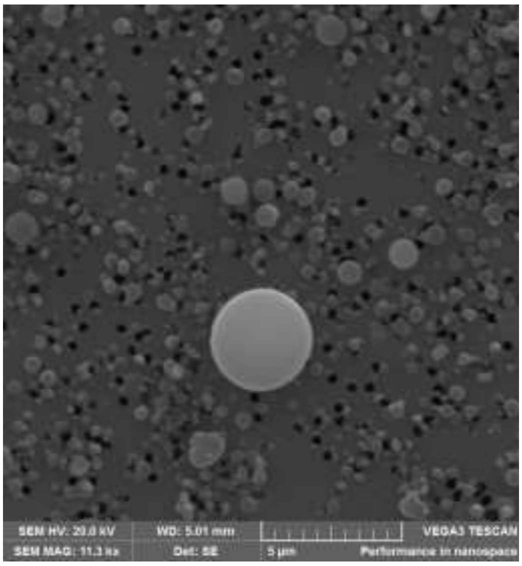

Figure 4: Giant tar ball particles from the ignition phase of a BLUD fire

Figure 5 shows that the liquid aerosol droplets from coal fires form tar balls and bead-like accretion chains along the length of the fibre material. It can be seen that these super-micron particles primarily consist of individual tar ball particles.
The nearly perfect tar ball appearance of the particles implies that the minerals in coal are almost completely melted during combustion (Wu *et al*., 2011). Although small bead-like aggregates exist, the surfaces of the tar ball particles are quite smooth suggesting that the aggregation and condensation of vaporised species are not the important factor in super-micron particle formation.

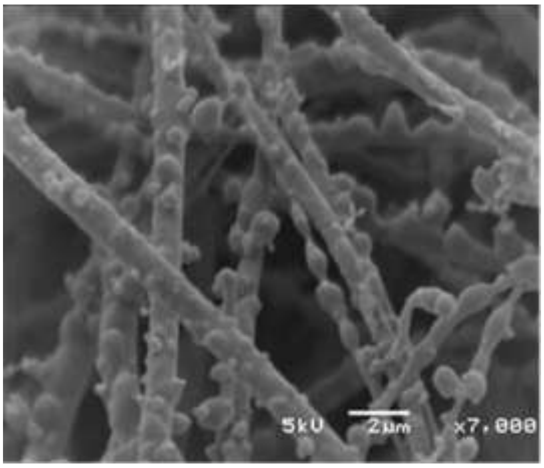

Figure 5: SEM micrograph showing the presence of bead-like particle aggregates from a BLUD fire ignition method during pyrolysis stage I.

3.4 Morphology of coal particles

Figure 6 shows the morphology of particles collected on a quartz filter, which include the submicron and ultra-fine particles. It is seen that the particles on this stage are dominated by individual spherical particles. The morphology of the particles shown in Figure 6 indicates that for particles in between super-micron and ultra-fine particles, condensation of vapour phase species or aggregation of nucleates could be an important formation mechanism.

For tar balls like particles, the specific surface area increases with decreasing particle diameter. Therefore, this mechanism would be more pronounced for smaller particles (i.e.the contribution of vaporised species/nucleates would be more significant for the formation of smaller particles) (Wu *et al*., 2011).

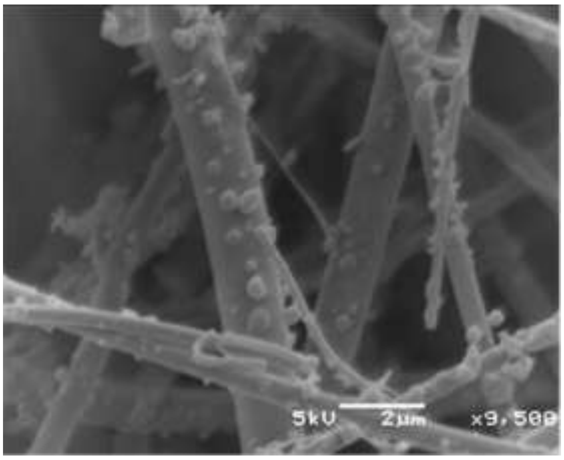

Figure 6: SEM micrograph showing the presence of bead-like particle aggregates from a TLUD fire ignition method during pyrolysis stage I

3.5 Identification of diffusion accretion chains

In Particle morphologies (sampled at < 1 m from the braziers) were investigated for the BLUD and the TLUD ignition method in both the high and low ventilation rate brazier.

Figure 7 shows micrographs of the particles formed during the flaming phase of BLUD and TLUD fires when using a high ventilation brazier.

Results show that during the initial pyrolysis stage (phase I) of the fire, spherical particles are formed in BLUD fires (Figure 7a), whereas conglomerate chained particles are evident in TLUD fires (Figure 7b). During pyrolysis (stage II), 'giant' conglomerates are formed from BLUD fires (Figure 7c); whereas in the TLUD fires fine mode conglomerate particles are formed (Figure 7d).

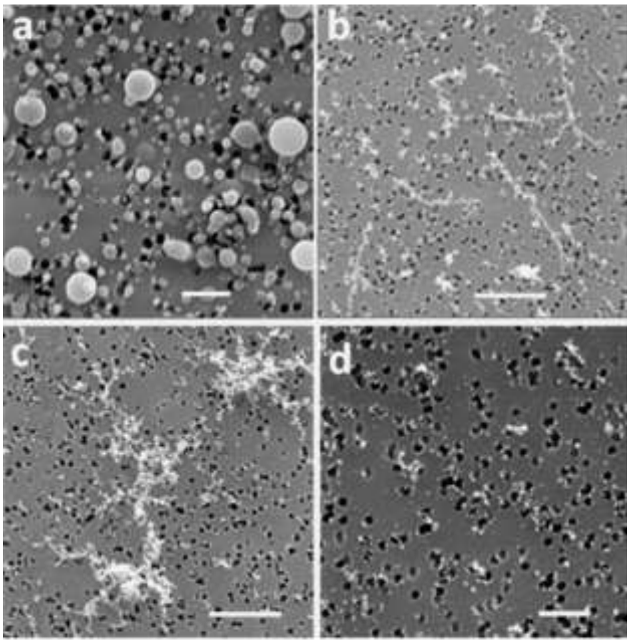

Figure 7. Ageing particles sampled from BLUD and TLUD fires; a) Tar ball particles from BLUD fires (pyrolysis stage I); b) numerous condensation spherules and diffusion accretion chains from TLUD fires (pyrolysis stage I); c) dendritic particles for BLUD during pyrolysis stage II; and d) fine soot particles for TLUD during the coking phase. Scale bars = 2 µm (a & d); 5 µm (b & c)

Figure 8 shows an electron micrograph with numerous diffusion accretion chains. These agglomerates have not been reported in previous studies on coal combustion, although there have been observed in experiments involving biomass burning smoke (China *et al*., 2014; Chakrabarty et al., 2009; Chakrabarty *et al*., 2006, Pósfai *et al*., 2004; Pósfai *et al*., 2003). These diffusion accretion chains are formed from bimolecular homogeneous nucleation with water vapour, and they grow by coagulation and condensation.

Low volatile organic compound (LVOC) released from the burning coal undergoes polymerisation reactions with OH radicals in droplets, yielding larger molecular weight and less water-soluble species. Due to the Raoult effect, the equilibrium size of the droplet is reduced. As the size of the droplet decreases, the solution becomes concentrated and the rate of polymerisation increases, which results in turning the organic polymer largely insoluble in water. Spherical tar balls observed in this study are believed to remain as dry, low-vapour pressure solid particles.

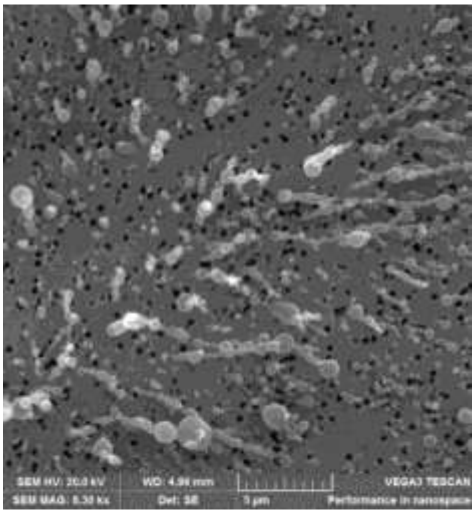

Figure 8. Numerous spherical tar balls particles and diffusion accretion chains.

We hypothesise that tar ball particles from fixed-bed domestic coal combustion may have been formed by the ejection of liquid tar droplets (pyrolysis stage I products of coal burning) from the pores of the burning coal, followed by rapid thermal transformation upon passing through the flame or glow zone of the fire. The flame chemistry in the fire zone or multiphase chemical reactions in the smoke plume may contribute to the ageing of the ejected tar droplets forming accretion chains or aggregates. During pyrolysis stage II, dendritic particles comprised of much smaller primary condensation spherules were collected on the filters regardless of the ignition method.

Figure 9 shows an EDS spectrum of tar ball particle produced from smouldering combustion conditions in the BLUD method of igniting a coal fire in a brazier. The majority of the identified spherical particles contained only C and O. Other particles contained C and O plus other elements such as Si, S, Mo, K, Al in trace amounts (Figure 9). This result is consistent with previous observations of atmospheric tar-ball particles (Niemi *et al*., 2006).

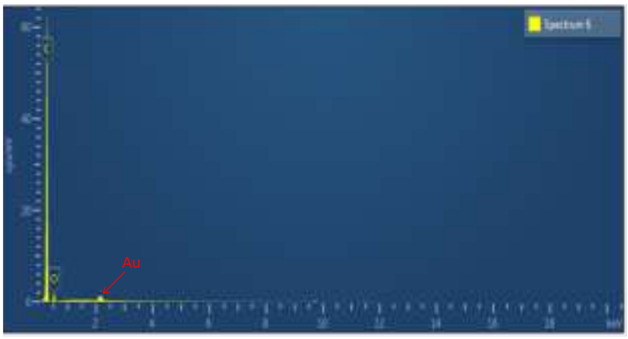

Figure 9. Typical EDS spectrum from a tar ball particle containing only C and O. (The gold peaks are artefacts that originate from the gold-coated membrane filters)

4 Conclusion

We have shown in this study that tar ball particles are emitted from domestic coal combustion in informal braziers. During the ignition phase, electron micrographs revealed continuous layers of merged tar-like deposits with no discrete particles visible. During pyrolysis stage I and II, filters collected particles that (mostly) retained their morphology on impact, showing appearance on the electron micrographs of discrete particles with a range of morphologies. Images of filters sampled during pyrolysis phase showed that that the fire ignition method and ventilation rates influence aerosol formation and morphology of the emitted particles. Perfectly spherical giant tar ball particles were observed in ageing smoke from smouldering combustion conditions typical of poorly ventilated BLUD fires. The spherical organic particles were found as individual spherical particles and as aggregates forming diffusion accretion chains.

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