Ultrafine Particulate Matter (PM$_{0.1}$) Formation under Pulverized Coal Combustion and Oxyfiring Conditions

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1. Introduction

The main drawback of the large use of coal for power generation are greenhouse gases, primarily carbon dioxide, and pollutant emissions such as nitrogen and sulfur oxides and particulate matter. Next generation coal power plants require a carbon dioxide capture and sequestration system in order to be environmental sustainable [1]. Oxy-combustion technologies are becoming widely used to allow carbon dioxide capture either in new plants or in retrofitting existing air blown furnaces. Retrofitting requires oxygen enriched concentrations in recirculated flue gas to satisfy the heat exchange request [2]. The change in combustion atmosphere and the potential change in local particle temperature between oxy-fired and air-fired combustion may have an effect on the ash formation mechanisms and hence the ash composition and quality. Ash formation mechanism in conventional coal combustion systems has been extensively studied. On the contrary, how oxy-combustion conditions affect ash formation is still under investigation [3]. This is particular true for ultrafine ashes whose formation is strongly affected by the temperature and the gas phase composition surrounding the coal particles. Indeed, both direct vaporization of volatile metals [4], which react in the gas phase and subsequently nucleate or condense on the surface of existing particles, and of refractory species, after their reduction to suboxides [5], are strongly affected by local flame temperature and oxygen concentration. The process involving ash transformation is also coupled with carbonaceous particle formation due to pyrolysis of tar and volatile organic compounds released during coal devolatilization [6]. The ultrafine ashes (D<100nm) represent just a small percentage of total ash mass at the exhaust of a coal furnaces [7]. Nevertheless, the ultrafine fraction is of great concern because of its toxic effects [8]. Ultrafine ashes are not easily removed by filtering devices and can be emitted in the atmosphere [9] so that they may imply a significant pollution problem.

The aim of this paper is to measure the size distribution functions (PSDF) of coal ultrafine ashes formed in a laboratory scale combustion reactor. The reactor is operated in air and high oxygen concentrations to assess the oxygen content effect on particle sizes and composition.

2. Experimental

2.1. Coal properties

Three U.S. coals of different ranks, Utah Skyline high volatile bituminous (UTS), black thunder Powder River Basin sub-bituminous (PRB) and Montana lignite (MTL), and two high volatile bituminous, Colombian (COL) and Indonesian (IDN), coals have been used. All coals have low sulfur content (>0.6%) while ash content ranges from 4.94% in PRB coal to 8.83% in UTS coal. The properties and ash composition listed in Tab.1, broadly vary among the selected coals. A Carbon Black powder (N762, Phillips Petroleum Co.) is also used to assess the contribution of carbonaceous matter to PM$_{0.1}$. 

2.2. Pulverized coal combustion reactor

The reactor consists of a fuel lean flat laminar premixed flame sustained by ethanol vapor and operated at atmospheric pressure. Coal particles, monodisperse in size, are homogeneously added into the flame so that their oxidation occurs into the flame exhaust gasses. The flame is stabilized on a burner consisting of two coaxial stainless steel tubes and a flat plate positioned 90 mm downstream the burner mouth. A Silicon Carbide honeycomb (1 inch 300CPSI, CTI s.a.) covers the top of the inner tube (18 mm ID) to laminarize the flow. Tube wall temperature is kept constant at 65°C. Sheath argon (9.0 l/min) is flowed through the ring (24 mm ID and 34 mm OD) between the tubes to prevent surrounding air entrainment and minimize flame flickering. The burner is fed with 2.33 l/min (STP) of oxidant stream and 0.30 cm³/min of ethanol, in the form of 80.2.33 l/min (STP) of oxidant stream and 0.30 cm³/min of ethanol, in the form of 80

Table 1. Properties of the used coals

<table>
<thead>
<tr>
<th>Species</th>
<th>UTS</th>
<th>PRB</th>
<th>MTL</th>
<th>COL</th>
<th>IDN</th>
</tr>
</thead>
<tbody>
<tr>
<td>HHV [MJ/kg]</td>
<td>29.3</td>
<td>21.1</td>
<td>18.3</td>
<td>28.7</td>
<td>30.3</td>
</tr>
<tr>
<td>Proximate analysis, wt% on coal as received</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ash</td>
<td>8.83</td>
<td>4.94</td>
<td>6.90</td>
<td>6.11</td>
<td>7.40</td>
</tr>
<tr>
<td>Volatile</td>
<td>38.60</td>
<td>33.36</td>
<td>25.02</td>
<td>38.31</td>
<td>40.20</td>
</tr>
<tr>
<td>Moisture</td>
<td>3.18</td>
<td>23.65</td>
<td>37.20</td>
<td>4.90</td>
<td>3.11</td>
</tr>
<tr>
<td>Fixed C</td>
<td>49.39</td>
<td>38.01</td>
<td>30.89</td>
<td>50.68</td>
<td>49.29</td>
</tr>
<tr>
<td>Ultimate analysis, wt% on coal as received</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>70.60</td>
<td>53.72</td>
<td>40.56</td>
<td>70.95</td>
<td>71.68</td>
</tr>
<tr>
<td>H</td>
<td>5.41</td>
<td>6.22</td>
<td>2.63</td>
<td>5.32</td>
<td>5.62</td>
</tr>
<tr>
<td>N</td>
<td>1.42</td>
<td>0.78</td>
<td>0.62</td>
<td>1.32</td>
<td>1.38</td>
</tr>
<tr>
<td>S</td>
<td>0.53</td>
<td>0.23</td>
<td>0.48</td>
<td>0.40</td>
<td>0.53</td>
</tr>
<tr>
<td>O by diff</td>
<td>13.21</td>
<td>34.11</td>
<td>11.62</td>
<td>11.00</td>
<td>10.28</td>
</tr>
<tr>
<td>Ash composition, wt% on ash</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>60.89</td>
<td>30.46</td>
<td>26.79</td>
<td>47.05</td>
<td>44.47</td>
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<tr>
<td>Al₂O₃</td>
<td>14.52</td>
<td>14.78</td>
<td>13.57</td>
<td>23.94</td>
<td>22.28</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>5.09</td>
<td>5.20</td>
<td>6.16</td>
<td>5.99</td>
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<tr>
<td>MgO</td>
<td>1.39</td>
<td>5.17</td>
<td>10.02</td>
<td>1.43</td>
<td>1.41</td>
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<tr>
<td>CaO</td>
<td>6.11</td>
<td>22.19</td>
<td>24.73</td>
<td>3.29</td>
<td>1.98</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.41</td>
<td>1.94</td>
<td>0.24</td>
<td>2.03</td>
<td>1.14</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.57</td>
<td>0.35</td>
<td>0.29</td>
<td>1.40</td>
<td>2.31</td>
</tr>
<tr>
<td>MnO</td>
<td>0.02</td>
<td>0.01</td>
<td>0.07</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.33</td>
<td>8.83</td>
<td>14.13</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
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</table>

Table 2. Gas composition and temperature.

<table>
<thead>
<tr>
<th>Species</th>
<th>Exhaust gas composition (+/-0.5) [vol%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>5.0</td>
</tr>
<tr>
<td>CO₂</td>
<td>9.5</td>
</tr>
<tr>
<td>H₂O</td>
<td>14.0</td>
</tr>
<tr>
<td>N₂</td>
<td>71.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>HAB</th>
<th>Gas temperature (+/-30) [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5mm</td>
<td>1730</td>
</tr>
<tr>
<td>25mm</td>
<td>1590</td>
</tr>
<tr>
<td>50mm</td>
<td>1290</td>
</tr>
</tbody>
</table>

2.3. Measurements techniques

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 (29.5 l/min). 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 [9-11]. Dilution is required to control coagulation during sampling and to reduce particle concentration within the electrometer detection range. The DMA was operated in three modalities, selected changing the maximum voltage applied to the electrostatic classifier and the sheath air flow rate. The nominal mobility diameter (MD) ranges from 0.6nm to 28nm and from 2.1nm to 100nm in the high flux (50l/min) low and high voltage modes, respectively. The range is further enlarged (2.9nm-151nm) operating the DMA in the low flux (25l/min) high voltage mode. All measurements were performed positioning the sampling pinhole on axis 50mm downstream the burner. This distance corresponds to residence time in the reactor of 60-65ms [11]. Measured number weighted PSDFs are averaged on more than 10 scans and corrected for dilution. The PSDF in the whole 1-151nm range is reconstructed merging results at high, intermediate and low dilutions [10]. The volume weighted PSDFs are obtained by multiplying each point of the number weighted PSDFs by the corresponding particle volume, calculated with the approximation of spherical particles. Diameter are considered $D_0=0.5nm$ smaller than the mobility diameter in accordance with literature [12]. PSDFs are subsequently fitted adding modal lognormal distributions. The aerosol generated in the low oxygen condition was also sampled (0.8l/min) on axis 50mm above the burner using a vertical tube probe (8mm ID) and bubbled for 1h into 15cc of pure water. The bubbler was ice-cooled to condense combustion water. UV-visible spectra of water samples, previously filtered with 500nm fiber glass filter, were measured on an Agilent 8453 Diode Array spectrophotometer by using a standard 1 cm path-length cuvette.

3. Results and discussion

Both number and volume PSDFs from UTS coal combustion at low oxygen concentration are plotted in Fig.1. This illustrative PSDF clearly shows the multimodal nature of ultrafine coal ashes and the huge number concentration (order of $10^{12}$ cm$^{-3}$) of particles smaller than 30nm. 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 weighted PSDF showing concentration that range from hundredth of ppb to unitary ppb.

3.1. Air-blown coal combustion

The yields on coal mass basis of ultrafine ashes from the combustion of the five coals at low oxygen concentration are plotted in Fig.2 as a function of mobility diameter. They range from some tenths up to few cubic millimeter per coal gram implying that ultrafine particles,
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assumed to have unit density, are from ~1% (UTS) to ~3% (IDN) of total ash mass. All the
PSDFs show that the largest fraction of PM$_{0.1}$ is
due to two classes of particles, those smaller than
10nm and those larger than 30nm. Each of the
two classes is composed of two peaks, whose
relative contribution depends on the coal type.
Mode(I), centered between 1.5nm and 2.5nm,
surprisingly accounts for a considerable fraction,
from 15% (MTL, PRB) up to 50% (COL, IDN),
of ultrafine particles. Particles smaller than 10nm
are at least 35% (UTS) because of the mode(II)
located at 5nm that is prevalent for MTL (45%)
and PRB (36%) coals. Mode(III) centered at
18nm accounts for matter, less than 10%, in the
intermediate size range. Mode(IV), accounting
for 5-12% of PM$_{0.1}$ is recognized at 45nm while
the remaining part of PM$_{0.1}$ belong to the
mode(V) that sweeps beyond the measurement
range centering around 180nm.

Figure 2 also shows the monomodal PSDF
centered at 2.5nm resulting from carbon black
oxidation at the same low oxygen concentration.
Oxidation of carbon black in the flame reactor
leaves ~0.01% of particles not oxidized at 50mm
above the burner. These particles have sizes in
the 1-5nm range and derive from fragmentation
of black carbon, as observed for soot oxidation in
a flow reactor [13] or surface oxidative
detachment. The particles formed during carbon
black oxidation have the same sizes of mode(I)
particles from coal combustion. Results from carbon black oxidation indicate that the
carbonaceous matter can contribute to the PM$_{0.1}$ from air blown pulverized coal combustion.

The UV-visible absorption spectrum of MTL coal ashes, collected by bubbling in water, is
plotted in Fig.3. Almost the same spectra were measured also for UTS and PRB coal ashes.
The absorption spectra show strong signal in the UV range, which decreases approaching a
low and noisy asymptotic value for wavelength larger than 350nm. A shoulder, stronger for
the UTS coal ashes, is also evident around 215nm while three absorption bands can be
identified, after spectra magnification, at 257nm, 264nm and 271nm, respectively. The
absorption spectra are similar to those of organic carbon nanoparticles with size below 5nm
detected in rich combustion of gaseous hydrocarbons [14]. The shoulder and the nonzero
asymptotic value could be due to small amounts of elemental carbon. The attribution of the
small bands to specific compounds has not yet been attempted.

3.1. Coal oxyfiring
The PSDFs of PM$_{0.1}$ formed burning the five coals in oxygen enriched environments are
plotted in Fig.4 as function of particle mobility diameter. Two extremely high oxygen
concentrations of 48.0% and 76.5%, were investigated to amplify the effects of oxyfiring

![Figure 2. PSDFs of PM$_{0.1}$ from combustion in 5.0%vol of oxygen: (□)UTS; (Ο)PRB; (Δ)MTL; (*)COL; (+)IDN. The fitted PSDFs are plotted with dotted lines. The solid line fits results burning Carbon Black (◊).](image)

![Figure 3. UV-Visible absorbance of the water sample from MTL coal combustion in 5%vol of oxygen.](image)
conditions on ash formation. Ultrafine particle yields range from few up to several cubic millimeter per coal gram in both conditions so that it is from three (MTL-48% O2) to seven times (UTS-76%O2) higher respect to conventional air-blown coal combustion. Particles are rather uniformly distributed in the ultrafine size range and each mode of the PSDFs gives a significant contribution to the particle volume fraction. Five modes have been identified also in the investigated oxyfiring conditions. The modal relative importance depends on the coal type and the oxygen concentration.

Mode(I) is again centered at 1.5-2nm and it accounts for a percentage of PM0.1 ranging from 4.3% (PRB) to 9.2% (COL) and from 2.6% (UTS) to 4.2% (COL) at oxygen concentration of 48.0% and 76.5%, respectively. The yield of such small particles is only slightly smaller than that measured in air combustion. Mode(II) particles are slightly larger (7nm) larger than those measured in air combustion. The larger size probably depends on different ash nucleation locations in the reactor involving longer residence times before sampling [11].

As for air blown combustion, particles smaller than 10nm totally account for a significant percentage of PM0.1 also in oxyfiring condition. Particularly they are from 21.9% (IND) to 51.3% (MTL) and from 8.3% (COL) to 25.2% (MTL) of PM0.1 for oxygen concentration of 48.0% and 76.5%, respectively. The yields of particles belonging to third and forth modes, still centered at 18nm and 45nm, respectively, are largely promoted by oxygen enriched environments. Appreciable differences have also been found among the five coals and the two enhanced oxygen concentrations. Mode(III) represents a fraction ranging from 14.7% (COL) to 47.6% (PRB) and from 12.3% (COL) to 57.13% (MTL) for the intermediate and high oxygen concentrations, respectively.

Results obtained at the intermediate oxygen level using the O2/N2 only slightly differ from that obtained using the O2/CO2 mixture because of a larger contribution of mode(IV). This enhancement of mode(IV) is anyway lower than that observed for increased oxygen concentration. Mode(V), located around 200nm, still sweeps the dimensional range under investigation but it seems to be not largely affected by oxygen concentration. In oxygen concentrations of 48% and 76.5%, carbon black oxidation produces the bimodal PSDFs, also reported in Fig.4. A small fraction (<0.01%) of carbonaceous matter survives extremely high oxidative conditions in the form of particles smaller than 5nm. The yield of this matter is comparable to that of mode(I) detected during coal oxyfiring. These results strongly indicate that carbonaceous matter could account in a large extent to mode(I) particles, also during coal combustion in oxygen enhanced conditions.
4. Final remarks
Five pulverized coals, covering a wide range of characteristics, have been oxidized in a flow reactor designed on purpose while the size distribution functions of incipient particles have been measured by a high resolution differential electrical mobility technique. The fraction of the particles captured in water have been also analyzed by UV-visible absorption spectroscopy whereas a carbon black powder has been oxidized in the same conditions of temperature and oxygen concentration to assess the contribution of unburnt carbon to ultrafine particles. Results have clearly shown that the PSDFs of coal ultrafine ash consist of five well distinct modes. Carbonaceous particles having size between 1nm and 3nm largely account for the smallest mode of coal fly ashes. Absorption spectra have revealed that such small particles mainly have an organic structure while some elemental carbon could also survive. A detailed data analysis suggests that the selective nucleation of ash components and their coagulating growth could be responsible for the larger modes of the PSDFs.

5. Acknowledgments
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7. References