Formation characteristics and elemental health effects of PM$_{2.5}$ during O$_2$/CO$_2$ combustion of pulverised coal

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What is inhalable particulate matter (PM$_{10}$)?

Solid or liquid particles suspended in the air

- **Human Hair**: ~70 µm average diameter
- **PM$_{2.5}$**: <2.5 µm in diameter
- **PM$_{10}$**: <10 µm in diameter
- **Fine Beach Sand**: 90 µm in diameter

*Image courtesy of EPA, Office of Research and Development*
Formation mechanism of PM$_{2.5}$

Coal

- Char fragmentation
- Fine coal particles
- Transformation of excluded minerals

Product

- Homogeneous / Heterogeneous coagulation / Reaction

Vaporization

Ultrafine mode

- $< 1$ μm

Central mode

- 1-3 or 5 μm

Coarse mode

- $> 3$-5 μm

PM$_{2.5}$ is mainly constituted of ultrafine mode and central mode particles

(Sarofim 1977; Flagan 1978; Linak 2002; Seames 2003; Dunxi Yu 2007)
Iron (Fe) and sulfur (S) have the quite adverse health effects comparing with other dominating elements in particulate matter.
Oxy-fuel Combustion technology

A promising technology for coal-fired power plants to control CO₂ emissions, as well as NOₓ, SO₂, and Hg emissions.

(Buhre 2005; Wall T. 2006)
Compared to the air (O₂/N₂) combustion:

- Carbon dioxide may undergo gasification reaction with carbon from coal/char surface, the change of CO/CO₂ in char particles surface will affect the gasification of refractory oxides.
- Lower temperatures in the surface of char particles and less char fragmentation and minerals gasification.

(Krishnamoorthy 2003; Suriyawong 2006; Sheng 2008)

**Oxy-fuel combustion (O₂/CO₂ combustion) has a significant impact on the formation and properties of PM, especially PM₂.5.**
To study the formation and properties of PM$_{2.5}$ generated during coal combustion under O$_2$/CO$_2$ and air(O$_2$/N$_2$) conditions.
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Experimental

Experimental system: Drop tube furnace
Coal sample: DT bituminous, NMG lignite, XLT lignite (All Chinese)
Feeding rate: 0.3 g/min  Temperature: 1573K
Atmospheres: O₂:CO₂=1:9 1:4 3:7, O₂:N₂=1:4 (by volume)
Particle size analyze: DLPI  Element analyze: XRF

<table>
<thead>
<tr>
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<th>Proximate analysis (wt% , ad)</th>
<th>Ultimate analysis (wt% , ad)</th>
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<tbody>
<tr>
<td></td>
<td>M</td>
<td>A</td>
</tr>
<tr>
<td>DT</td>
<td>1.8</td>
<td>27.8</td>
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<tr>
<td>NMG</td>
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<td>11.7</td>
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<tr>
<td>XLT</td>
<td>15.5</td>
<td>15.6</td>
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Low temperature ash elemental composition (LTA, wt%)

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<tr>
<th></th>
<th>Na₂O</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>P₂O₅</th>
<th>SO₃</th>
<th>K₂O</th>
<th>CaO</th>
<th>MnO</th>
<th>Fe₂O₃</th>
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<tr>
<td>DT</td>
<td>0.1</td>
<td>0.4</td>
<td>36.6</td>
<td>40.9</td>
<td>0.3</td>
<td>14.8</td>
<td>0.2</td>
<td>1.3</td>
<td>0.1</td>
<td>5.3</td>
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<tr>
<td>NMG</td>
<td>1.5</td>
<td>2.4</td>
<td>16.9</td>
<td>46.0</td>
<td>0.6</td>
<td>9.9</td>
<td>0.3</td>
<td>14.5</td>
<td>0.2</td>
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<tr>
<td>XLT</td>
<td>2.0</td>
<td>1.8</td>
<td>11.7</td>
<td>23.5</td>
<td>0.8</td>
<td>19.4</td>
<td>1.2</td>
<td>27.3</td>
<td>0.1</td>
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Coal feeder

Coal particles
primary gas

Secondary gas

Secondary gas

Vertical Furnace

Injection probe

Sampling probe

Cyclone

<10 µm

>10 µm

<table>
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<tr>
<th>Stage</th>
<th>After Filter</th>
<th>DLPI</th>
<th>Vacuum pump</th>
<th>Exhaust</th>
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<td>6.60</td>
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<td>13</td>
<td></td>
<td>9.80</td>
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Schematic Diagram of Cascade Impactor.
The identification of central mode in PM$_{2.5}$

PSD of DT: **Tri-modal.** A definite inflection point at approximately 2µm on the shoulder of the coarse mode, that is similar to O$_2$/N$_2$ combustion which was studied previously.

PSD of Al: The increase of composition between 0.258 and 2.36µm implies that they are belonged to central mode.

(Dunxi Yu, Proceeding of combustion institute, 2007)
Compared to the $O_2/N_2$ combustion:

- Carbon dioxide may undergo gasification reaction with carbon from coal/char surface, the change of $CO/CO_2$ in char particles surface will affect the gasification of refractory oxides.

- Lower temperatures in the surface of char particles and less char fragmentation and minerals gasification.

(Krishnamoorthy 2003; Suriyawong 2006; Sheng 2008)
The ultrafine mode (PM$_{0.2}$) includes the first four stages of LPI, the central mode (PM$_{0.2-2.5}$) includes the stages of 5-10.

**NMG**: The competition between reducing atmosphere and combustion temperature lead to PM$_{0.2}$ concentration is the least in 20% O$_2$.

**The difference of two coals**: the difference in the mode of occurrence of the main ash-forming elements within PM, which results in different characteristic of vaporization.
The influence of oxygen content

Total sulfur concentration:
DT: $O_2 \uparrow$, $PM_{0.2} \uparrow \downarrow$, $PM_{0.2-2.5} \uparrow$
NMG: $O_2 \uparrow$, $PM_{0.2} \downarrow \uparrow$, $PM_{0.2-2.5} \uparrow$

Iron concentration:
$O_2 \uparrow$, $PM_{0.2} \uparrow$, $PM_{0.2-2.5} \uparrow$

PM$_{0.2}$: Competition between reducing atmosphere and combustion temperature; the difference in the mode of occurrence of the main ash forming elements.

The difference of sulfur convert into PM$_{0.2}$: The competition among homogeneous nucleation, heterogeneous condensation and particles coalescence. (Sulfur $\rightarrow$ sulfate $\rightarrow$ PM)

(Kauppinen, Environ Sci Technol, 1990)
O$_2$/CO$_2$ combustion versus O$_2$/N$_2$ combustion

**O$_2$/CO$_2$: PM$_{0.2}$ ↓、PM$_{0.2-2.5}$ ↓**

- Carbon dioxide may undergo gasification reaction with carbon from coal/char surface, the change of CO/CO$_2$ in char particles surface will affect the gasification of refractory oxides;
- The specific heat capacity of CO$_2$ is larger than that of N$_2$;
- The diffusion rate of O$_2$ in CO$_2$ is lower than that in N$_2$.

Resulted in the lower combustion temperature of coal particle
The differences of PM$_{0.2}$ formation between O$_2$/CO$_2$ and O$_2$/N$_2$ combustion are not so significant (Previous Page), but the high temperature in O$_2$/N$_2$ combustion increase the gasification ratio of refractory elements.

XLT lignite has a high alkali metals content (LTA), the optimum temperature of sulfur and alkali metals reaction is around 1400K, that is close to particle temperatures of O$_2$/CO$_2$ atmosphere.

( Wibberleya , Fuel , 1982 )
Sulfur present in PM$_{2.5}$ as sulfur, sulphuric acid, sulfurous acid and sulfate.

Breathing excessive sulfur compound may generate irritant to eye and nose, sulfurous acid is a impetus to asthma, especially to children.

Sulfur in central mode of PM$_{2.5}$ is slightly less or even larger than sulfur concentration in ultrafine mode.

As the combustion condition changes, sulfur concentration in PM$_{2.5}$ from different coals presents different characteristic.

Iron is a typical transition element, it can catalyse the formation of ROS (reactive oxygen species), which is likely to bring arteriosclerosis and cancer.

Iron compound in ultrafine particles can combine with other trace elements like chromium, then it catalyse the formation of human free radical and increase the pressure in cardiovascular system.

( Amdur, Environ Health Perspect, 1989 )

( Lighty, J Air Waste Management, 2000 )
Tri-modally distribution are observed in O$_2$/CO$_2$ combustion with peak around 0.15µm, 1.58µm and larger than 10µm.

O$_2$/CO$_2$ combustion can be effective in reducing PM$_{2.5}$ formation, and decreasing oxygen content results in a reduction of PM$_{2.5}$ formation, too.

Sulfur concentration in central mode of PM$_{2.5}$ is slightly less or even larger than sulfur concentration in ultrafine mode, and iron mostly exists in central mode of PM$_{2.5}$.

As the combustion condition changes, sulfur concentration in PM$_{2.5}$ from different coals presents different characteristic.

**We should be more thorough in our study about sulfur formation in PM$_{2.5}$.**

The mode of occurrence of sulfur, and how to transfer to PM$_{2.5}$
Thanks for your attention!

Thanks to National Natural Science Foundation of China
(Grant No. 50325621, 50721005, 50720145604)