Study of coal devolatilization and combustion under oxy-steam conditions with high H₂O concentrations

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12th ECCRIA Conference, 5-7 September, Cardiff (UK)
Oxy-fuel combustion of coal

**Carbon capture technology:** firing coal in $O_2$ diluted in a recycled stream of $CO_2$, rendering pure $CO_2$ as flue gas ready to storage

**1st generation oxy-fuel combustion systems**

Flue gas is recycled to control the combustion temperature

IEAGHG “Oxyfuel combustion of pulverised coal” 2010/7
Oxy-fuel combustion of coal

Main challenges:

- **Operational**
  - Control the heat transfer profile of the combustion process
  - Reaching a high CO$_2$ concentration in the flue gas

- **Chemical**
  - Ignition, burnout, emissions

- **Economical**
  - Cost of oxygen (energy penalty)
  - Cost of transport of the product flue gas

Different gas properties lead to changes in the adiabatic flame temperature, heat transfer, emissivity, hydrodynamics...
Oxy-fuel combustion of coal

2nd generation oxy-fuel combustion systems

Energy efficient integration and optimization of the process, recovery of low temperature heat

Fast approaching demonstration stage (IEA CCT reports)
3rd generation of Oxy-fuel combustion

Minimizing or eliminating the flue gas recycle

- Reduction in size
- Reduction in capital cost
- Flexibility

Oxy-steam combustion

Avoidance of energy spent in gas recycling, flue gas separation and purification

≈ Energy penalty of steam production (highly integrated)

Sheng 2014
Oxy-steam combustion

- Volumetric flow rate through boiler and auxiliary equipment is reduced
- Higher radiative and convective heat transfer
- Low NO\textsubscript{x} and excess O\textsubscript{2}
- 90%CO\textsubscript{2} (db) in final flue gas (less infiltration issues)
- Adiabatic flame temperature would allow 30-40% O\textsubscript{2}

Up to 40% scale reduction in unit size

High energy integration (Canmet, Seepana 2010)

Cp Steam>>> Cp CO\textsubscript{2}: lesser amount of steam is needed to create the same moderation

Better O\textsubscript{2} diffusion values
Oxy-steem combustion

- Volumetric flow rate through boiler and auxiliary equipment is reduced
- Higher radiative and convective heat transfer
- Low NO\textsubscript{x} and excess O\textsubscript{2}
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Up to 40% scale reduction in unit size
high energy integration
(Canmet, Seepana 2010)

<table>
<thead>
<tr>
<th></th>
<th>Air Combustion</th>
<th>Dry Oxy-combustion</th>
<th>Wet oxy-combustion</th>
<th>Oxy-steem combustion</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Windbox O\textsubscript{2}</strong></td>
<td>21</td>
<td>21 - 30</td>
<td>21 - 30</td>
<td>30 - 40</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>79</td>
<td>0 - 10</td>
<td>0 - 10</td>
<td>0 - 1</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>-</td>
<td>60 - 80</td>
<td>40 - 60</td>
<td>-</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>-</td>
<td>-</td>
<td>10 - 40</td>
<td>60 -70</td>
</tr>
<tr>
<td>others</td>
<td>-</td>
<td>NO\textsubscript{x}, SO\textsubscript{2}</td>
<td>NO\textsubscript{x}, SO\textsubscript{2}</td>
<td>-</td>
</tr>
<tr>
<td><strong>Flue gas O\textsubscript{2}</strong></td>
<td>2 - 6</td>
<td>2 - 6</td>
<td>2 - 4</td>
<td>2 - 5</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>65 - 75</td>
<td>0 - 10</td>
<td>0 - 10</td>
<td>0 - 1</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>7 - 18</td>
<td>60 - 85</td>
<td>50 - 70</td>
<td>35-45</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>4 - 18</td>
<td>8 - 16</td>
<td>30 - 48</td>
<td>50-60</td>
</tr>
<tr>
<td>others</td>
<td>NO\textsubscript{x}, SO\textsubscript{2}</td>
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<td>NO\textsubscript{x}, SO\textsubscript{2}</td>
<td>NO\textsubscript{x}, SO\textsubscript{2}</td>
</tr>
</tbody>
</table>
**OxyHidro project**

*Oxy-stea coal combustion. Towards third-generation oxy-combustion*

Spanish Ministry of Economy and Competitiveness, contract ENE2015-67448-C2

**Design and Reactor Start Up**

- **Kinetics Devolatilization**
- **Oxidation 0 – 80% H₂O**

**Testing 0 - 40% H₂O**

- **Combustion yield**
- **Heat transfer**
- **Emissions**

**Ashes deposition**

**Mineral matter evolution 0 – 80% H₂O**

**Corrosion**

**Oxidation and corrosion 0 – 80% H₂O**

**Condensed**

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OxyHidro project

“Oxy-steam coal combustion. Towards third-generation oxy-combustion”
Spanish Ministry of Economy and Competitiveness contract ENE2015-67448-C2

Kinetics Devolatilization Oxidation 0 - 80% H₂O
Numerical simulation 0 – 80% H₂O

Combustion yield
Heat transfer
Emissions

Testing 0 - 40% H₂O

Ashes deposition
Corrosion
Condensed

Mineral matter evolution 0 – 80% H₂O
Oxidation and corrosion 0 – 80% H₂O

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Determinition of kinetic parameters

There is a range of T where kinetic parameters obtained by TGA can be extrapolated to high temperature as long as Regime I is maintained.

Determinación de parámetros cinéticos


**Regime I:** 
Reaction kinetics control

**Regime II:** 
Internal diffusion & Reaction kinetics control

**Regime III:** 
Bulk diffusion controlled

"There is a range of $T$ where kinetic parameters obtained by TGA can be extrapolated to high temperature as long as Regime I is maintained."

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Coal reactivity in Steam-TGA

- Non-isothermal experiments: **20 K/min**, 353-1173 K
- **Steam** concentration: **0, 20, 40, 70 vol.%**
- **Oxygen** concentration: **0, 20, 30 vol%**
- **N₂** or **CO₂** to balance

<table>
<thead>
<tr>
<th></th>
<th>Anthracite</th>
<th>Blend</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Proximate analysis</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture (%, a.r.)</td>
<td>1.8</td>
<td>5.9</td>
</tr>
<tr>
<td>Ash (%, dry)</td>
<td>26.9</td>
<td>27.8</td>
</tr>
<tr>
<td>Volatile (%, dry)</td>
<td>5.5</td>
<td>26.4</td>
</tr>
<tr>
<td>Fixed Carbon (%, dry)</td>
<td>67.6</td>
<td>45.8</td>
</tr>
<tr>
<td><strong>Ultimate analysis</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C (wt.%, daf)</td>
<td>92.9</td>
<td>73.8</td>
</tr>
<tr>
<td>H (wt.%, daf)</td>
<td>2.1</td>
<td>4.2</td>
</tr>
<tr>
<td>N (wt.%, daf)</td>
<td>1.2</td>
<td>1.6</td>
</tr>
<tr>
<td>S (wt.%, daf)</td>
<td>1.2</td>
<td>6.6</td>
</tr>
<tr>
<td>O (wt.%, daf)</td>
<td>2.6</td>
<td>13.8</td>
</tr>
<tr>
<td>LHV (MJ/kg, dry)</td>
<td>23.6</td>
<td>20.16</td>
</tr>
</tbody>
</table>

**Netzsch STA-449-F3**

able to work under **100 % H₂O**
Devolatilization in Steam-TGA

- **Steam concentration:** 0, 20, 40, 70 vol.%
- **CO$_2$** to balance

- **Devolatilization was not observed in the case of anthracite**
- **Gasification at high temperature occurred in the presence of steam and/or CO$_2$**
Devolatilization in Steam-TGA

**COAL BLEND**

Pyrolysis  Gasification

**Kinetics calculation**

Coats-Redfern integral method

\[
\frac{d\alpha}{dt} = A \cdot \left( \frac{E}{RT} \right) \cdot (1-\alpha)^n
\]

\( n = 1 \)

**Temperature (K)**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>DTG (wt.% min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>-3.0</td>
</tr>
<tr>
<td>600</td>
<td>-2.5</td>
</tr>
<tr>
<td>800</td>
<td>-2.0</td>
</tr>
<tr>
<td>1000</td>
<td>-1.5</td>
</tr>
</tbody>
</table>

**% H\(_2\)O**

<table>
<thead>
<tr>
<th>% H(_2)O</th>
<th>N(_2)</th>
<th>CO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>40</td>
<td>25</td>
</tr>
<tr>
<td>20</td>
<td>35</td>
<td>30</td>
</tr>
<tr>
<td>40</td>
<td>40</td>
<td>35</td>
</tr>
<tr>
<td>70</td>
<td>45</td>
<td>40</td>
</tr>
</tbody>
</table>

**E\(_a\) in dry N\(_2\) > E\(_a\) in wet oxy-fuel > E\(_a\) in oxy-steam**
Direct oxidation in Steam-TGA

**COAL BLEND**

- **Oxygen concentration:** 20 and 30 vol.%
- **N₂ or CO₂ to balance**

**Two different stages in direct oxidation**

- **Devolatilization (pyrolysis)**
- **Char oxidation**

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**Temperature (K)**

<table>
<thead>
<tr>
<th>400</th>
<th>600</th>
<th>800</th>
<th>1000</th>
<th>1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% H₂O</td>
<td>20% H₂O</td>
<td>40% H₂O</td>
<td>70% H₂O</td>
<td></td>
</tr>
</tbody>
</table>

**Mass loss (%)**

<table>
<thead>
<tr>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>100</th>
</tr>
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</table>

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**Temperature (K)**

<table>
<thead>
<tr>
<th>400</th>
<th>600</th>
<th>800</th>
<th>1000</th>
<th>1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% O₂, CO₂</td>
<td>20% O₂, N₂</td>
<td>30% O₂, CO₂</td>
<td>30% O₂, N₂</td>
<td></td>
</tr>
</tbody>
</table>

**Mass loss (%)**

<table>
<thead>
<tr>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>100</th>
</tr>
</thead>
</table>

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**DTG (%/min)**

<table>
<thead>
<tr>
<th>-10</th>
<th>-8</th>
<th>-6</th>
<th>-4</th>
<th>-2</th>
<th>0</th>
</tr>
</thead>
</table>

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Direct oxidation with steam addition

Coal blend, 30% O₂ in CO₂

Increasing H₂O content

- Delay in devolatilization of coal??
- Reduction in combustion reactivity??

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Direct oxidation with steam addition

Increasing H$_2$O content → No significant effect on oxidation
Direct oxidation with steam addition

Anthracite

Temperature (K)

20% $O_2$

$0\% H_2O$

$20\% H_2O$

$40\% H_2O$

$70\% H_2O$

$0\% H_2O, N_2$

Temperature (K)

$0\% H_2O$

$20\% H_2O$

$40\% H_2O$

$70\% H_2O$

$0\% H_2O, N_2$

DTG (%/min)

Temperature (K)

$20\% O_2$

$30\% O_2$

$0\% H_2O$

$20\% H_2O$

$40\% H_2O$

$70\% H_2O$

$0\% H_2O, N_2$

mass loss (%)

0% $H_2O$

20% $H_2O$

40% $H_2O$

70% $H_2O$

0% $H_2O, N_2$

0% $H_2O$

20% $H_2O$

40% $H_2O$

70% $H_2O$

0% $H_2O, N_2$
Direct oxidation with steam addition

Anthracite, 30% O₂ in CO₂

Deconvolution

Temperature (K)

DTG (%/min)

Increasing H₂O content   Effect on ignition and burnout in oxidation

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Direct oxidation with steam addition

**Anthracite, 30% O₂ in CO₂**

![Graph showing the effect of increasing H₂O content on ignition and burnout in oxidation.](image)

**Deconvolution**

Increasing H₂O content  Effect on ignition and burnout in oxidation
Characteristic temperatures

- Ignition temperature ($T_i$)
- Maximum combustion rate temperature ($T_{peak}$)
- Burnout temperature ($T_{bo}$)
Anthracite characteristic temperatures

Anthracite, 30% O₂ in CO₂

Deconvolution

20% H₂O favours oxidation by OH radical effect

gasification?

20% O₂
30% O₂

H₂O concentration (vol.%)

Temperature (K)

T_i

T_bo

T_peak
Coal blend characteristic temperatures

Coal blend 30% O₂ in CO₂

20% H₂O favours oxidation by OH radical effect

40-70% H₂O slightly increases T_bo in low rank coal
Kinetic study: data zones

Data zones considered for the kinetics calculation of devolatilization and oxidation processes

Coats-Redfern integral method

\[ \frac{d\alpha}{dt} = \frac{A}{\beta} \cdot e^{\left(\frac{E}{RT}\right)} \cdot (1-\alpha)^n \]

n=1
Kinetic study: activation energy calculations

conventional combustion (20% O$_2$ + 80% N$_2$)
oxy-fuel combustion (20% O$_2$ + 80% CO$_2$)
water-recycle oxy-fuel combustion (20%O$_2$ + 40% H$_2$O + 40% CO$_2$)
oxy-steam combustion (20% O$_2$ +70% H$_2$O + 10% CO$_2$)
Kinetic study at 800 – 1200 K

\[ k(T) = A \cdot e^{-\frac{E}{R \cdot T}} \]

Similar kinetics in Oxy-steam to in wet oxy-fuel
Conclusions

When comparing coals and technologies as a function of steam presence:

1. Devolatilization and direct oxidation in the presence of high steam concentrations was significantly influenced by the coal rank.

2. Replacing CO₂ with 20% H₂O produced a decrease in ignition temperatures (OH radical effect).

3. For high-volatile content coals, addition of 40% and 70% H₂O increases burnout temperature.

4. In terms of activation energy and Arrhenius k, no significant differences were found when comparing wet oxy-fuel and oxy-steam combustion technologies.
Thank you for your attention

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Combustion process is delayed in the presence of CO$_2$ compared with N$_2$/O$_2$

Coal reactivity increases with the oxygen content and DTG curve is shifted to lower temperatures
Direct oxidation vs. char oxidation

Different behaviour:
coal vs char
in T and reactivity

Coal blend

Char of coal blend

20% O₂

20% H₂O