Effects of Flue Gas Recirculation on NO and N₂O formations in Coal Combustion

Ryo Yoshiie\textsuperscript{a}, Yasuaki Ueki\textsuperscript{b}, Ichiro Naruse\textsuperscript{a*}

\textsuperscript{a} Department of Mechanical Science & Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 4648603, Japan
\textsuperscript{b} EcoTopia Science Institute, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 4648603, Japan
E-mail address: naruse@mech.nagoya-u.ac.jp.

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Background

Previous reports:
NO\textsubscript{X} emissions

Oxy-fuel coal combustion < Air coal combustion
(the absence of N\textsubscript{2} in gas and lower flame temperature)

There have been few reports describing NO\textsubscript{X} formation under oxy-fuel combustion conditions, including the quantitative effect of additional re-circulated NO and N\textsubscript{2}O.
Objectives

Oxy-fuel (with flue gas recirculation) ⇔ Air

- Combustion behaviors (1073K~1223K)
- NOx (NO + N₂O) emissions

Contents

CO₂-O₂ atmosphere

Combustion experiment

Flue gas re-circulation

(NOx addition to the inlet CO₂-O₂)
Simulated oxy-fuel

{ Combustion experiment
Elemental reaction analysis

NOx emissions

Simulated oxy-fuel
Drop tube furnace for coal combustion experiment

**Fuel injection part**
- Continuous feeding
- Entraining gas: CO₂+O₂ or Air

**Reaction part**
- Temperature controlled by electric heater
- Residence time: 2s

**Sampling part**
- Iso-kinetic sampling
- Gas analysis
- Particle analysis

Diagram showing:
- Primary gas
- Mass flow controller
- Secondary gas
- Heater unit
- Dilution gas
- Water in
- Water out
- Sampling probe
- Filter
- Gas sample unit
- Oxygen (O₂)
- Carbon Dioxide (CO₂)
- Air
- Argon (Ar)
**Coal properties**

<table>
<thead>
<tr>
<th>Coal</th>
<th>Volatile matter</th>
<th>Fixed carbon</th>
<th>Ash</th>
<th>Moisture</th>
<th>Ultimate analysis [wt.% d.a.f]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>30.3</td>
<td>56</td>
<td>13.7</td>
<td>2</td>
<td>C: 80.97, H: 9.32, N: 1.47, O: 7.79, S: 0.45</td>
</tr>
</tbody>
</table>

**Experimental conditions**

- **Atmosphere**: CO\(_2\)+O\(_2\) (Air)
- **CO\(_2\):O\(_2\)**: 79:21
- **Primary gas [L/min]**: 0.22 (O\(_2\)) (1.05 (Air))
- **Secondary gas [L/min]**: 0.83 (CO\(_2\)) (3.85 (Air))
- **Dilution gas (Ar) [L/min]**: 3.04 (CO\(_2\))
- **Dilution rate (Sample gas : Ar = 1 : 4)**: 1.23
- **Stoichiometric air ratio**: 1.2
- **Pressure [atm]**: 1
- **Coal feed rate (g/min)**: 0.5 ± 0.05
- **Sampling distance from injector [mm]**: 1300
- **Furnace temperature [K]**: 1073, 1123, 1173, 1223
Carbon conversions under air and CO$_2$-O$_2$ combustion

- High concentrations of CO$_2$ → Low reaction rate, low heat transfer

Carbon conversions: CO$_2$-O$_2$ < air @ all temperature
Combustion experiment under flue gas re-circulation condition

In oxy-fuel system, minor components in flue gas was re-circulated to the combustion zone. Focusing on NO and N2O

Procedures to make up re-circulated gas with additional NO and N2O

<table>
<thead>
<tr>
<th>Gas</th>
<th>O₂</th>
<th>NO</th>
<th>N₂O</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vol%</td>
<td>21</td>
<td>(\alpha x_{i-1})</td>
<td>(\alpha y_{i-1})</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Initial gas composition at the inlet in \(i^{th}\) recycle experiment

- \(i\) : recycle times (\(i=0\) to 5)
- \(x_i\) : NO concentration in flue gas in \(i^{th}\) recycle experiment (\(x_0=0\))
- \(y_i\) : N₂O concentration in flue gas in \(i^{th}\) recycle experiment (\(y_0=0\))
- \(\alpha\) : dilution ratio defined by additional O₂ to the flue gas
1st step to simulate flue gas re-circulation condition

Inlet gas approaches to oxy-fuel with increase in gas recycling times

O₂-fuel ratio 1.2

2

8

O₂

CO₂

VM

FC

2

8

1st re-circulation experiment (i=1)

VM = Volatile matter
FC = Fixed Carbon

CO₂-O₂ combustion experiment (i=0)

Flue gas

NO

N₂O

Ar
NO concentrations at the reactor outlet with gas recycle times

NO in flue gas: not accumulate

NO under oxy-fuel combustion < NO under air combustion

Higher temperature ➔ Smaller difference
$N_2O$ concentration at the reactor outlet with gas recycle times

- **1073K $N_2O$**
- **1223K $N_2O$**

$N_2O$ in flue gas: accumulate due to additional $N_2O$

$N_2O$ under oxy-fuel combustion $> N_2O$ under air combustion

Higher temperature $\Rightarrow$ Smaller difference
Elemental reaction analysis

Based on
- 52 chemical species, 323 elemental reactions (GRI-mech 3.0)
- 4 surface reactions (BRAIN-C, NEDO, 1989)

Pressure and temperature: constant through reaction time (3s)

Assumption for compositions of volatiles from coal

\[ \text{NH}_3, \text{HCN}, \text{H}_2, \text{C}_2\text{H}_4, \text{CO} \]

N \[ \rightarrow \] \( \text{NH}_3 : \text{HCN} = 1 : 1 \)

Rest of H \[ \rightarrow \] \( \text{H}_2 : \text{C}_2\text{H}_4 = 1 : 1 \)

Balance C \[ \rightarrow \] \( \text{CO} \)

\( \text{O}_2 \) fuel ratio \[ \rightarrow \] 1.2

\( \text{CO}_2 : \text{O}_2 = 8 : 2 \)

\[ \text{mol} \% \]

\begin{align*}
\text{NH}_3 & \quad 0.00040 \\
\text{HCN} & \quad 0.00040 \\
\text{H}_2 & \quad 0.01147 \\
\text{C}_2\text{H}_4 & \quad 0.01147 \\
\text{CO} & \quad 0.02763 \\
\text{O}_2 & \quad 0.17089 \\
\text{CO}_2 & \quad 0.68356 \\
\text{FC} & \quad 0.09419
\end{align*}
Output under oxy-fuel combustion can be derived as a convergence.

Procedures to make up re-circulated gas (Sim.)

O₂-fuel ratio 1.2

CO₂-O₂ combustion simulation (i=0)

Flue gas

Re-circulated gas

1st re-circulation simulation (i=1)
NO concentration with reaction time under air, CO$_2$-O$_2$ and oxy-fuel combustion conditions

**Oxy-fuel combustion**

NO accumulation doesn't happen in spite of additional NO

Consistent with exp.
N$_2$O concentration with reaction time under air, CO$_2$-O$_2$ and oxy-fuel combustion conditions.

- Additional N$_2$O
- Oxy-fuel combustion
- N$_2$O accumulation happens due to additional NO
- Consistent with exp.

Nagoya University
1. Carbon conversion under CO$_2$-O$_2$ combustion was lower than that under air combustion.

2. NO concentration from coal combustion in CO$_2$-O$_2$ atmosphere was lower than that in air, and it did not increase in spite of additional NO input under oxy-fuel condition at 1073K. However, NO emissions accumulated under oxy-fuel conditions at 1223K.

3. N$_2$O concentration from coal combustion in CO$_2$-O$_2$ atmosphere was higher than that in air, and it accumulated under oxy-fuel condition at 1073K. The accumulation of recycled N$_2$O and the differences between the outcomes of oxy-fuel and air combustion had practically disappeared at 1223K.