Nitrogen Release during Pyrolysis in an Oxycombustion Process

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Overview

• Motivation for Oxy-fuel Combustion
• Previous studies
• Objective
• Approach
• Bituminous Coal Results
• Sub-bituminous Coal Results
• Density and Swelling
• Conclusion
Motivation for Oxy-Fuel

• Possible CO$_2$ regulations
  – Exit stream of CO$_2$/H$_2$O
  – Lower volume of gases in furnace
    • About a 20% reduction after recycling

  – Reduces NO$_x$ emissions
  – 0.4 lb/MMBtu in 2000
  – 0.17 lb/MMBtu in 2008
  – 0.14 lb/MMBtu in 2018
Oxycombustion Power Plants

From Mackrory and Tree
Documented NO\textsubscript{x} Reduction

Burhe, et al cited the following findings in a 2005 Progress in Energy and Combustion Science:

• NO\textsubscript{x} decrease of 50%
  – Energy and Environmental Research Corporation

• “Significantly decreased” NOx emissions
  – International Flame Research Foundation

• 25% decrease in NO\textsubscript{x}, though it increased with increasing O2 concentration
  – Kiga & co-workers

• Below 0.15 lb/MMBtu in pilot scale
  – B&W

• Decreased NO\textsubscript{x} emission
  – CANMET
Property Differences

Mackrory Conclusions

- Oxy-fuel produces higher CO, hydrocarbon, NH$_3$, and HCN concentrations in fuel-rich zones than air at same SR
- High CO in oxy-fuel is primarily due to thermal dissociation of CO$_2$ above 1500K, with minor influence from CO$_2$ gasification of char
- Differences between air and oxy-fuel combustion in a once-through combustor may result in slightly lower NO$_X$ from oxy-fuel.
Objectives

• Identify the differences, if any, between air and oxy-fuel single particle nitrogen release
• Identify the mechanism of difference in nitrogen release
• Compare results to CPD model to further validate the model
Approach

• Find four stable temperature conditions, with peak temperatures at 100 K intervals (1600, 1700, 1800, 1900 K) to simulate oxy-fuel conditions
• Collect char of 3 coals at each temperature condition
• Perform ultimate, proximate, and ICP analysis
• CO₂ used as diluent gas for Oxy-fuel experiments
• N₂ used as diluent gas for air experiments
• Create plots of mass and nitrogen release vs temperature
Flat Flame Schematic

- Simulates single particle affects
- Feed rate ~ 1 gram/hr
- 1 inch height has a residence time of ~ 15 ms
- 2 inches ~26 ms time
Temperature Profile

- 1700 K Oxy-fuel profile
- Adiabatic Flame Temperature of 1778 K
- Measured with type B thermocouple
- Temperature adjusted for radiation affects
Mass & Nitrogen Release

\[
MR_{daf} = \frac{1 - \frac{x_{Ti,coal}}{x_{Ti,ash}}}{1 - \frac{x_{Ti,coal}}{x_{Ti,coal}}} \\
N\text{ Release}_{daf} = 1 - \left(1 - MR_{daf}\right) \left(\frac{x_{N,daf\ char}}{x_{N,daf\ coal}}\right)
\]

- Mass release calculated using Elemental Tracer Analysis (ETA)
- ETA performed for Si, Ti, and Al, then averaged
- N Release uses averaged ETA and N content of coal and char from elemental analysis
Mass Release - Pittsburgh #8

![Graph showing mass release vs. temperature]

- **Mass Release (daf)**
- **Temperature (K)**

- **Oxy-fuel**
- **CPD Model**
Nitrogen Release – Pittsburgh #8
Mass Release - Illinois #6

![Graph showing mass release vs. temperature for air and oxy-fuel combustion.](Image)
Nitrogen Release – Illinois #6

Nitrogen Release (daf) vs Temperature (K)

- Air
- Oxy-fuel
- CPD Model
Results for Bituminous Coals

• Both Oxy-fuel mass and nitrogen release mirrored the Air results and the CPD model for the Illinois #6

• The Pittsburgh 8 shows a difference from the CPD model within experimental error
Mass Release – Black Thunder

![Graph showing the relationship between temperature (K) and mass release (daf). The graph includes data points for Air (2001), Oxy-fuel, Air (2008) - 2 inch, and Air (2008) - 1 inch. The graph shows a clear trend of increasing mass release with increasing temperature.]
Nitrogen Release – Black Thunder

![Graph showing nitrogen release versus temperature](image)

- **Nitrogen Release (daf)**
- **Temperature (K)**

- Green diamonds: Air (2001)
- Red triangles: Oxy-fuel
- Yellow diamonds: Air (2008) - 2 inch
- Purple squares: Air (2008) - 1 inch

- Blue line: CPD Model
Results - Subbituminous Coal

• Coal needs to be fully pyrolyzed to complete mass release
  – 1 inch N$_2$ is not fully pyrolyzed
  – 1 inch CO$_2$ is likely not either

• 2 inch N$_2$ has about the same mass and nitrogen release as the 1 inch CO$_2$
  – Possible effects
    • Gas Property Differences
    • Gasification
CPD Model

• Chemical Percolation Devolatilization
  ▪ Designed by Dr. Fletcher et al. in 1989
  ▪ Models devolatilization based on chemical structure of parent coal

• Cpdcpnlg version modified by Perry (1999)
  ▪ Calculates nitrogen release for tar, light gas
  ▪ Uses curve fits of C-13 NMR data to model structure
  ▪ Other inputs include: velocity, temperature, proximate analysis, ultimate analysis
CPD Model Validation

A. BT 1600

B. BT 1700
More CPD Validation
Density and Swelling

\[
\frac{m}{m_0} = \left( \frac{\rho}{\rho_0} \right) \left( \frac{d}{d_0} \right)^3
\]

- Bulk Density found using tap density method
- Density shows no trend with temperature
- Coal Chars show slight shrinkage
Conclusion

• There is no apparent difference at high temperatures for the bituminous coals
• The sub-bituminous coal (BT) exhibits increased mass and nitrogen under oxy-fuel conditions for a 15 ms residence time
  – Possible effects
    • Gasification
    • Gas Property Differences
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