Nitrogen Evolution in Oxy-fuel Combustion

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Background and Objective

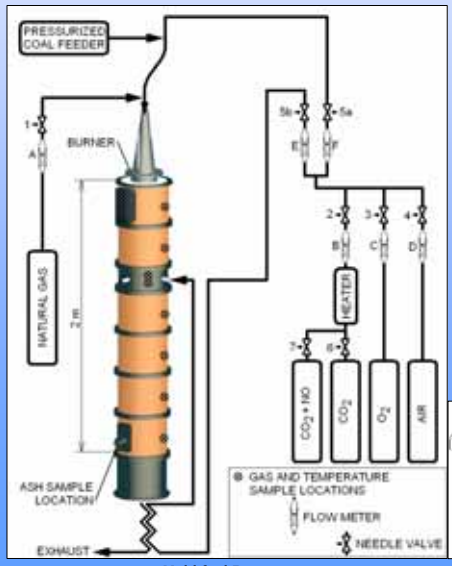
- Pilot scale oxy-fuel tests show an unexpected reduction in NO_x emissions
- Early research suggests that reduction of recycled NO_x is the dominant mechanism (Okazaki and Ando, 1997) but…
- …the mechanisms behind this reduction are not yet understood (Sarofim, 2007).

Our objective is to determine the causes of NO_x reduction in oxy-fuel combustion and thereby understand how NO_x reduction might be maximized.

Possible NO_x Reduction Mechanisms

- Near-elimination of thermal- and prompt-NO_x
- More attached flame
- Elevated NO concentrations
- Reduction of recycled NO_x in the fuel-rich zone
- Temperature increases
- Increased residence time in fuel-rich regions
- Equilibrium considerations
- Reduced NO formation from char
- Enhanced heterogeneous reburning
- Increased importance of gasification reactions

Experiments and Modeling



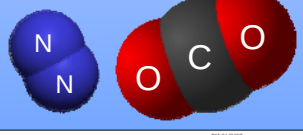
Multi-fuel Reactor Configured for Staged Oxy-fuel Combustion

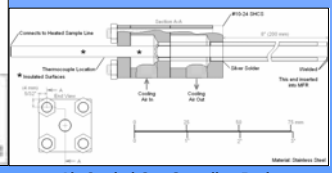
Gas analysis is performed using a HORIBA PG-250 portable gas analyzer for O_2, CO, and NO.

The new gas sample probe is air-cooled.

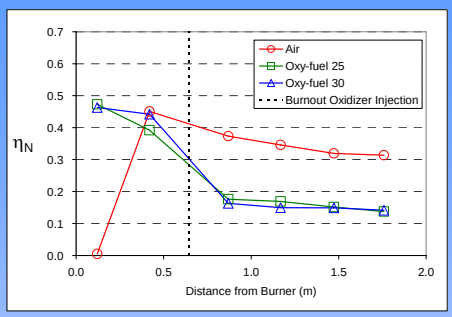
Addition of high spatial resolution gas sampling ports has just been completed.

An MKS FTIR gas analyzer with a heated sample line is being added to allow measurement of SO_2, SO_3, HCN, NH_3, CO_2 and other species.





Air-Cooled Gas Sampling Probe

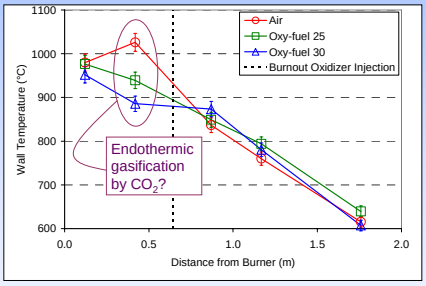


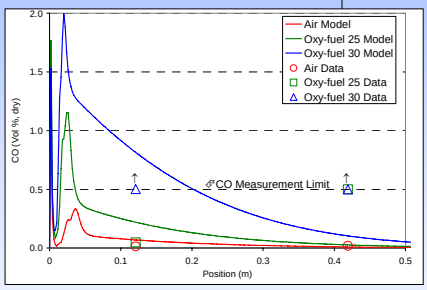
←Illinois #6 coal, SR_1 = 0.78, SR_2 = 1.09
Oxy-fuel 25 = 25% O_2, 75% CO_2 by mass
Oxy-fuel 30 = 30% O_2, 70% CO_2 by mass

Nitrogen conversion efficiency data shows apparently faster rates of NO destruction in the oxy-fuel cases leading to lower effluent NO in oxy-fuel independent of NO recycling.

Initial NO formation appears similar for all cases but higher spatial resolution data are required to identify peak NO levels and the location where conditions change from oxidizing to reducing.

Wall temperatures in oxy-fuel cases are unexpectedly lower in the reducing zone. Combined with the high measured CO values this suggests that endothermic gasification by CO_2 becomes significant under oxy-fuel conditions. ↓

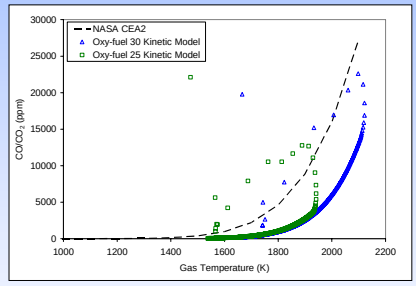


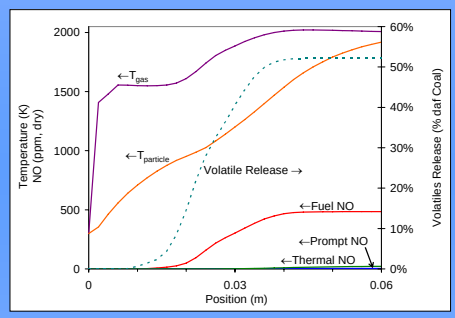


Model predictions of CO concentration correspond closely to equilibrium→

←Equilibrium dissociation of CO_2 to form CO can explain experimentally observed trends in CO near the burner, but not further downstream.

Other researchers report high concentrations of CO in oxy-fuel reducing zones without adequate explanation.





Conceptual Design of the Computational Model

Oxy-fuel combustion is modeled in MATLAB using Cantera for gas phase kinetics, and the CPD-NLG model for devolatilization and fuel-N release.

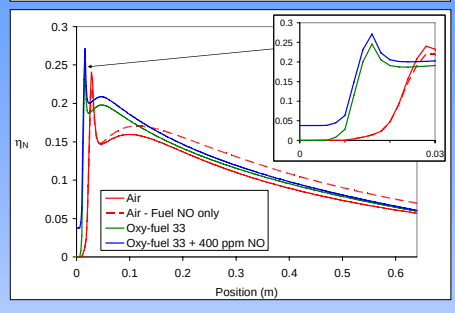
A series network of CSTR's simulates a plug flow reactor (1-D).

Homogeneous NO_x mechanisms:
- **Thermal**
- **Prompt**
- **Fuel**
- **Advanced reburning (Bowman, 1997)**

Char combustion & gasification is not yet incorporated.

The model predicts NO in the air case is mainly fuel-NO suggesting that elimination of prompt- and thermal-NO is not a significant mechanism.

The coal flame is stabilized with natural gas (first temperature rise). The model supports the assertion that the stoichiometry and temperature of the natural gas flame produce negligible NO_x.



Despite ~50% longer residence time in the oxy-fuel case, spatial rates of NO destruction are similar to the air case.

High concentrations of NO in reactants are predicted to suppress NO formation (as reported in literature).

High concentrations of NO also increase the NO destruction rate such that all recycled NO is effectively destroyed (as reported in literature).

The thermal- and prompt-NO mechanisms are responsible for some NO reduction.

Conclusions

- Oxy-fuel combustion can produce lower NO emissions independent of recycling, by apparently faster NO destruction rates in reducing zones.
- Gas phase kinetic modeling using known NO mechanisms can predict trends observed experimentally elsewhere: Suppression of NO formation by recycled NO, nearly complete destruction of all recycled NO etc. but cannot predict the results seen here.
- As measured by others, high CO levels exist in the reducing zone of oxy-fuel flames. Thermal dissociation of CO_2 can only partially explain this observation. Another possible source of CO is gasification of char by CO_2 which is suggested by our temperature data.
- A possible explanation for the greater NO reduction in oxy-fuel is NO reaction with CO on the char surface with char components (such as Ca) acting as catalysts. Such a mechanism should be coal dependent.

Future Work

Future work is planned as follows:

Stage 1: High spatial resolution NO, O_2, CO data with 3 coals
- identify peak NO levels and size of reducing zones, study coal-type dependence, close N balance with fly ash samples

Stage 2: Dope reactants with NO
- determine effects of NO recycling

Stage 3: Measure HCN, NH_3, CO_2, SO_2, SO_3, and other species by FTIR

Stage 4: Collect simulated superheater ash deposits
- look for indicators of altered corrosion tendencies in oxy-fuel combustion

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