A Mechanistic Investigation of Nitrogen Evolution and Corrosion with Oxy-fuel Combustion

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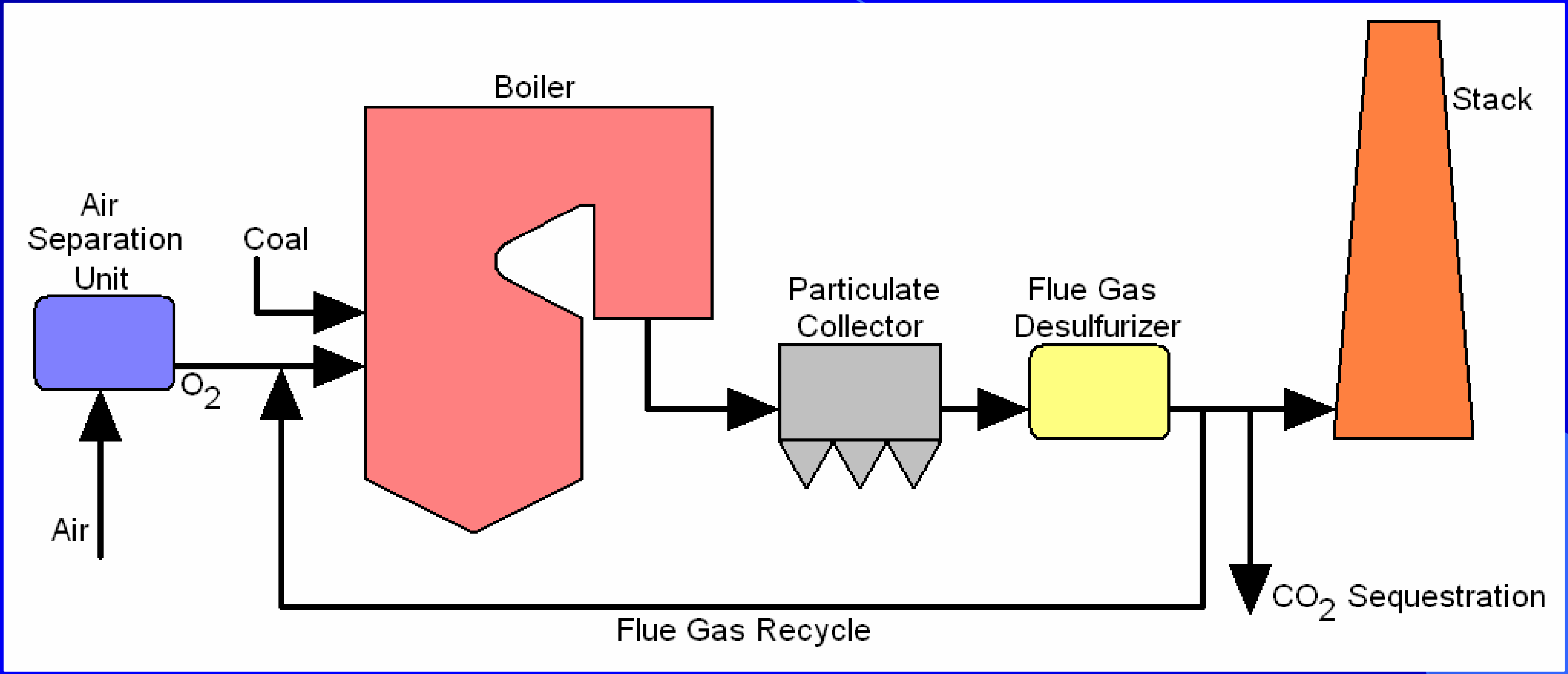
Introduction

Oxy-fuel combustion is the practice of using premixed oxygen and recirculated product gas in place of air as the fuel oxidizer

Motivation

- Increased CO_2 concentration in the exhaust stream for more economical capture
- Improved control of flame temperature (Ignition, NO control)
- Smaller flue gas cleaning equipment
- A reduction in NO_x has been reported

Oxy-fuel Combustion Flow Diagram



Background - Oxy-fuel Combustion Expectations

Paper studies show Oxy-fuel combustion is the most economical method for capturing CO_2

- Overall boiler efficiency will be reduced approximately 10% (absolute, i.e. 35% to 25%), primarily because of the energy required by the air separation unit (ASU).
- Oxy-fuel combustion is feasible with existing technologies
- Oxy-fuel combustion can be retrofit onto existing boilers

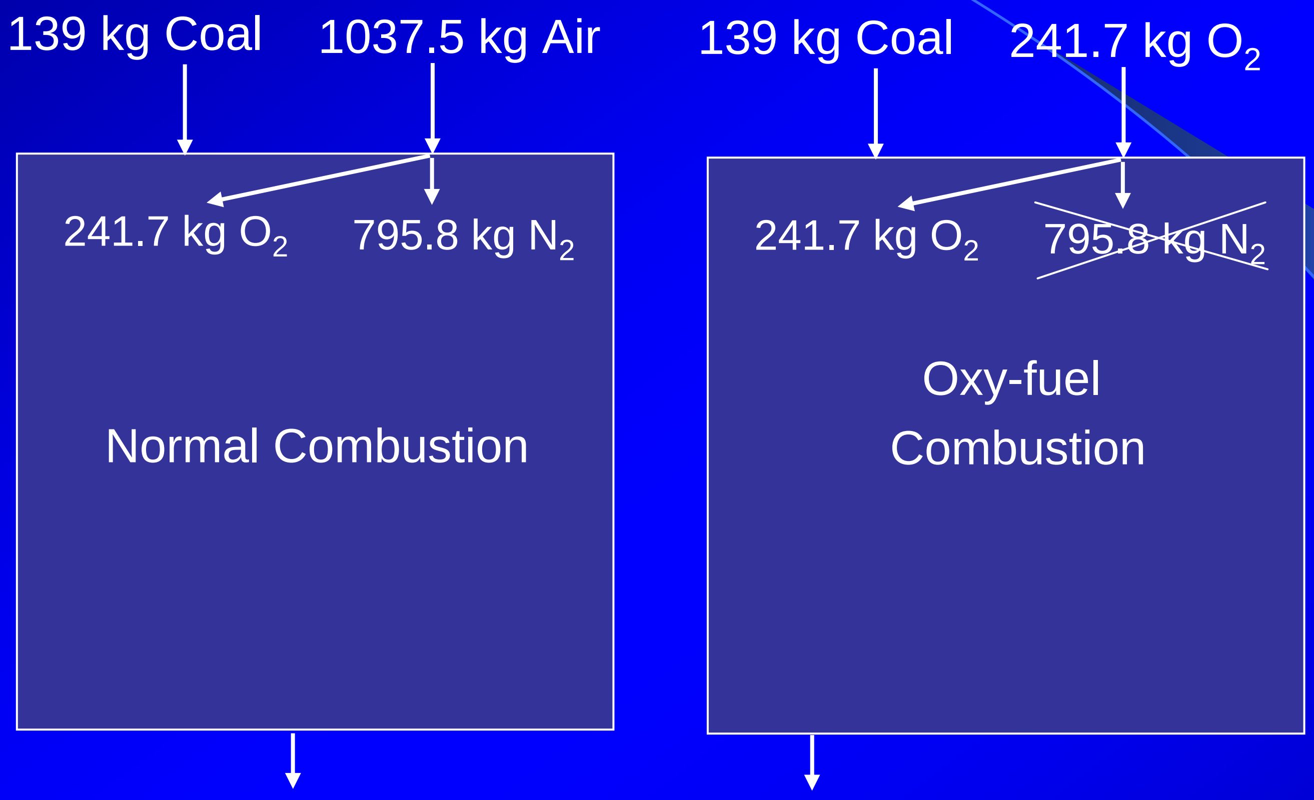
Background - Oxy-fuel Combustion Issues

Replacing N_2 with CO_2 produces the following changes

- CO_2 has a higher heat capacity than N_2. This lowers the flame temperature for equivalent O_2 to fuel ratios and changes heat loading of the boiler
- CO_2 is more dense than N_2 decreasing volume flow rate for the same mass
- CO_2 dissociates to CO at elevated temperatures which is endothermic and changes equilibrium concentrations of all other species
- The ratio of oxidizer (O_2) to diluent (N_2) is no longer fixed

Simple Oxy-fuel Combustion Calculations

Assuming complete combustion of a Wyodak, PRB, high moisture coal



139 kg Coal

1037.5 kg Air

241.7 kg O_2

795.8 kg N_2

Normal Combustion

139 kg Coal

241.7 kg O_2

241.7 kg O_2

~~795.8 kg N_2~~

Oxy-fuel Combustion

O_2 = 2.75 %
CO_2 = 14.3%
N_2 = 71.26 %
H_2O = 11.46%

O_2 = 9.57 %
CO_2 = 49.7 %
N_2 = 0 %
H_2O = 39.9 %

Note: Concentrations increase dramatically when N_2 is removed.

NO, SO_2, Na, Cl concentrations should all increase ~ 3.5 times

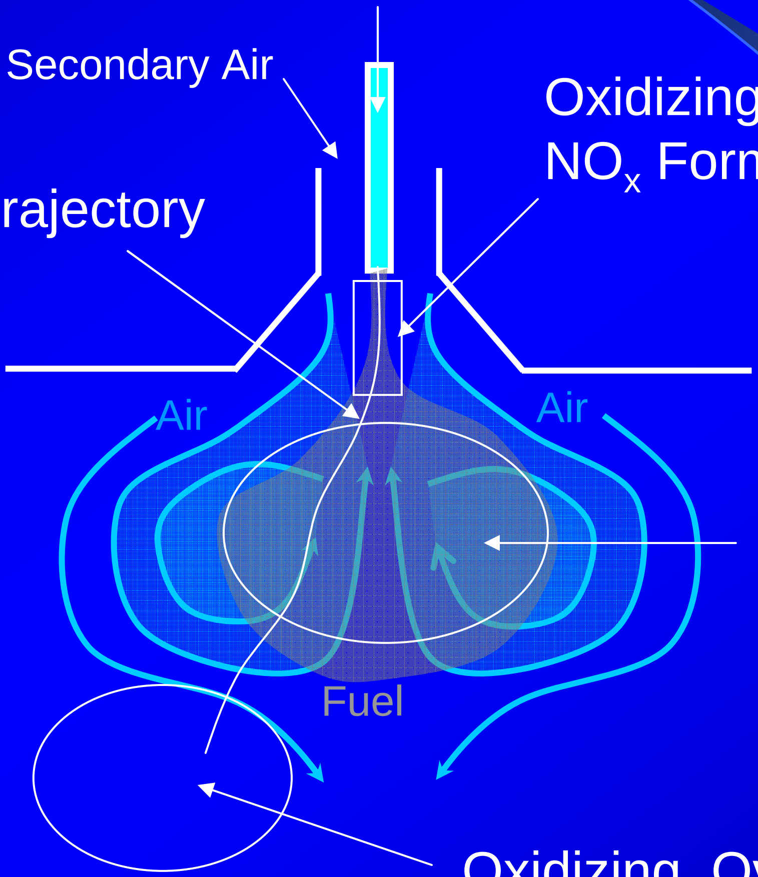
Flame Temp. would be very high

Objectives

- Determine the cause of NO_x reduction in oxy-fuel combustion
- Determine potential corrosion issues related to oxy-fuel deposits independent of increased concentrations

Nitrogen Evolution In Coal Combustion

Swirl Stabilized Low-NO_x Burner



Fuel and Primary Air

Secondary Air

Oxidizing, Overall Rich
NO_x Formation

Particle Trajectory

Reducing Zone,
Overall Rich,
NO_x Reduction

Oxidizing, Overall Lean

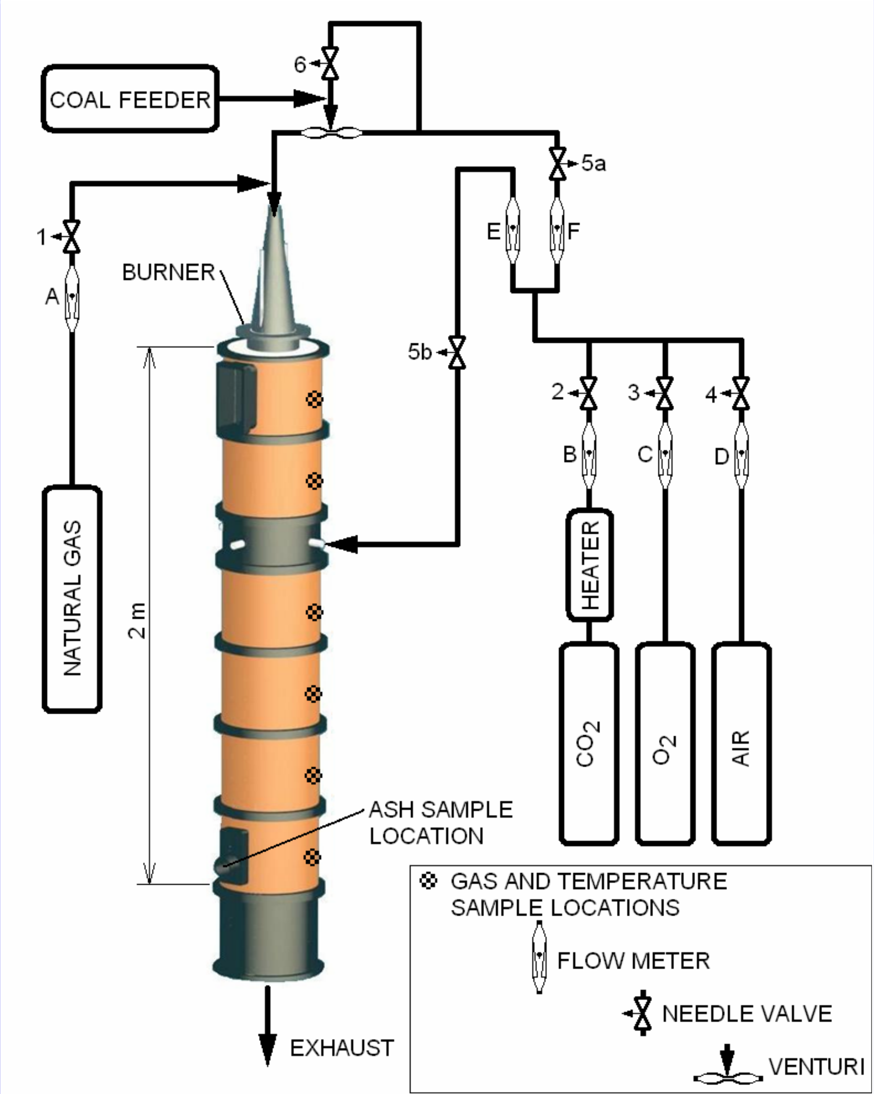
Potential Reasons For NO_x Reduction

- Near-elimination of thermal- and prompt-NO_x because air nitrogen is gone
- More attached flame reduces oxygen entrainment into reducing zone
- High NO concentrations inhibit NO formation
- Reduction of recycled NO_x in the fuel-rich flame zone
- Higher temperature increases NO reduction rates
- Reduced flow rates increase residence times in fuel-rich regions
- Higher temperatures push toward low equilibrium concentrations
- Increased N in volatiles allows reduced NO formation from char
- Enhanced heterogeneous reburning, increased CO levels promotes reburning
- Increased importance of gasification reactions, these reactions may alter temperature and species and thereby influence NO

Method

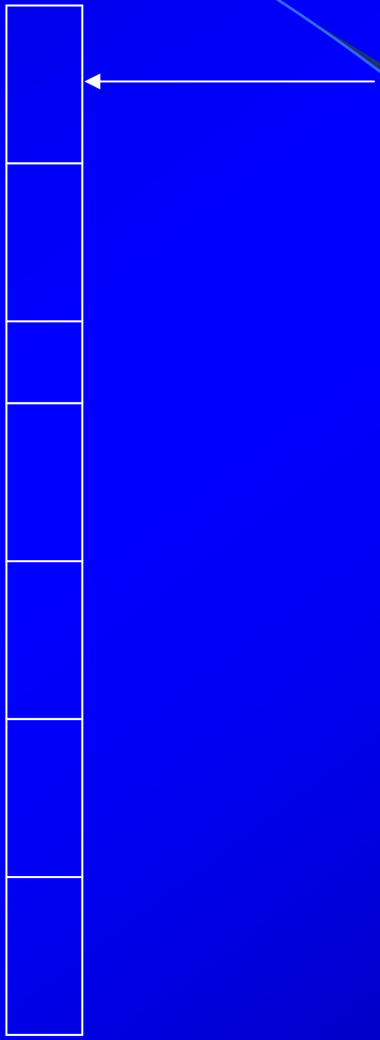
- Measure coal/char nitrogen release as a function of oxy-fuel recycle ratio (CO_2 to O_2 ratio) – Flat Flame Burner
- Measure NO_x and other flue gas concentrations as a function of (CO_2 to O_2 ratio) – Flat Flame and Multi-fuel Reactor (MFR)
- Measure NO destruction rates in Oxy-fuel combustion - MFR
- Measure deposition rates for normal and oxy-fuel combustion - MFR
- Collect SEM images containing Na, Cl, Fe, S, K, and carbon concentrations of normal and oxy-fuel combustion deposits - MFR

Experimental Set-up



Test Matrix - Unstaged

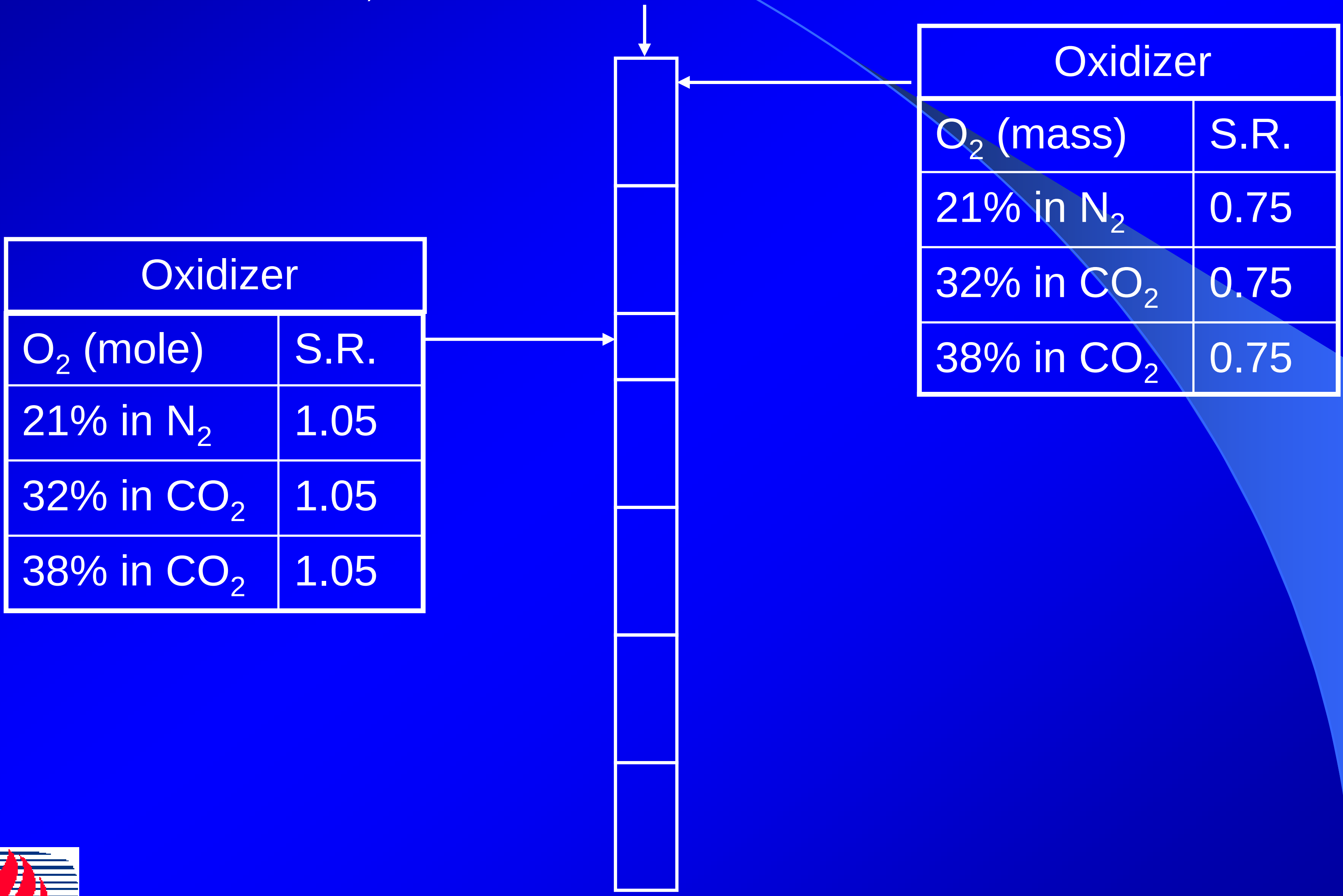
O_2, Coal, and Ch_4 are constant



O_2 (mass)	S.R.
23% in N_2	1.05
25% in CO_2	1.05
30% in CO_2	1.05

Test Matrix - Staged

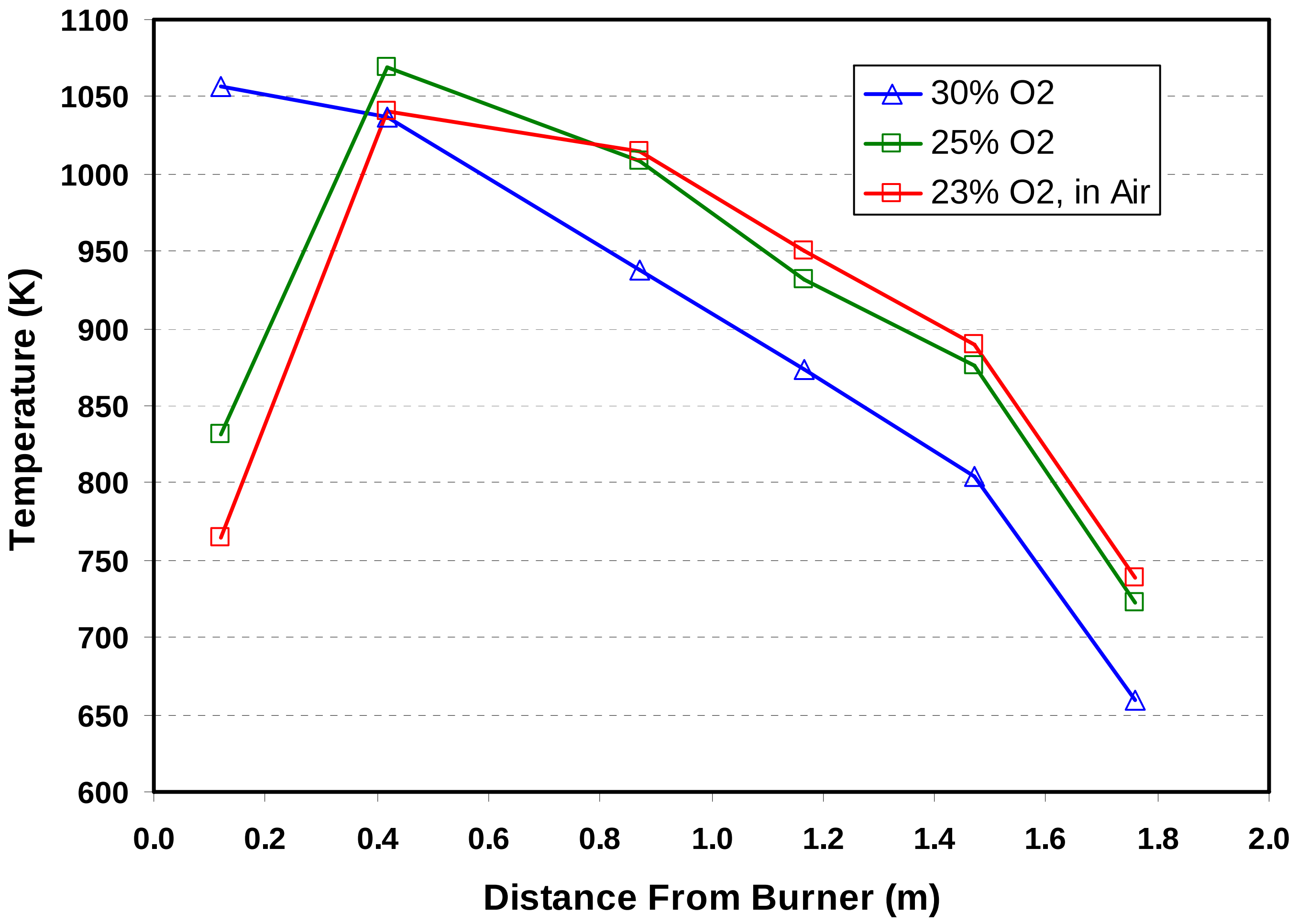
O_2, Coal, and CH_4 are Constant



Oxidizer	
O_2 (mole)	S.R.
21% in N_2	1.05
32% in CO_2	1.05
38% in CO_2	1.05

Oxidizer	
O_2 (mass)	S.R.
21% in N_2	0.75
32% in CO_2	0.75
38% in CO_2	0.75

Results – Unstaged, Temperature



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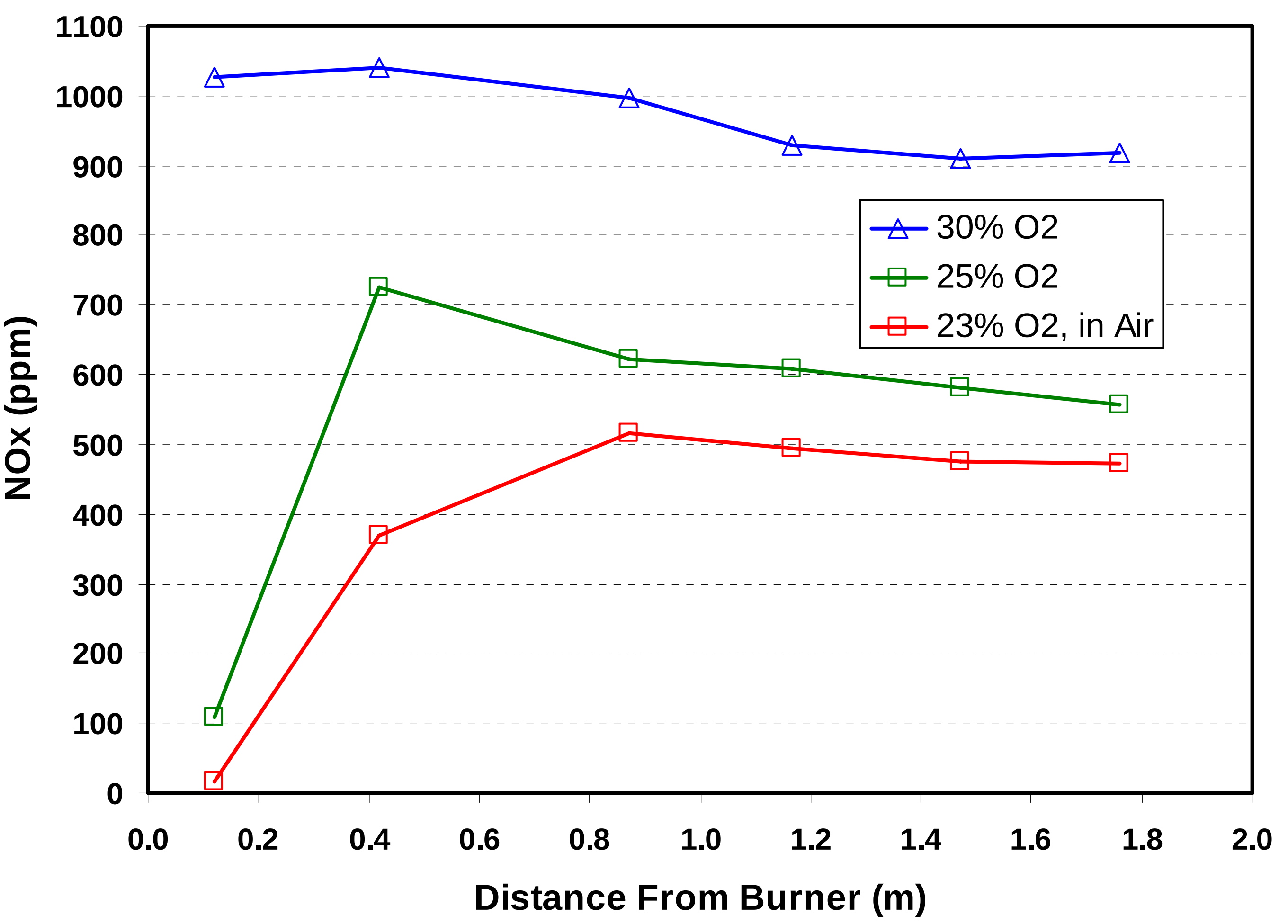
Results – Unstaged NO_x



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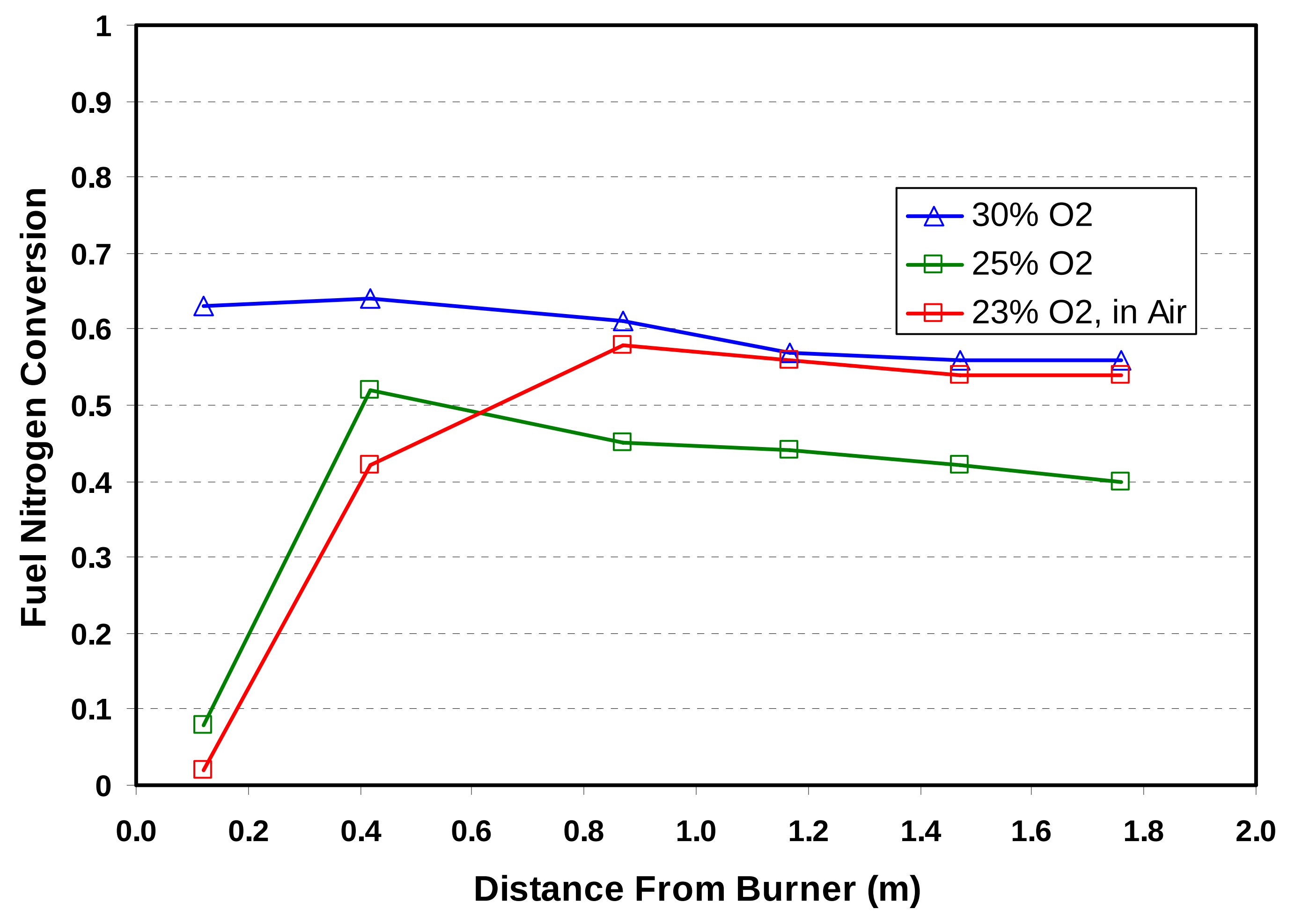
Results – Unstaged Nitrogen Conversion



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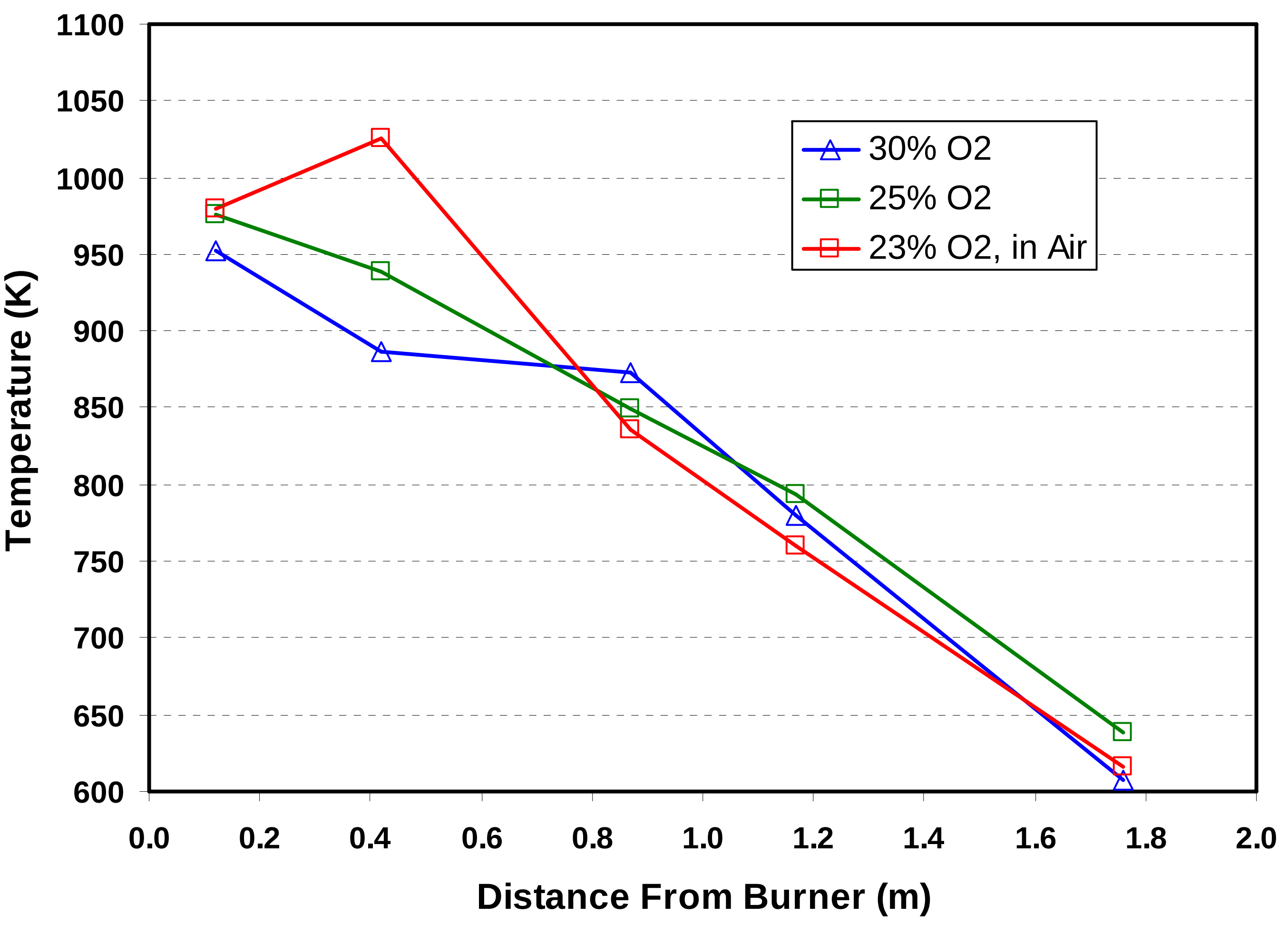
Results – Staged Wall Temperature



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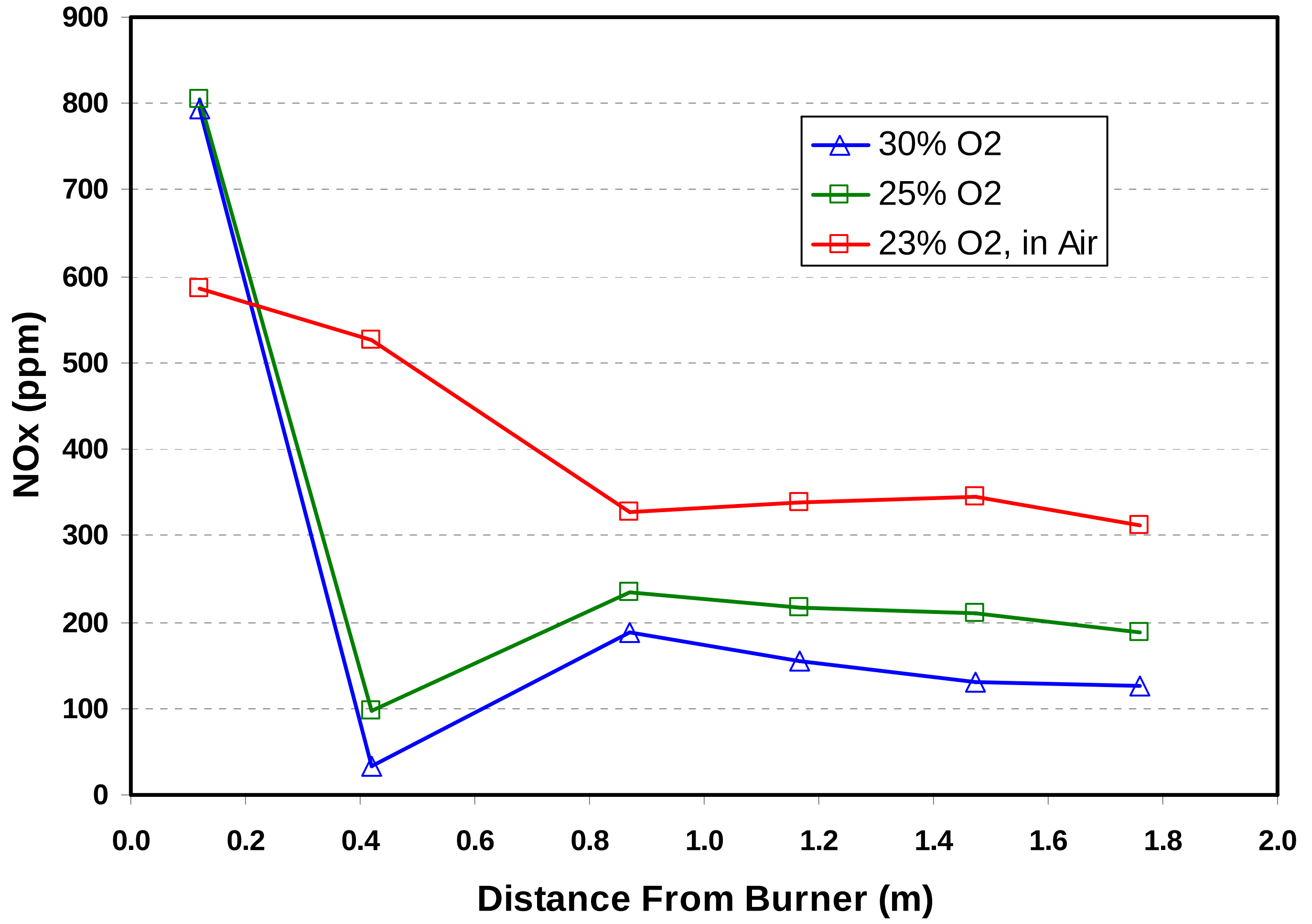
Results – Staged NO_x



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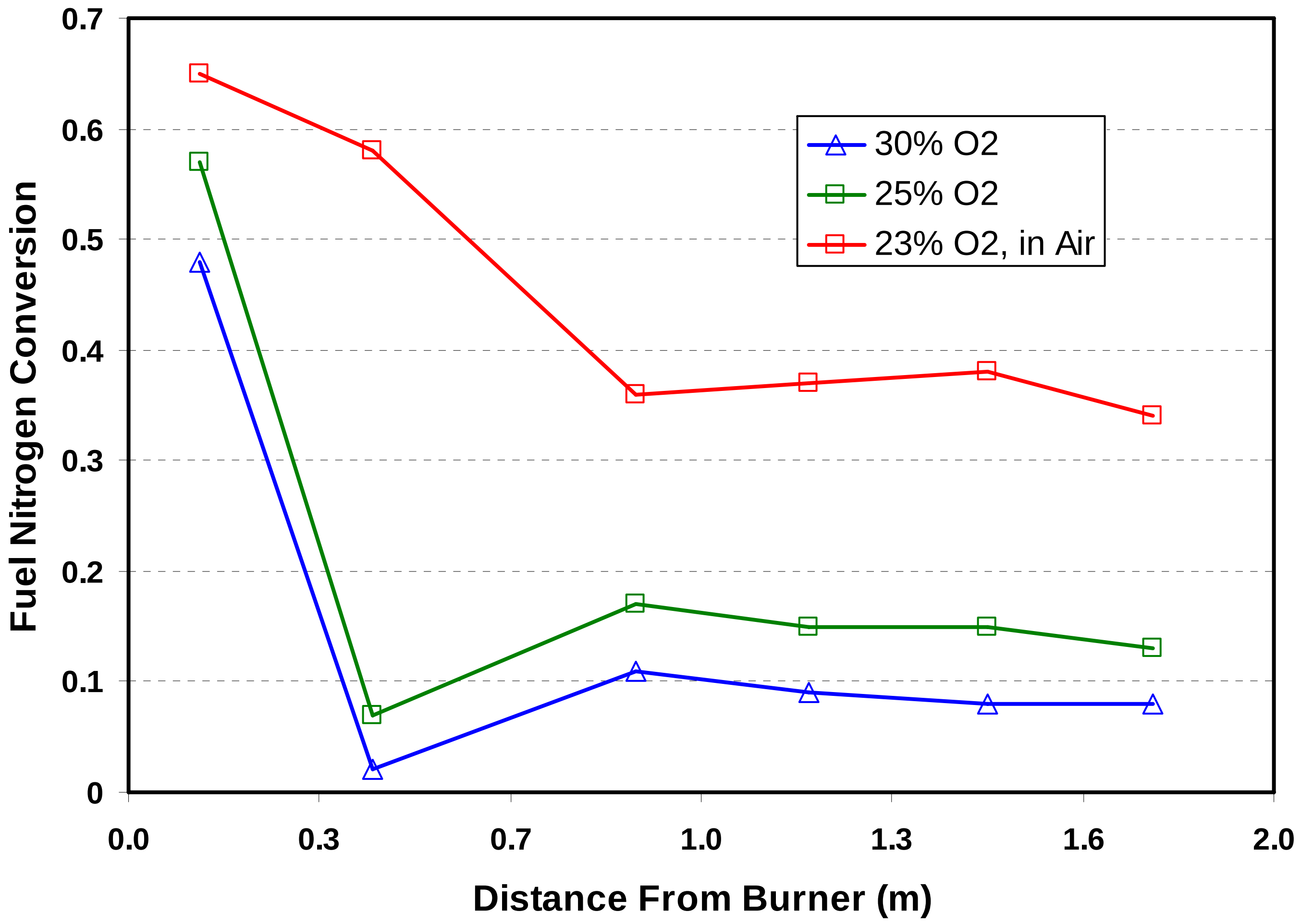
Results - Staged Nitrogen Conversion



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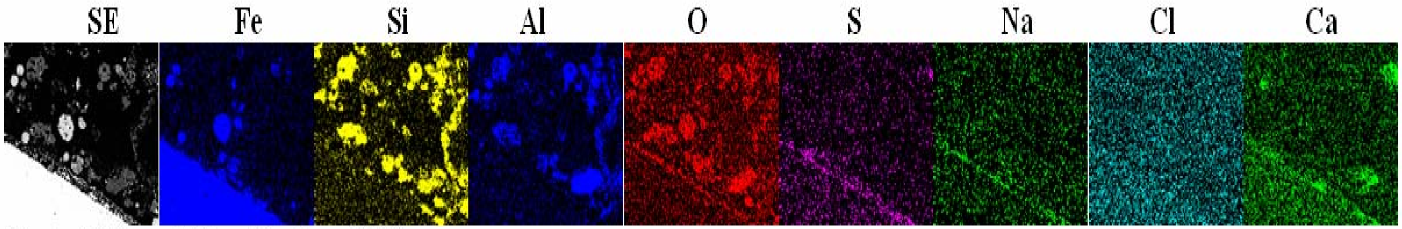
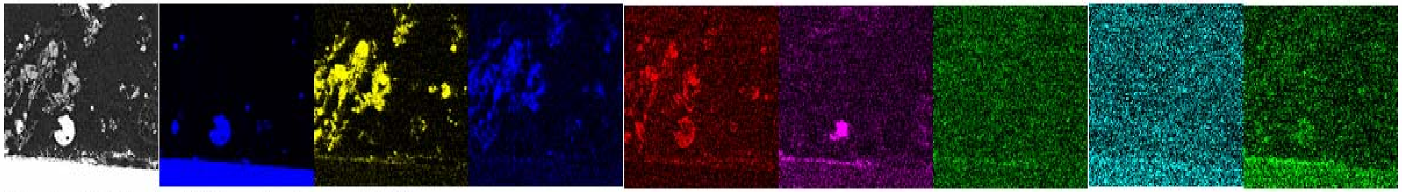
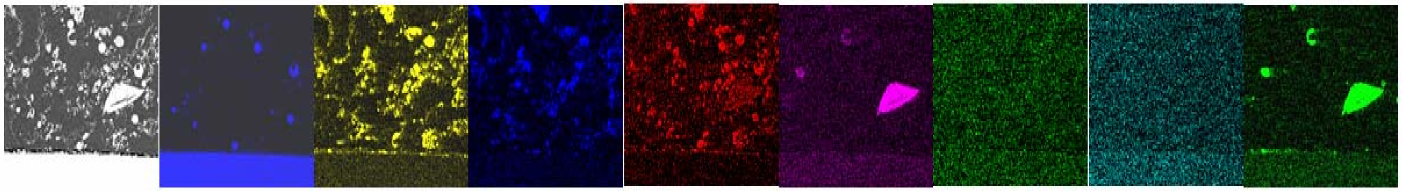
Results – Deposition Composition



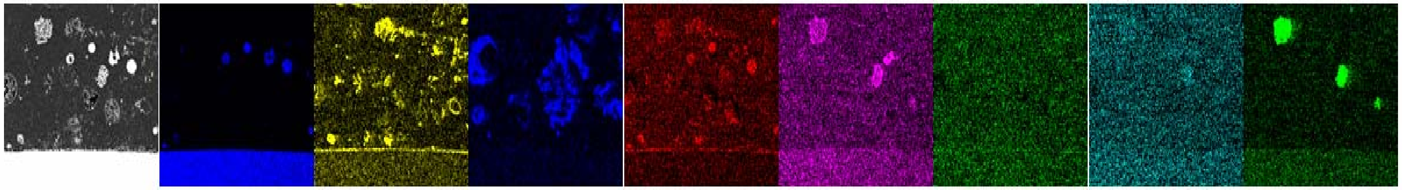
Illinois #6 (Normal) Magnification – 500X



Illinois #6 (Oxyfuel) Magnification – 400X



Illinois #6 (Normal) Magnification – 268X



Illinois #6 (Oxyfuel) Magnification – 200X

Ongoing Activities

- Add 500 ppm NO to incoming CO_2 and measure NO reduction in staged and unstaged combustion.
- Increase resolution of the measurements in the near burner region and measure NH_3 and HCN in addition to major species. Add additional staged conditions
- Model oxy-fuel combustion with chemical kinetic mechanism using a series of plug flow reactors

Summary and Conclusions

- Oxy-fuel combustion has been shown to reduce NO_x emissions in pilot scale testing.
- Recirculation of exhaust products will produce an approximate increase of 3.5 times the concentration of all gasses.
- Premixed unstaged combustion produced less nitrogen conversion to NO_x at equal flame temperatures.
- In staged combustion oxy-fuel combustion produced lower nitrogen to NO_x conversion even at higher adiabatic flame temperatures.

Summary and Conclusions

- The measurement of NO_x in oxy-fuel systems can be misleading because:
- Although similar amounts of nitrogen are originally converted to NO_x in both normal and oxy-fuel combustion, oxy-fuel combustion produced much higher NO_x reductions in the reducing zone.

1. The concentrations are not a relevant measure of NO_x when oxidizer molar flow rates are changing
2. CO_2 can influence chemiluminescence analyzers, causing a 15 – 20% reduction in analyzer response.

Questions

Simple Oxy-fuel Combustion Calculations

For ideal products, what happens to concentrations when flue gas is recycled?

139 kg Coal

241.7 kg O_2

Recycle Ratio =
y = fraction of
flue gas recycled

Total Mass Flow Rates (kg/hr)					Stoichiometry				
Coal	CH_4	Air	O_2	CO_2	Oxidizer to Burnout Section	Primary Stage SR	Sec. Stage SR	Oxidizer Mass % O_2	Oxidizer Molar % O_2
0.741	0.372	16.8	-	-	28%	0.75	1.05	23.3%	21%
0.744	0.370	-	3.886	11.37	28%	0.75	1.04	25.5%	32%
0.697	0.345	-	3.562	8.127	28%	0.73	1.02	30.5%	38%

Why ?

O_2 = 9.57 %
CO_2 = 49.7 %
N_2 = 0 %
H_2O = 39.9 %

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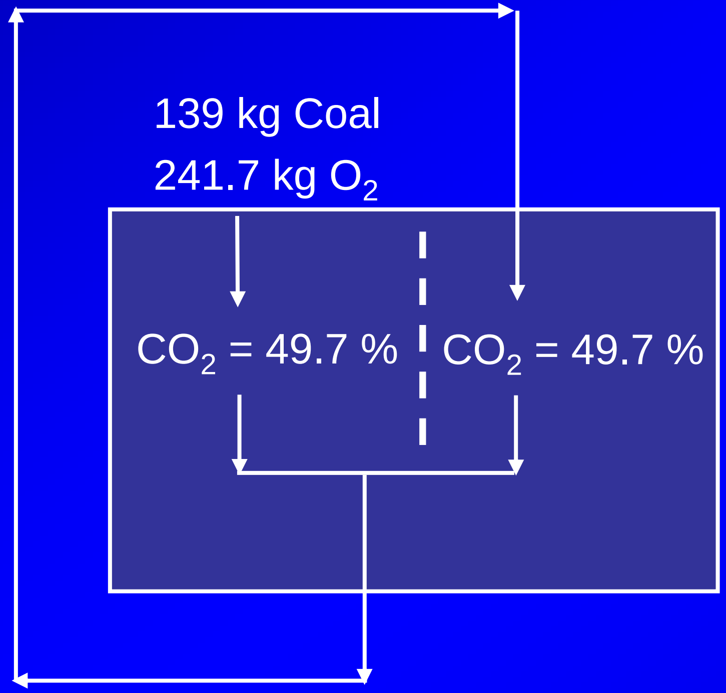
Simple Oxy-fuel Combustion Calculations

For non reacting products and ideal products of combustion – concentrations are independent of the recycle ratio

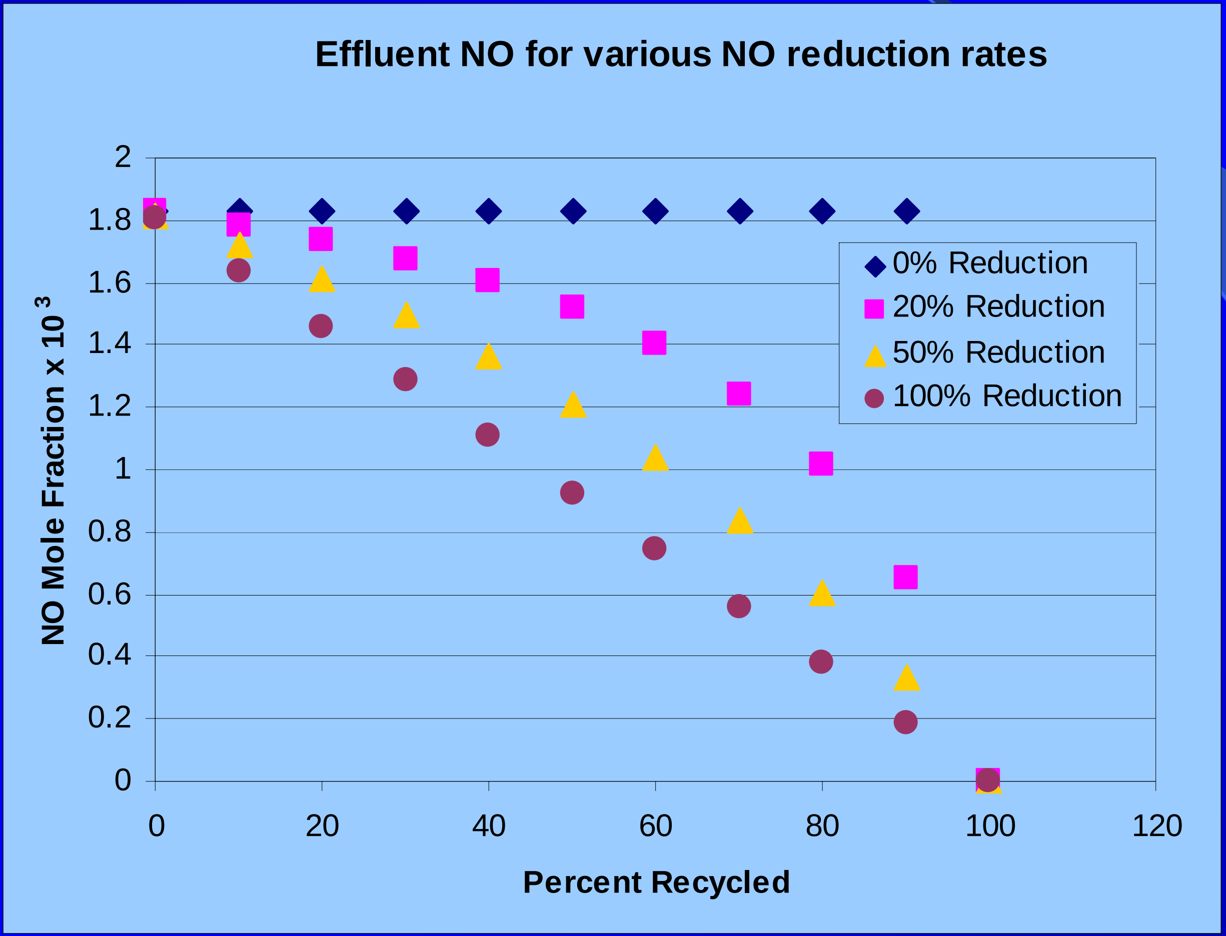


However: Experiments show this is not true for NO_x and SO_2 . NO_x, and SO_2 decreases with increasing recycle ratio

Therefore: NO_x and SO_2 in the recycle must be destroyed in the boiler

Simple Oxy-fuel Combustion Calculations

Calculations for complete conversion of fuel Nitrogen to NO as a function of recycle ratio, y, and NO destruction, X_d



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Why Is NO_x Lowered Through Oxy-fuel Combustion

Possible Reasons

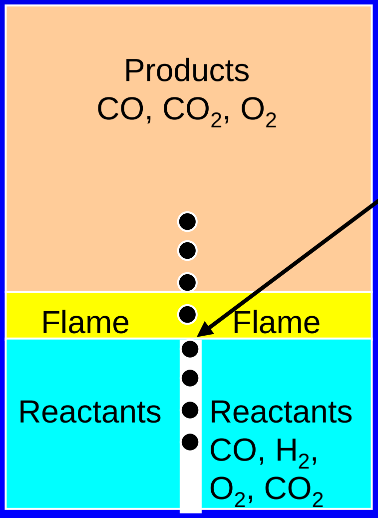
- Volatile and volatile nitrogen release increases causing increased reduction to N_2 in fuel rich regions, this is possible with increase temperatures and heating rates for particles (less is formed)
- Nitrogen is reduced as it passes back through fuel rich regions in the flame (NO is destroyed)
- High CO_2 alters equilibrium concentrations which affect NO formation (less is formed)

Objectives

- Investigate nitrogen evolution for oxy-fuel combustion
- Determine changes in ash deposition rate and composition for oxy-fuel versus normal combustion
- Evaluate potential for increased corrosion with oxy-fuel combustion

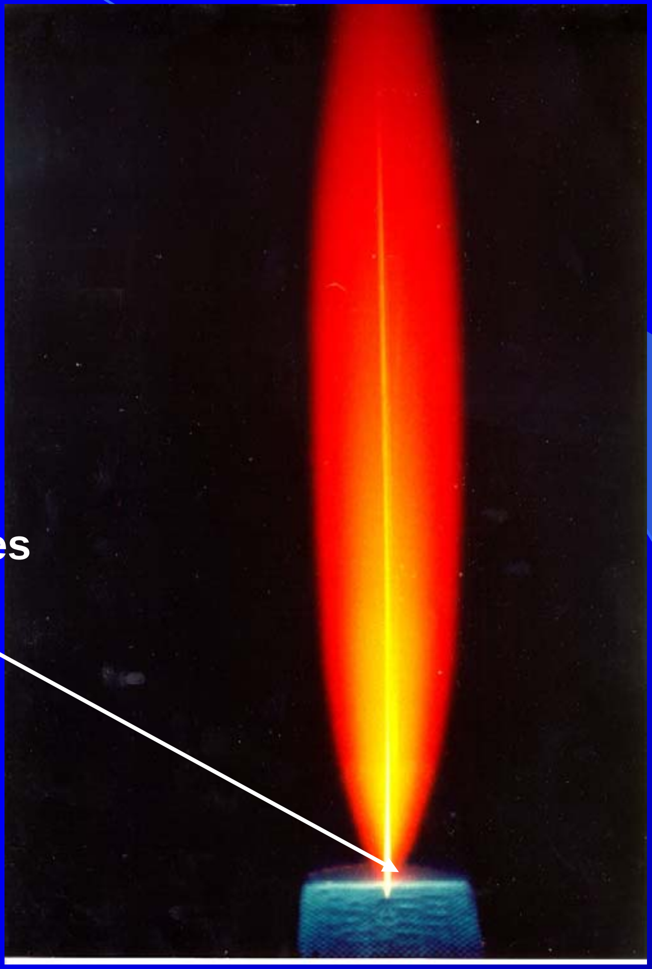
Apparatus – Flat Flame Burner

Measuring coal/char nitrogen release



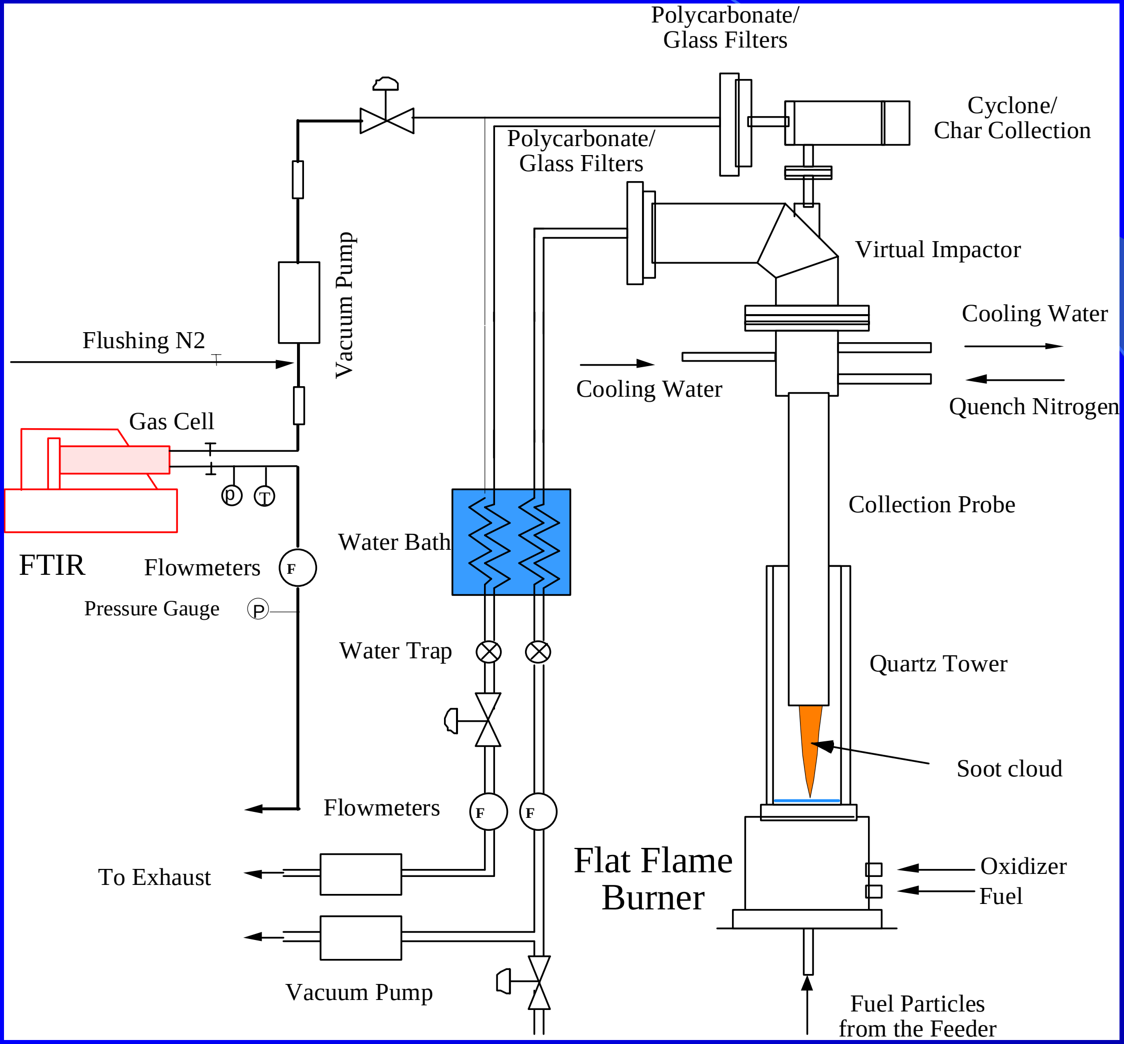
FFB Concept

Coal Particles



Apparatus – Flat Flame Burner

- Flat Flame Burner – Nitrogen release measurement



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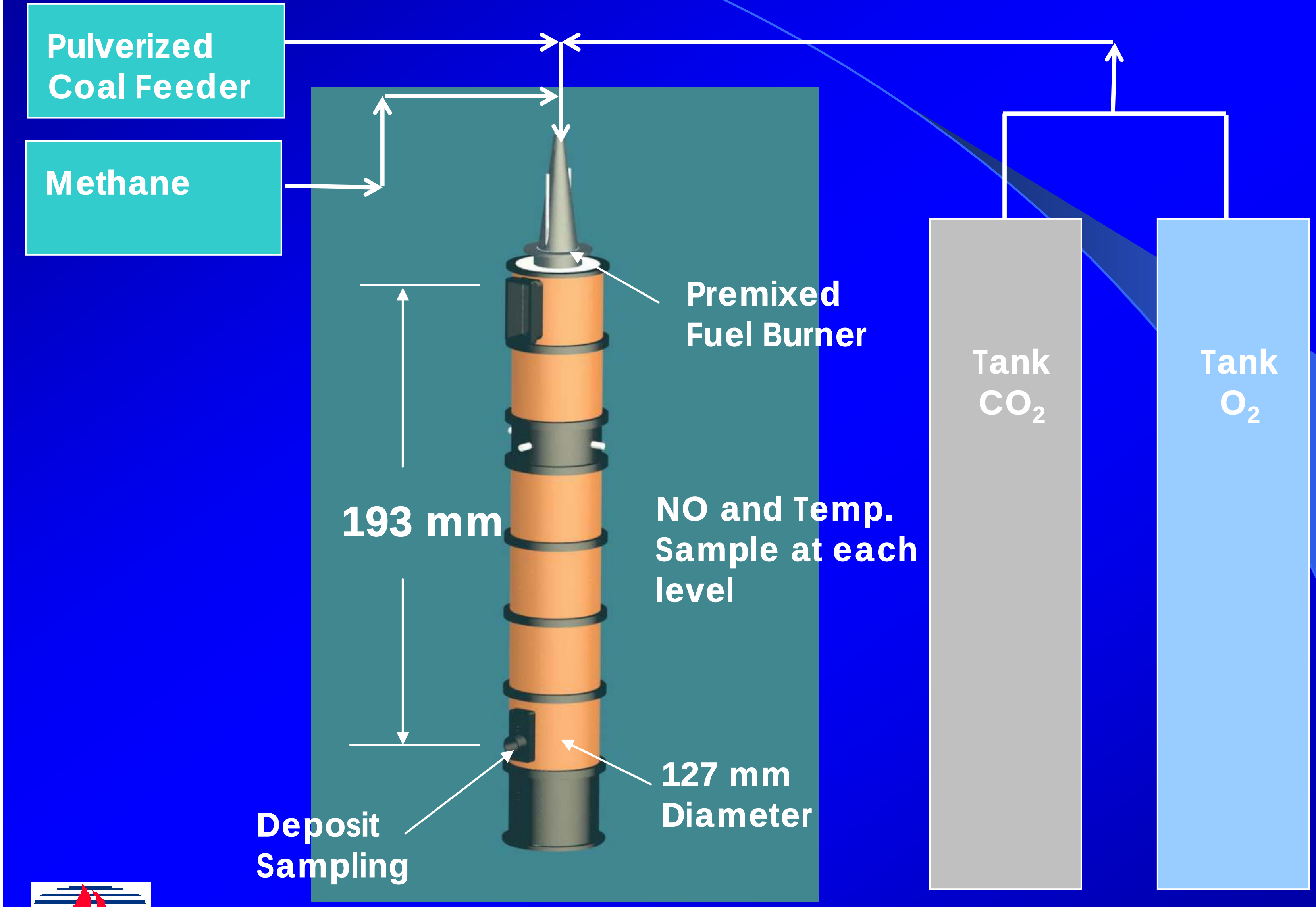
Flat Flame Burner - Measurements

Collect Char and gas samples for a matrix of

- Various O_2/CO_2 concentrations or temperatures (1100 – 1700 K)
- Three coals types: Pitt #8, PRB, Illinois #6

Measure gas concentrations including nitrogen species (NO, HCN, NH_3)

Apparatus – Multi-fuel Reactor



Pulverized Coal Feeder

Methane

Premixed Fuel Burner

193 mm

NO and Temp. Sample at each level

127 mm Diameter

Deposit Sampling

Tank CO_2

Tank O_2

Multi-fuel Reactor - Measurements

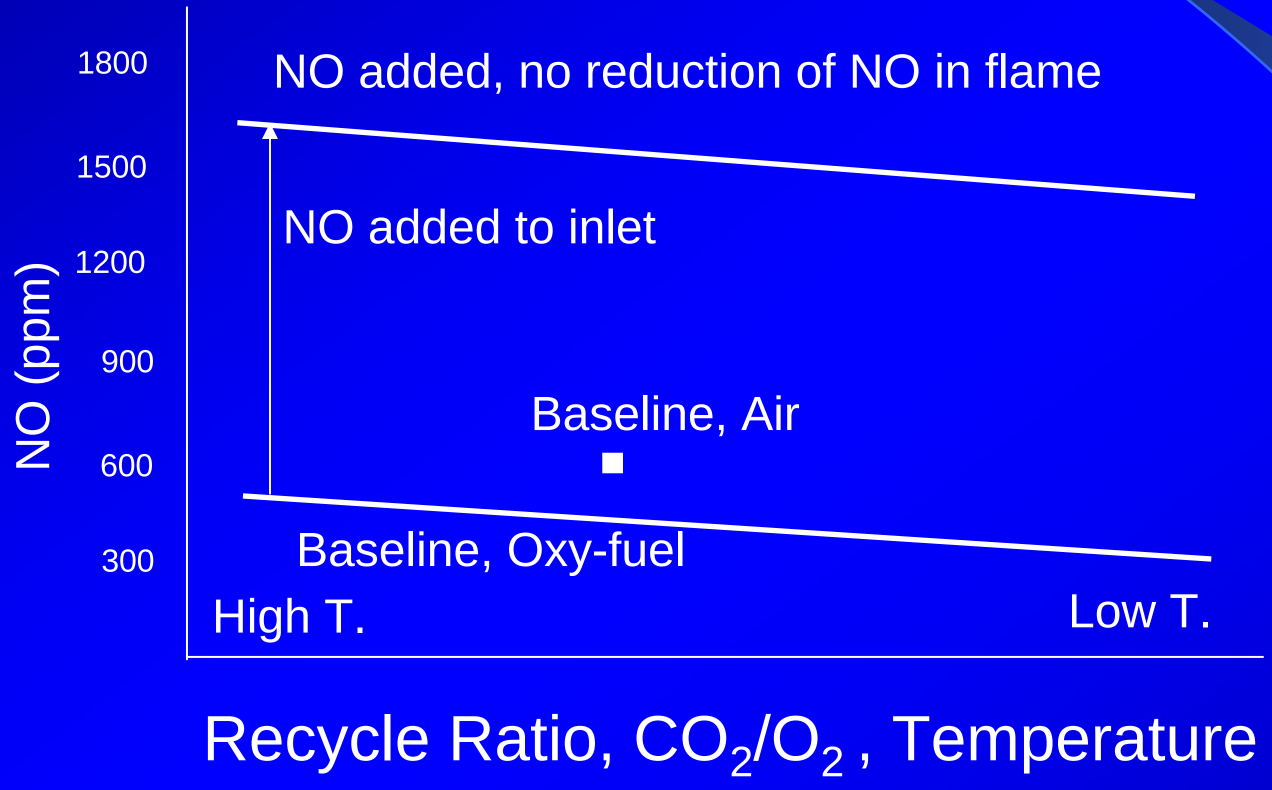
Fixed O_2/CO_2 concentrations (70% CO_2) and vary equivalence ratio (0.8 - .95)

- Measure axial centerline NO and temperature
- Measure ash deposition rate
- Analyze ash deposits – composition (S, Cl, K, Na, C, Fe) and morphology (particle shape, condensed layers, etc.)

Fix equivalence ratio ($\phi = 0.85$), vary CO_2/O_2 ratio or recycle ratio. Repeat above measurements

Add NO to input gas. Fix equivalence ratio ($\phi = 0.85$), vary CO_2/O_2 ratio or recycle ratio. Repeat above measurements

Anticipated Results



Result above or below indicates behavior relative to air combustion

A decrease in NO from that added indicates reduction in the flame

The change in slope indicates sensitivity of reduction reaction to temperature

Anticipated Results

NO reduction will be caused by: 1. reduction of recycled NO passing through fuel rich zone 2. enhanced volatiles release at elevated temperatures

NO reductions should be highest at low O_2/CO_2 ratios or low flame temperatures where reburning or advanced reburning type reactions are more efficient

Ash deposition rates should be similar for most oxy-fuel conditions but may change at high O_2/CO_2 ratios where high temperatures alter ash composition

Acknowledgements

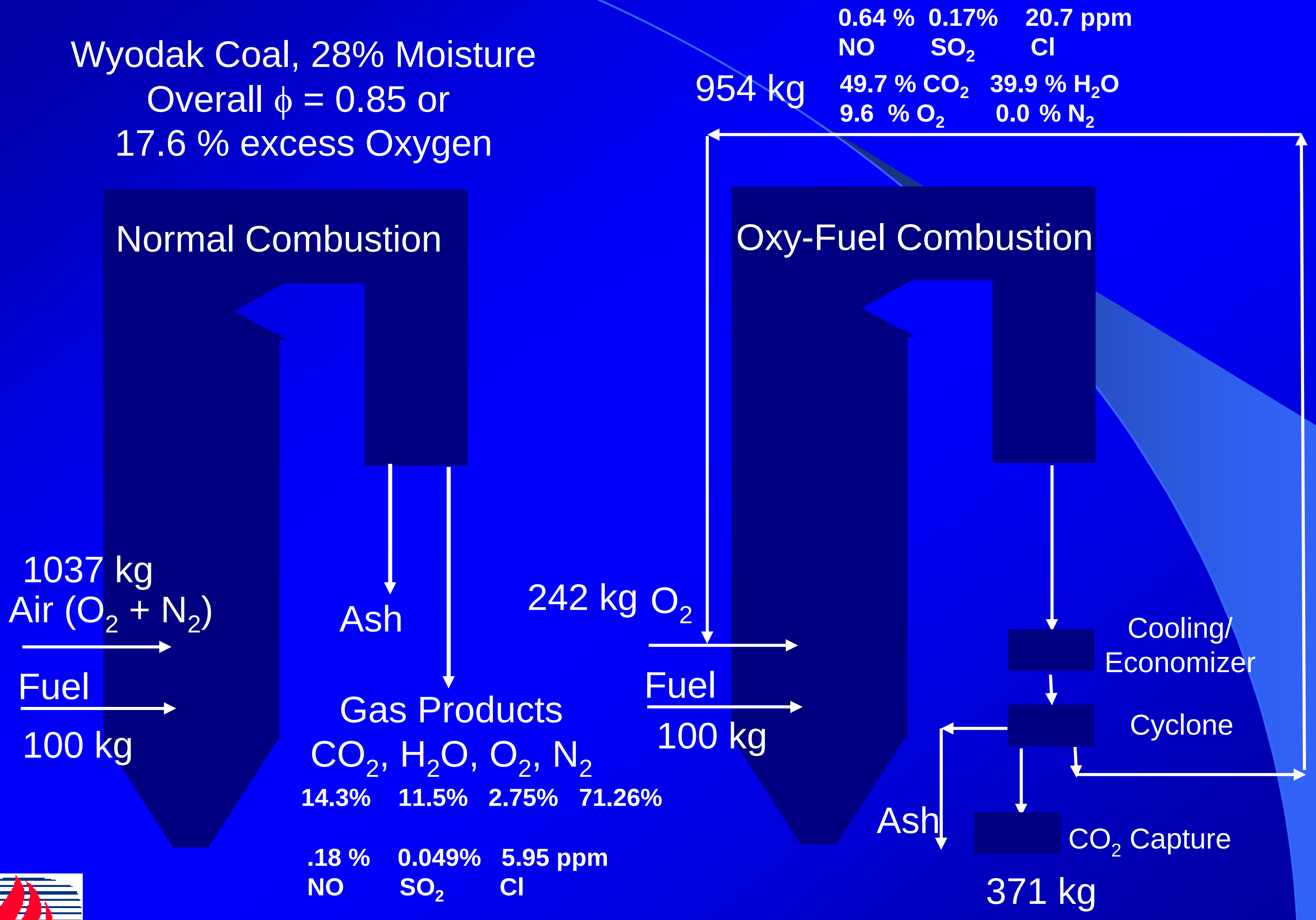
We would like to thank the DOE, UCR program for the funding to do this work

Air-Liquide for funding and technical support

Questions and Suggestions

Ideal Oxy-fuel Combustion

Wyodak Coal, 28% Moisture
Overall ϕ = 0.85 or
17.6 % excess Oxygen



Normal Combustion

1037 kg
Air (O_2 + N_2)

Fuel

100 kg

Ash

Gas Products

CO_2, H_2O, O_2, N_2

14.3% 11.5% 2.75% 71.26%

.18 %	0.049%	5.95 ppm
NO	SO_2	Cl

Oxy-Fuel Combustion

954 kg

0.64 %	0.17%	20.7 ppm
NO	SO_2	Cl

49.7 % CO_2 39.9 % H_2O
9.6 % O_2 0.0 % N_2

242 kg O_2

Fuel

100 kg

Cooling/
Economizer

Cyclone

Ash

CO_2 Capture

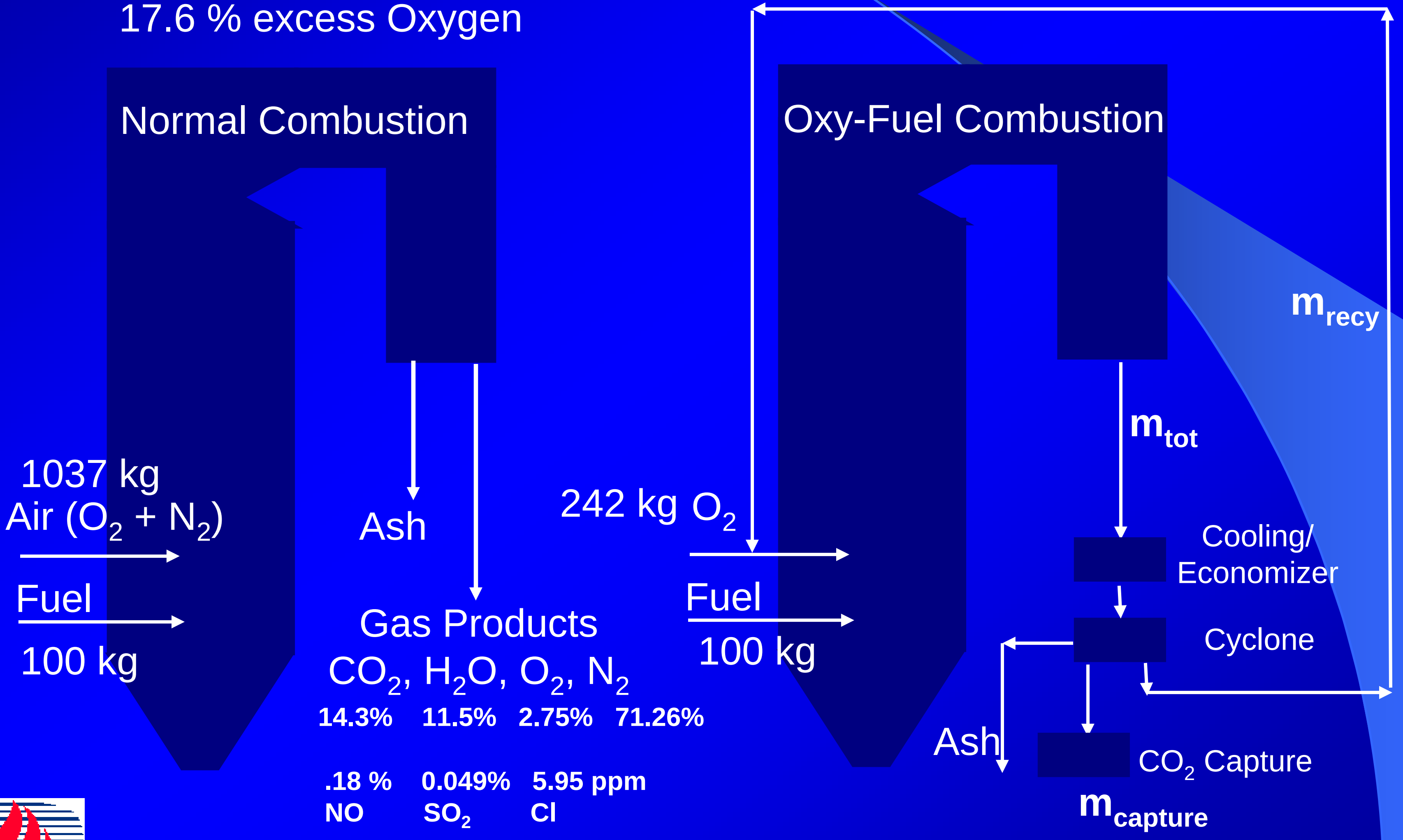
371 kg

Ideal Oxy-fuel Combustion

Wyodak Coal, 28% Moisture
Overall $\phi = 0.85$ or
17.6 % excess Oxygen

$m_{tot} = m_{recy} + m_{capture}$

y = recycle fraction = m_{recy} / m_{tot}



Normal Combustion

1037 kg
Air ($O_2 + N_2$)

Fuel

100 kg

Ash

Gas Products

CO_2, H_2O, O_2, N_2

CO_2	H_2O	O_2	N_2
14.3%	11.5%	2.75%	71.26%

NO	SO_2	Cl
.18 %	0.049%	5.95 ppm

Oxy-Fuel Combustion

242 kg O_2

Fuel

100 kg

m_{tot}

m_{recy}

Cooling/
Economizer

Cyclone

Ash

CO_2 Capture

$m_{capture}$

Ideal Oxy-fuel Combustion

- Effluent Concentrations are not a function of the mass recirculated
- Flame temperature is a strong function of the mass recirculated
- In order to achieve comparable temperatures and heat flux to existing boilers, recirculation ratios of 70 – 80% are required with O_2 concentrations of ~ 30%

Non-Ideal Oxy-fuel Combustion

- Assume some fraction x_{dest} of the NO passing through the reactor is destroyed

Oxy-fuel Combustion - Challenges

- Air Separation required to produce O_2 reduces overall efficiency relative to normal combustion
- Increased concentrations of CO_2 cause increased radiative heat transfer from combustion gas to wall
- Increased concentrations of product gases may lead to increased corrosion
- Air leakage into the return effluent is difficult to eliminate and control
- Volume flow rates decrease because CO_2 is more dense than N_2
- Oxygen concentrations in the intake need to be around 30% to produce acceptable burnout

Anticipated Results

- NO versus recycle ratio (60 – 80 %CO2) holding O_2 and fuel (phi) constant
- NO should decrease slightly as recycle increases due to temperature
- NO for a sweep of phi holding CO2 constant (70%)
- No should peak at O2 9%, decrease as O2 increases because of lower temperature
- Repeat with NO in the inlet to determine the NO destruction

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