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Advances in Thermochemical Conversion of Coal and Biomass to Energy and Fuels

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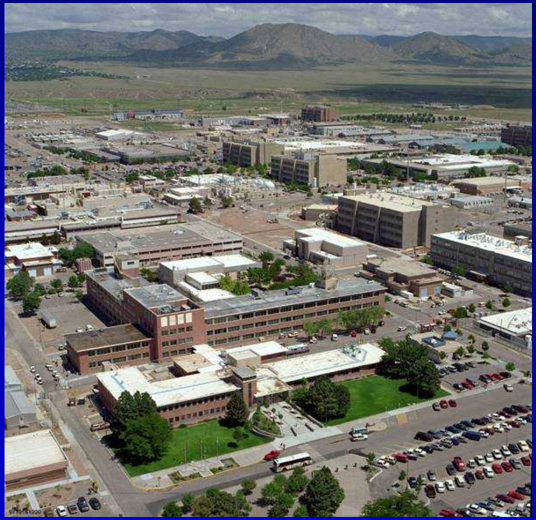
Outline of Presentation

- **Overview of Sandia Energy Research**
- **Current Research on Thermochemical Conversion of Coal and Biomass**
  - ✓ **Oxy-combustion of coal**
  - ✓ **Oxy-combustion of syngas**
  - ✓ **Gasification of coal**
  - ✓ **Combustion and Gasification of lignin**
- **Conclusions and Perspectives**

Sandia National Laboratories

- Sandia is a DOE Nuclear Weapons laboratory, based in Albuquerque, NM, with a secondary facility (with ~ 800 employees) located in Livermore, CA, adjacent to the Lawrence Livermore National Lab

Albuquerque, New Mexico



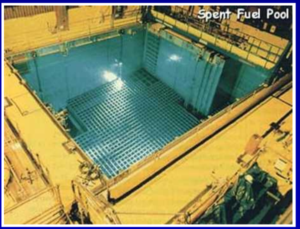
Livermore, California

- Approx. one-half of Sandia's efforts are devoted to nuclear weapons issues and one-half to energy and environment and homeland security

Sandia Energy Research

- **Solar research, primarily concentrating solar power (CSP)**
  - ✓ power tower technology – Solar One and Solar Two
  - ✓ compact solar power – stirling engine

- **Nuclear power**
  - ✓ nuclear waste repository design and evaluation
  - ✓ critical safety systems analysis



- **Wind power**

- **Fossil Energy**
  - ✓ geological engineering
  - ✓ drilling diagnostics

- **Biofuels**
  - ✓ advanced pretreatment and enzymatic hydrolysis of lignocellulosic biomass
  - ✓ algal biodiesel

Sandia's Combustion Research Facility

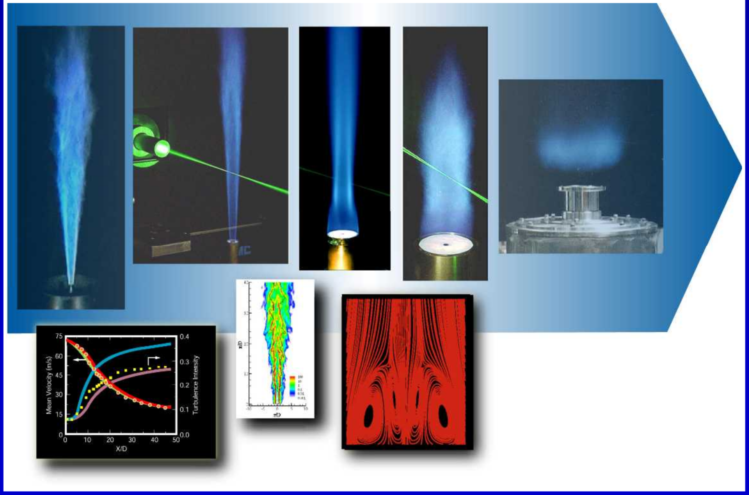
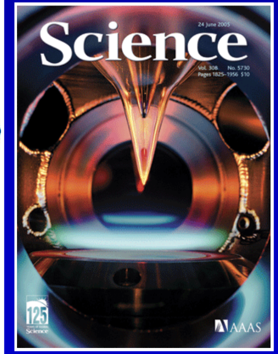
U.S. Dept. of Energy's premier collaborative research facility for both basic and applied combustion research

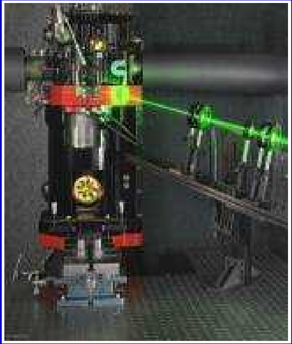
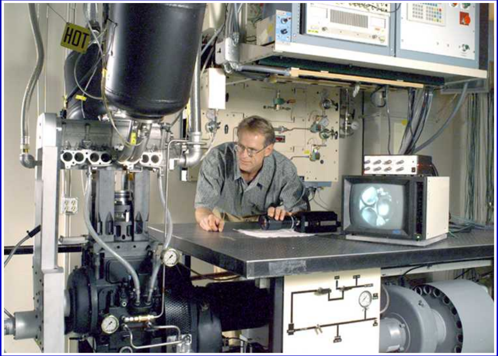
- ✓ 36 specialized labs
- ✓ dedicated teraflop Linux cluster
- ✓ 100 researchers: 36 PhD staff, 30 postdocs, 20 technicians + lab support
- ✓ ~ 80 visitors each year (university faculty, graduate students, industrial researchers)

Sandia's Combustion Research

Mixture of experimental and computational research, ranging from fundamental reaction chemistry to production-geometry heavy-duty diesel engines

- ✓ **experimental work emphasizes advanced laser diagnostics**
- ✓ **computational work includes master equation solutions, direct numerical simulation (DNS), large eddy simulation (LES), and simplified descriptions of turbulent mixing (LEM)**

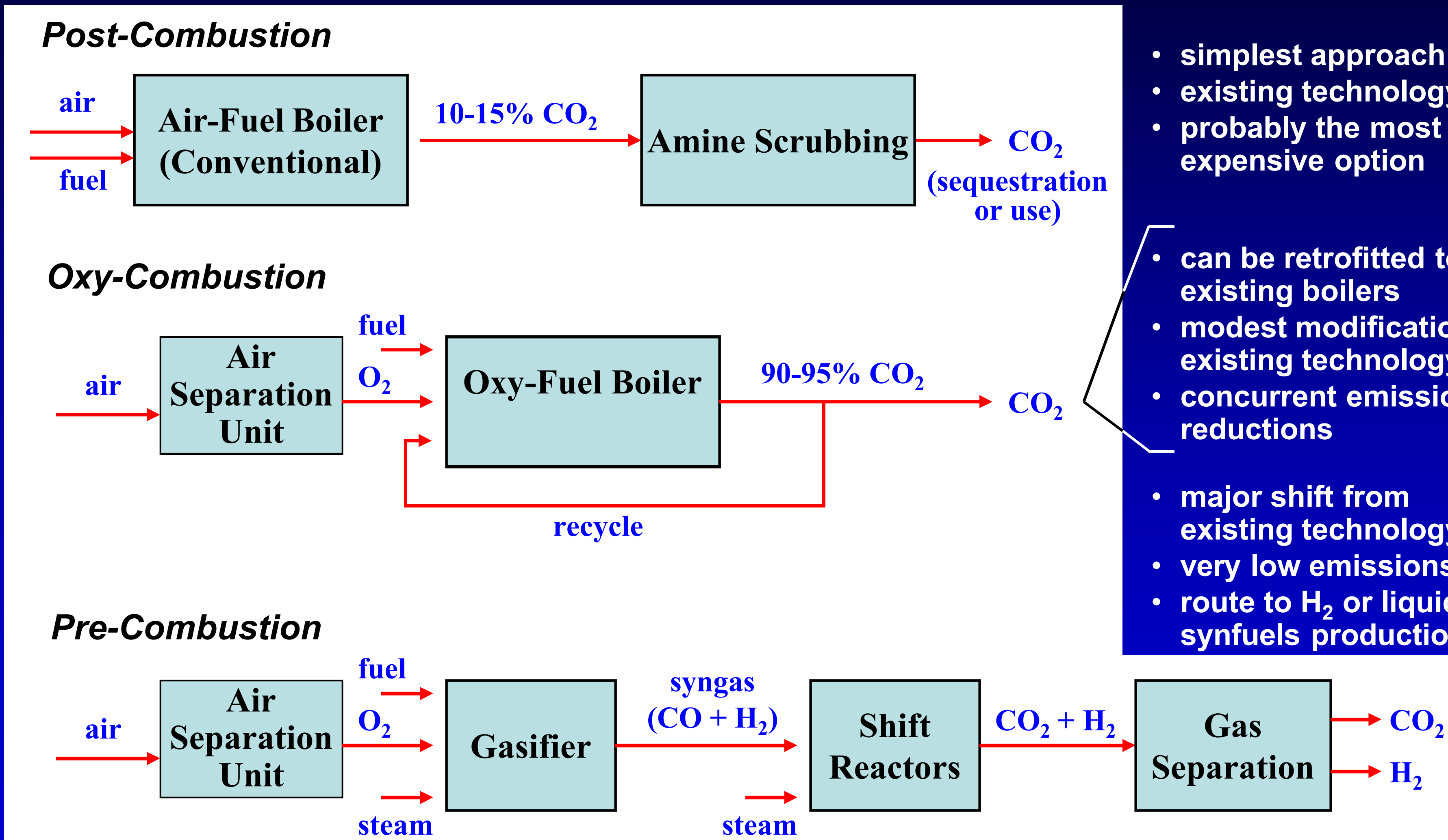



Thermochemical Conversion of Coal and Biomass

- Coal and biomass are two of the most abundant energy resources in the world
- Traditional conversion of these fuels to useful energy, by combustion in air to generate electricity, releases CO_2 and does not reduce need to import oil for use in the transportation sector
- Recent international assessments conclude that global climate change is occurring and that it is likely driven by CO_2 emissions from human activities
- U.S. DOE, together with many governments around the world, is supporting research to
  - ✓ determine lowest-cost method to generate electricity from coal and biomass while capturing CO_2 for sequestration (typ. in saline aquifers)
  - ✓ develop cost-effective processes for generating H_2 or other alternative transportation fuels from these feedstocks while capturing CO_2

3 Routes to Carbon Capture



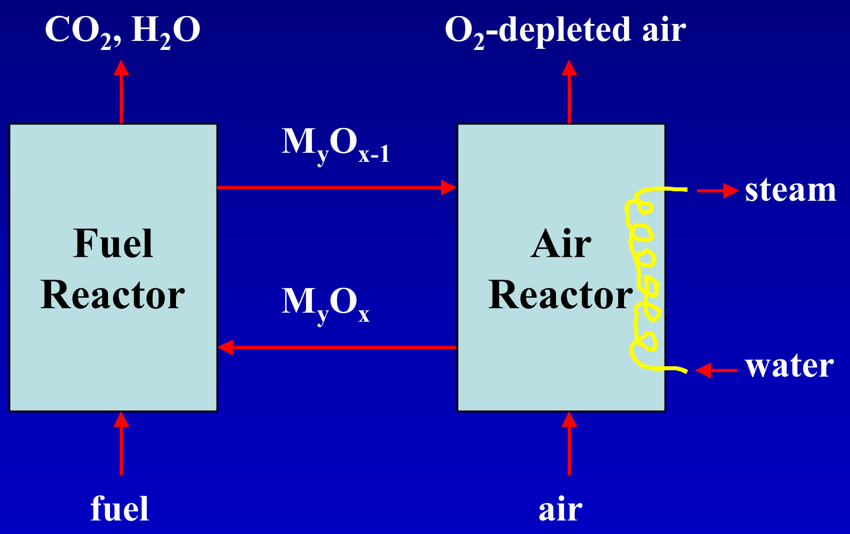
- simplest approach
- existing technology
- probably the most expensive option

- can be retrofitted to existing boilers
- modest modification of existing technology
- concurrent emissions reductions

- major shift from existing technology
- very low emissions
- route to H_2 or liquid synfuels production

Chemical Looping Combustion: Variant of Oxy-Combustion

- Alternative to expensive generation of oxygen from air is to react fuel with metal oxide to produce reduced metal and CO_2, then react reduced metal with air to regenerate metal oxide



- metal systems investigated include NiO/Ni, CuO/Cu, CoO/Co, Fe_2O_3/Fe_3O_4
- operates at 800-1000 °C; suitable for incorporating into fluidized beds
- may be operable at elevated pressures

- Critical issues are coking of metal surface, separation of ash from active metal oxide system, and long-term cyclic activity of metal system – technology is in its infancy

Oxy-Combustion of Coal: Worldwide Development

- A number of coal burners and furnaces have been operated in oxy-combustion mode to evaluate feasibility of approach
- Several pilot plants planned or undergoing construction around the world
  - ✓ Vattenfall Schwarze Pumpe, 30 MW_{th} pc (new), Germany
  - ✓ Babcock & Wilcox, 30 MW_{th} pc (retrofit), U.S.
  - ✓ CS Energy Callide, 90 MW_{th} pc (retrofit), Australia
  - ✓ Doosan Babcock Energy Renfrew, 40 MW_{th} pc (retrofit), Scotland
  - ✓ Ciuden, 30 MW_{th} pc (new) and 30 MW_{th} CFB (new), Spain

Schwarze Pumpe pilot plant

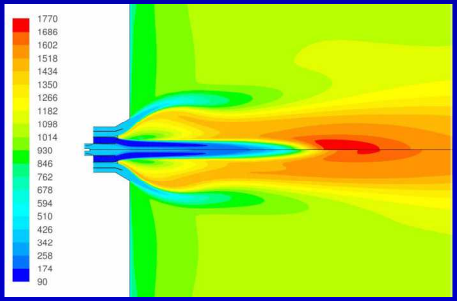
- Preliminary planning underway for larger scale demonstrations
  - ✓ Jamestown, 150 MW_{th} CFB (new), U.S.
  - ✓ Youngdong, 300 MW_{th} pc (new), South Korea

Oxy-Combustion of Coal and Biomass: Critical Technical Issues

- **Heat Transfer**
  - ✓ for retrofit applications, need to more or less match distribution of radiant and convective heat transfer
  - ✓ for new plants, can consider compact furnace designs with higher temperatures and more radiant heat transfer (little to no flue gas recycle)
- **Oxy-Fuel Burner Operation**
  - ✓ flame stability and length
  - ✓ carbon burnout
  - ✓ NOx formation
  - ✓ fly ash properties and carbonization of deposits
- **System Integration**
  - ✓ oxygen source purity
  - ✓ pollutant removal during flue gas compression
  - ✓ thermal integration of air separation and flue gas compression processes

Oxy-Fuel Combustion: What's Different?

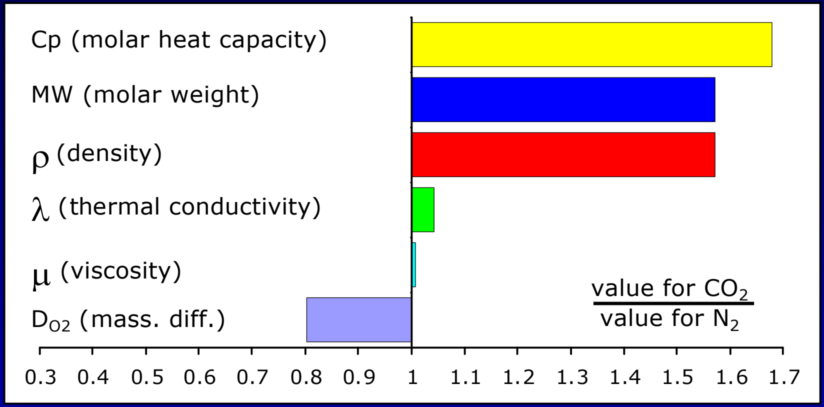
- **Elimination of nitrogen diluent and its partial replacement with recycled CO_2 results in**
  - ✓ **lower gas velocity**
  - ✓ **more concentrated product gases in the boiler**
  - ✓ **significant differences in gas transport properties**
  - ✓ **radiantly active gas medium (IR absorption and emission)**
- **Improved control over flame temperature, flame stabilization, and carbon burnout, by controlling O_2 level in different flow streams**



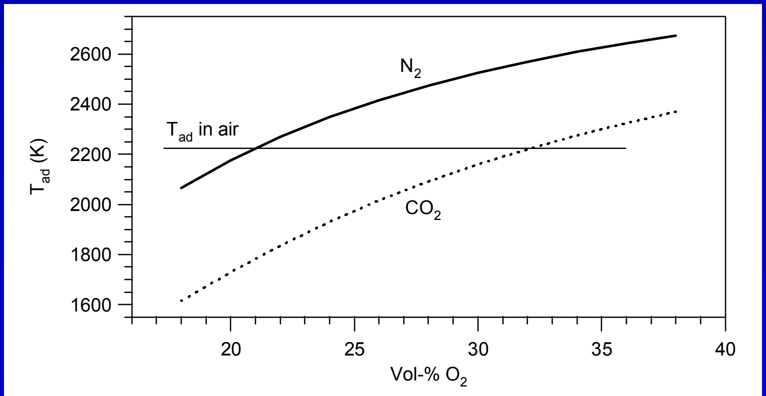
T field of simulated burner

Differences in Gas Transport Properties

Ratio of CO_2 properties to N_2 properties (at 1650 K)



High specific heat means need to use less dilution with CO_2 to match flame (and postflame) temperatures



Adiabatic flame temperature for CH_4 combustion

Example of CO_2 Effect

Consider convective heat transfer to steam tubes in a retrofit application

$$q/L = h\pi D\left(T_\infty - T_w\right)$$

If match gas temperatures, only difference in heat transfer is derived from *h*

$$h = Nu \cdot k/D$$

$$Nu = \left(0.4\,\mathrm{Re}^{1/2} + 0.06\,\mathrm{Re}^{2/3}\right)\mathrm{Pr}^{0.4}\left(\mu_\infty/\mu_w\right)^{1/4}$$

Whitaker formula

At 1000 K, $k_{CO_2} = 1.08\ k_{N_2}$ and $Pr_{CO_2} \approx Pr_{N_2}$

$$\mathrm{Re} = \rho VD/\mu$$

***V* ratio is 0.7 (with 30% O_2 in CO_2)**
***ρ* ratio is 1.6**
***μ* ratio is 1.0**

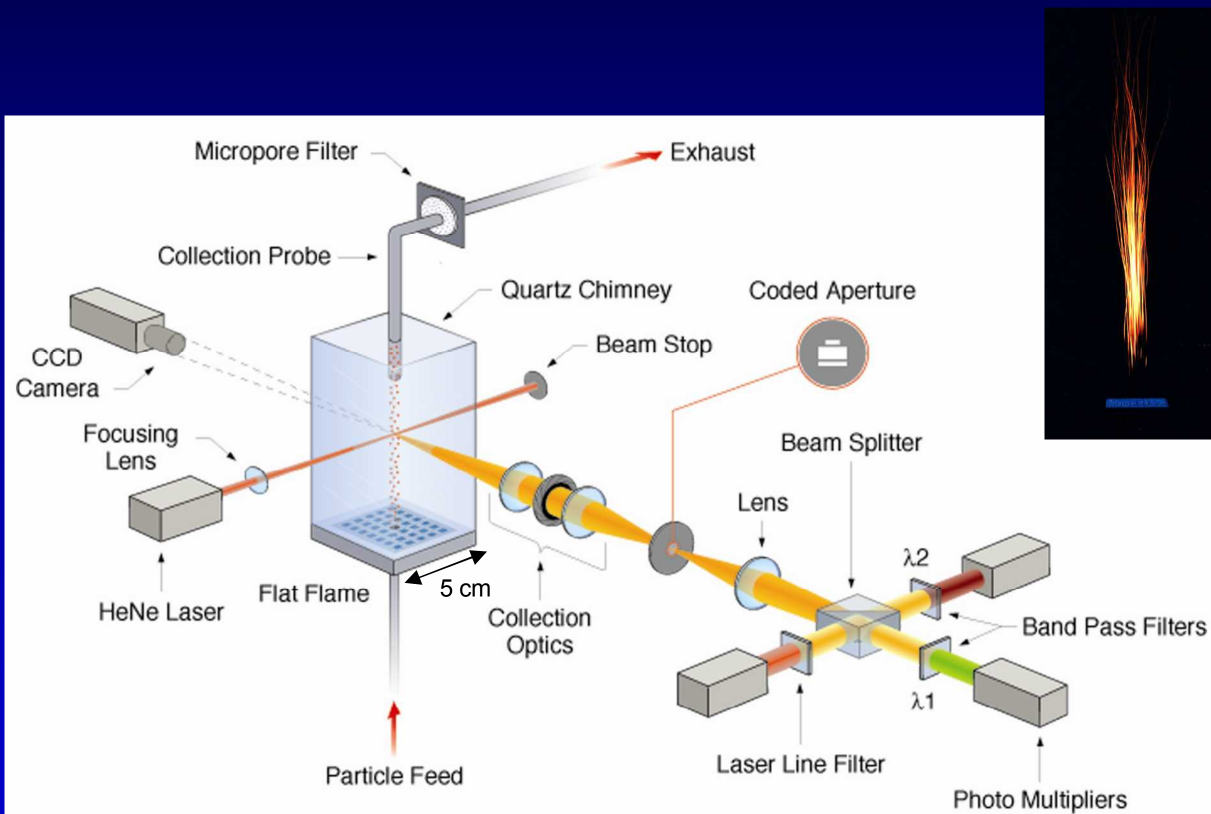
so $Re_{CO_2} = 1.12\ Re_{N_2}$

Therefore $h_{CO_2} \approx 1.13\ h_{N_2}$ – slightly greater convective heat transfer

Sandia Research on Oxy-Coal Combustion

- Single particle ignition and devolatilization rates
  - ✓ experiments using small entrained flow reactor
  - ✓ interpretation with analytical expressions
- Char combustion rates and kinetics
  - ✓ experiments using small entrained flow reactor
  - ✓ interpretation with analytical expressions and with single-particle combustion model
- NOx production
  - ✓ experiments using large entrained flow reactor
  - ✓ interpretation with plug flow particle combustion model and with single-particle combustion model

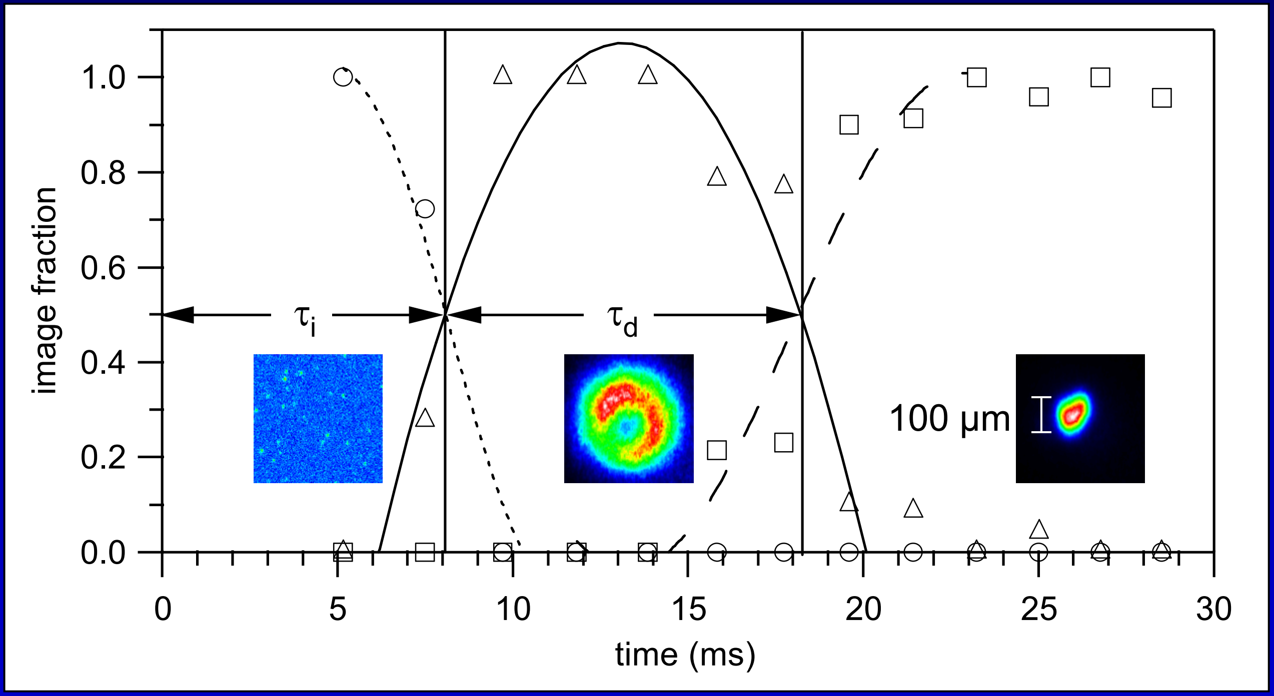
Experimental Setup: Combustion-Driven Optical Entrained Flow Reactor



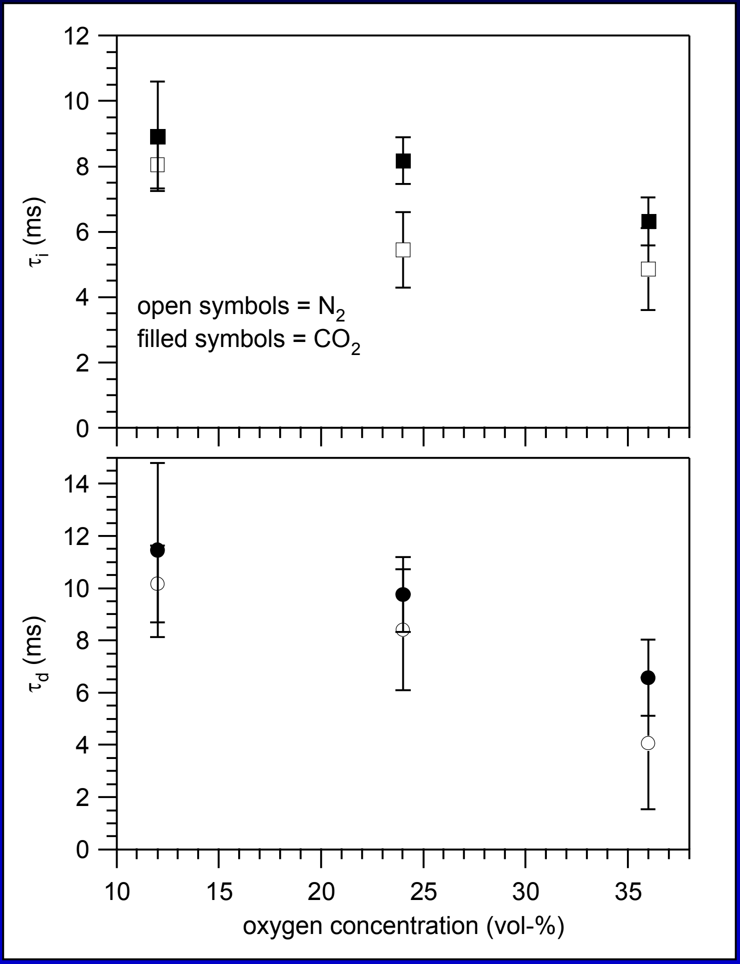
- 1 atm
- compact, flat flame burner
- fuel particles introduced along centerline
- quartz chimney
- coded-aperture, 2-color pyrometry diagnostic for char size, T, and velocity
- laser-triggered ICCD for single particle imaging

Characteristic Timescales from Single Particle Imaging

pre-ignition **devolatilization** **char combustion**



Trends in Measured Ignition and Devolatilization Times



Explanation of Measured Trends

- **Ignition time trends explained by adiabatic thermal explosion theory (1-step overall rxn)**

$$\tau_i = \frac{c_v \left(T_0^2 / T_a \right)}{q_c Y_{F,0} A \exp\left(-T_a / T_0 \right)}$$

– CO_2 increases local mixture c_v
– O_2 increases mixture reactivity

- **Devolatilization time trends explained by quasi-steady droplet combustion theory**

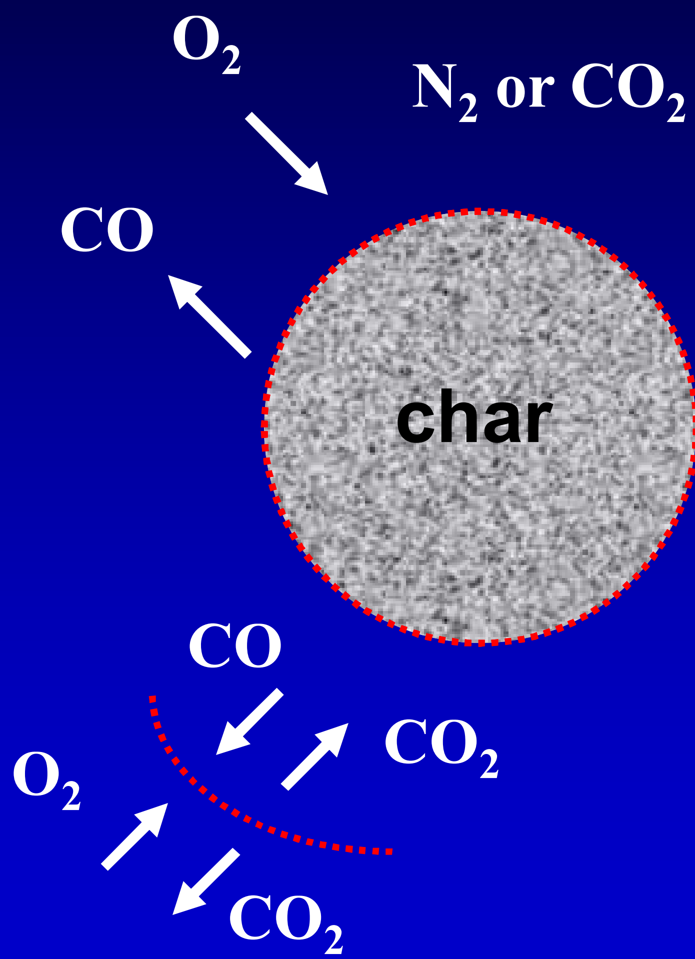
$$\dot{m} = \left(4\pi r_p \right) \left(\rho_p D_{fuel} \right) \ln\left(1 + B \right)$$

$$B = \left[c_{p,fuel} \left(T_\infty - T_p \right) + \left(Y_{o,\infty} / OF \right) h_c \right] / h_v$$

– D_{fuel} is 20% lower in CO_2
– $Y_{O,\infty}$ is part of Spalding B factor (increases diffusional flux of O_2)

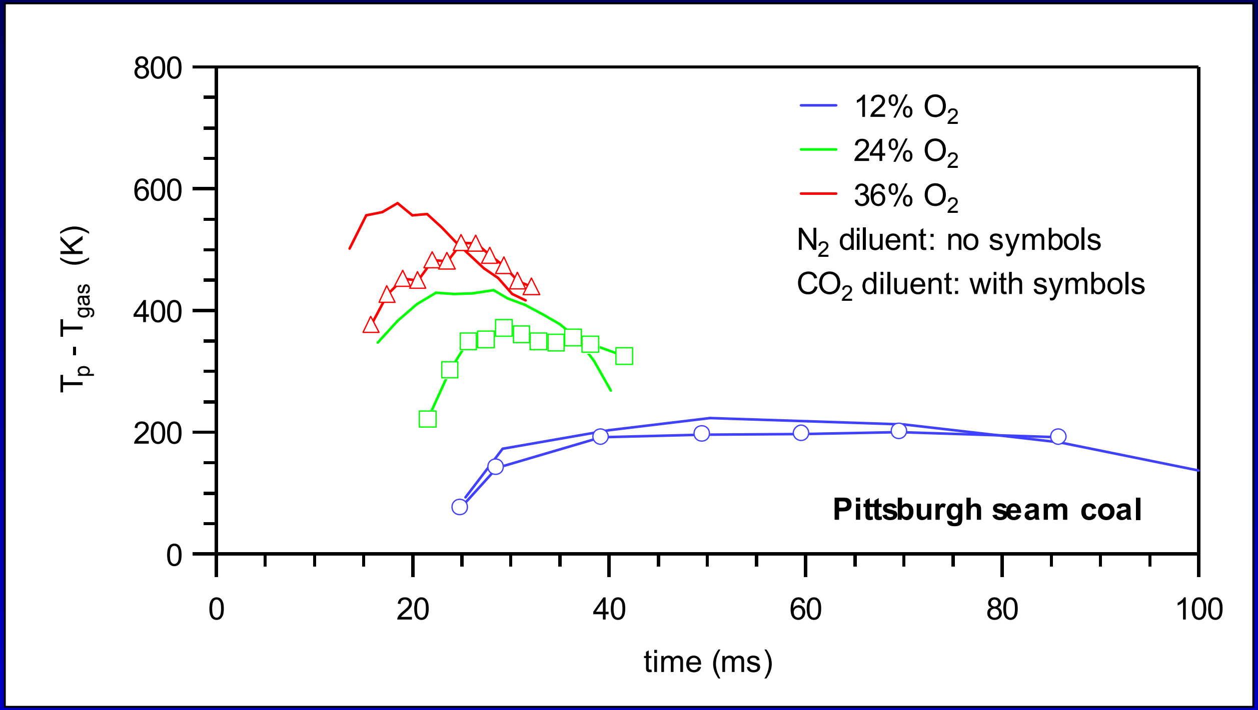
Potential Effects of CO_2 on Char Combustion

- Reduction of O_2 diffusion in particle boundary layer and within particle
  effect: burn rate ↓
- CO_2 reacts directly with char (Boudouard Reaction), but reaction is endothermic
  net effect: burn rate ↓?
- High ρC_p of CO_2 reduces CO flame T and heat transfer to particle (for 2-film model)
  effect: burn rate ↓
- CO_2 dissociation on char leads to surface site competition with O_2
  effect: burn rate ↓



Particle Temperature Measurements

Pittsburgh coal



- **Particles consistently burn hotter and earlier in N_2, implying higher char burning rate**

Burning Rate Analysis

- For each particle, construct an instantaneous energy balance, using a single-film combustion model:

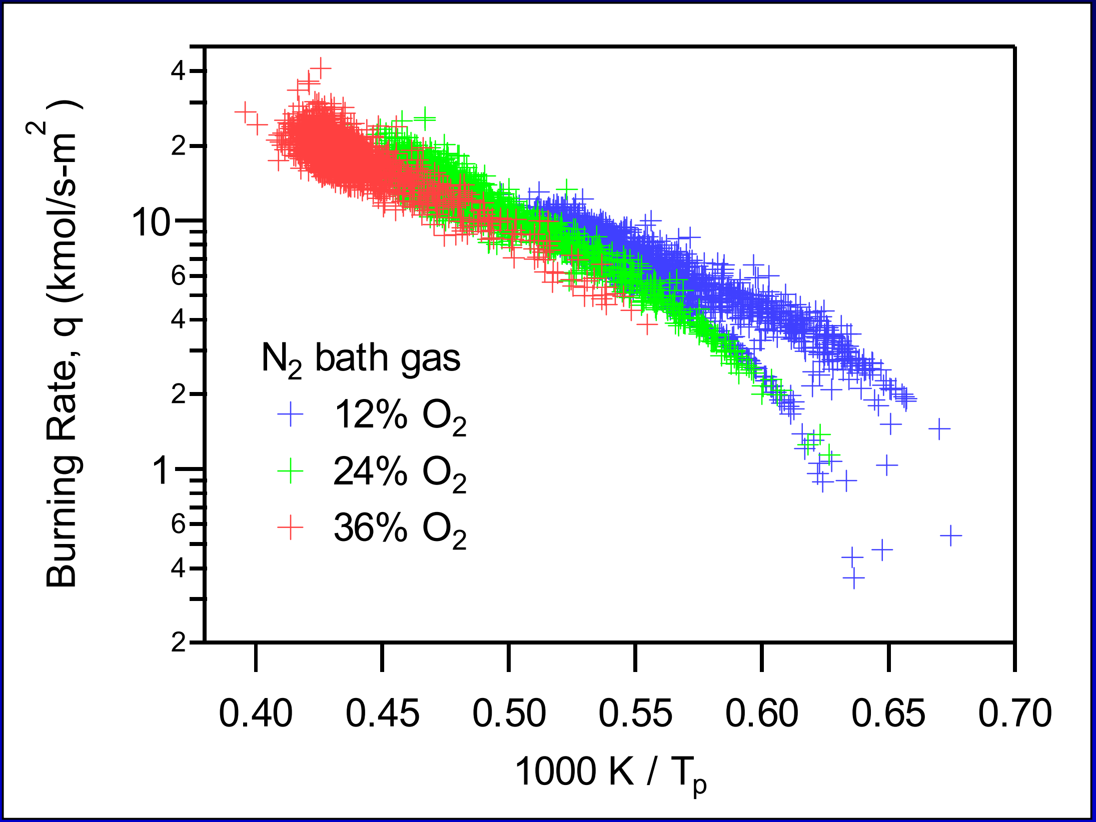
$$\underbrace{\frac{d_p \rho_p C_{v_p}}{6}\frac{dT_p}{dz}}_{\text{thermal inertia}} = \underbrace{-\varepsilon\sigma\left(T_p^4 - T_w^4\right)}_{\text{radiant loss}} \underbrace{-\frac{2\lambda}{d_p}\left[\frac{\kappa/2}{e^{\kappa/2}-1}\right]\left(T_p - T_g\right)}_{\text{convective loss}} + \underbrace{q\Delta h}_{\text{heat release}}$$

- Solve for surface-specific burning rate (of each particle), q

Surface-Specific Burning Rates

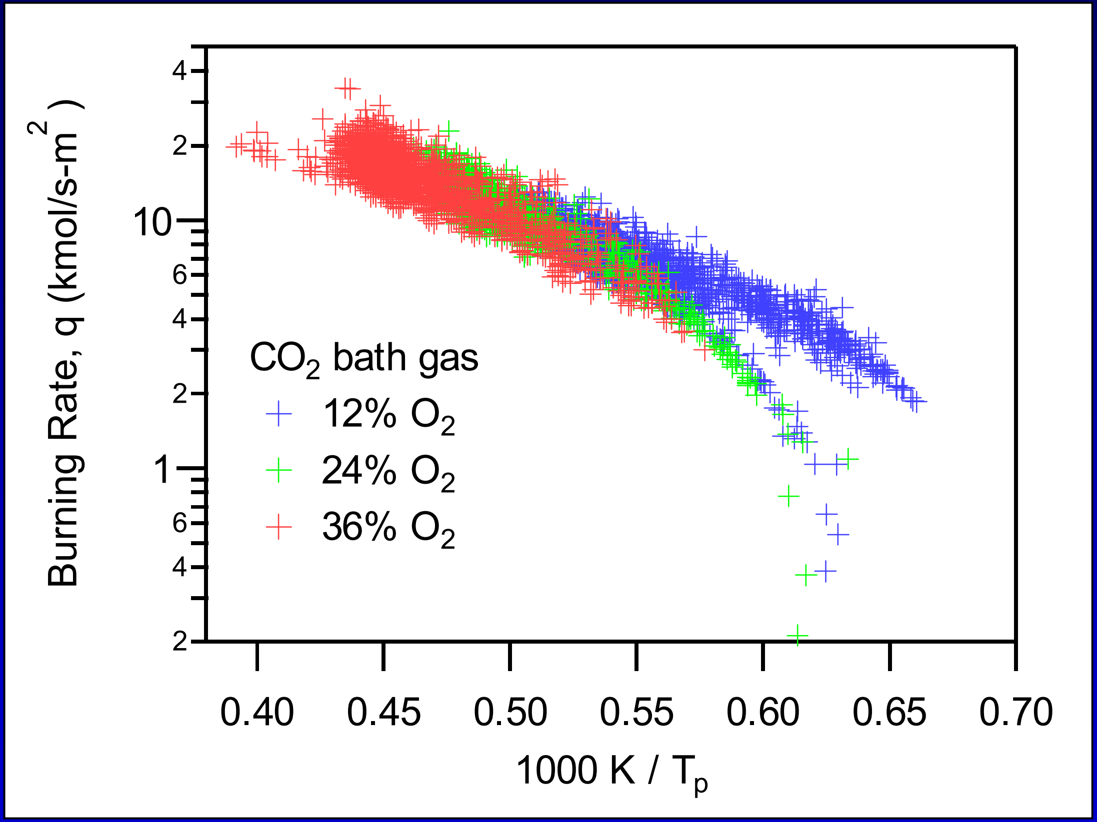
Pittsburgh coal

N_2 bath gas



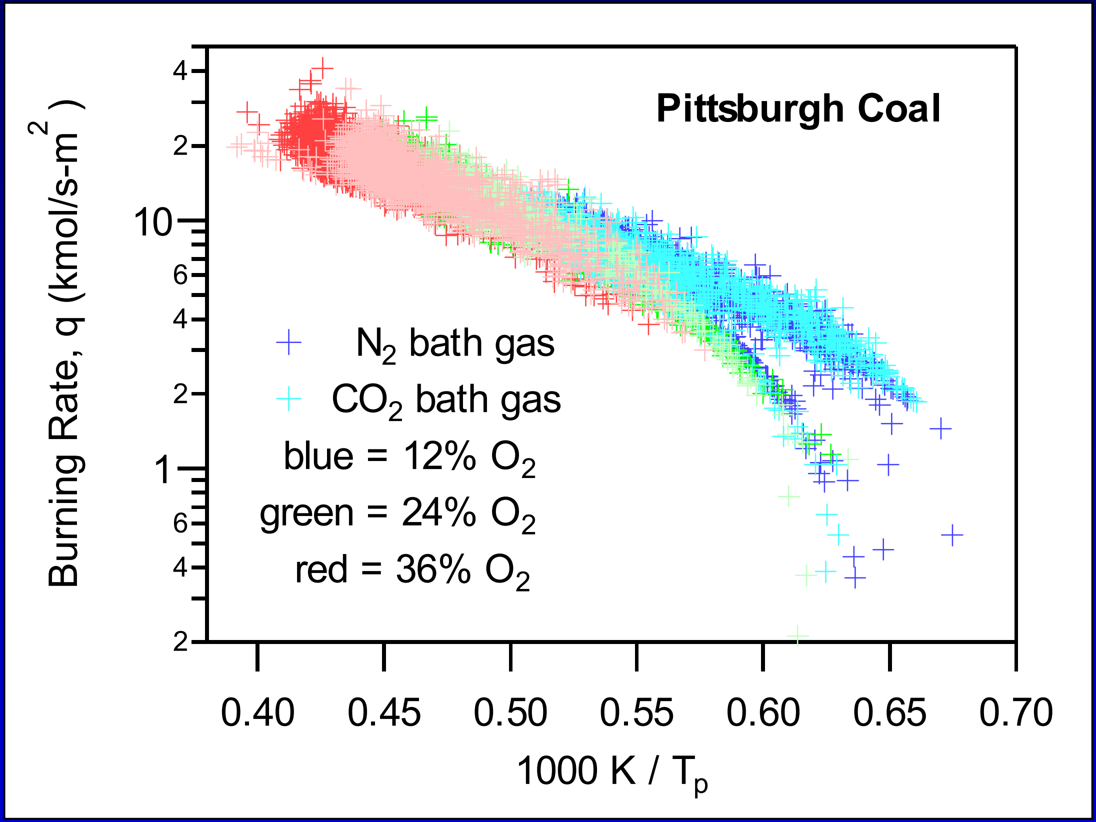
Surface-Specific Burning Rates

Pittsburgh coal
CO_2 bath gas



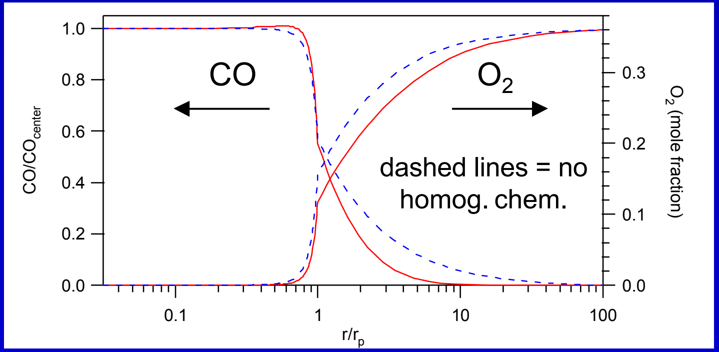
Surface-Specific Burning Rates

Pittsburgh coal
Both bath gases

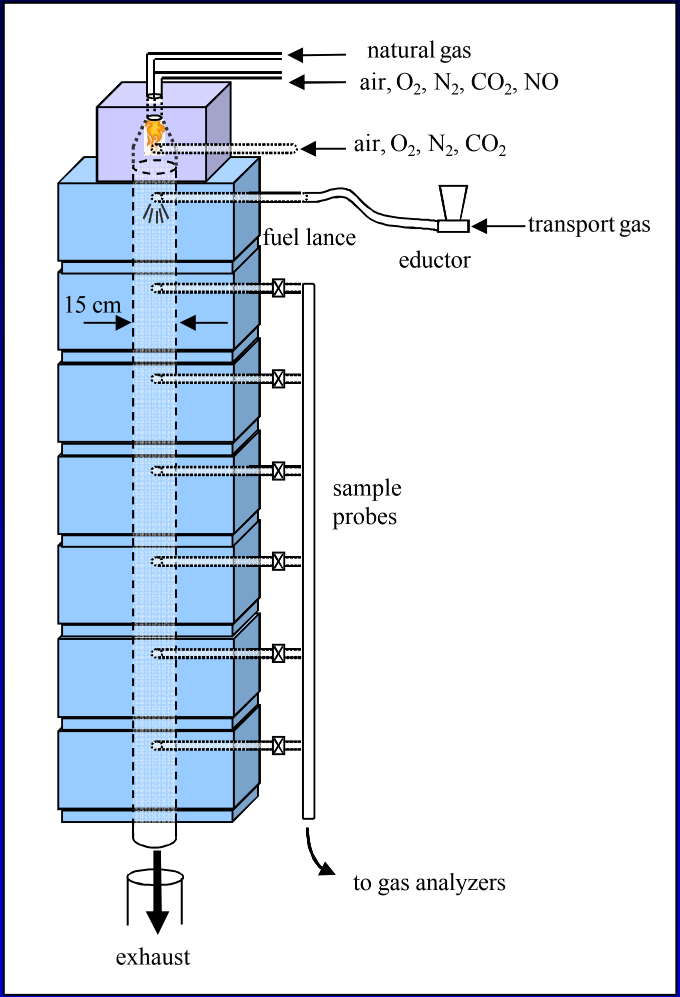


Interpretation of Results from Oxy-Coal Char Combustion

- **There are no significant (net) *kinetic* effects of CO_2 bath gas (at least for [O_2] > 12 vol-%)**
- **The lower *burning rate* measured in CO_2 is caused by lower diffusivity of O_2**
  - ✓ **analytical single-film calculations support this conclusion**
  - ✓ **single-particle combustion model with detailed gas transfer and full gas-phase chemistry also supports this conclusion**
- **Single particle model shows significant influence of partial CO conversion in boundary layer under enriched-O_2 conditions**



Experimental Setup: Multifuel Combustor



- 1 atm
- 150 mm dia, 4.2 m long SiC reaction tube with 7 independently controlled heater sections (up to 1350 °C)
- operates on air or specified mixtures of O_2 with N_2 or CO_2
- natural gas burner to preheat gases
- coal or char particles introduced at top of reactor
- Horiba CEM and micro-GC analysis of stable gases

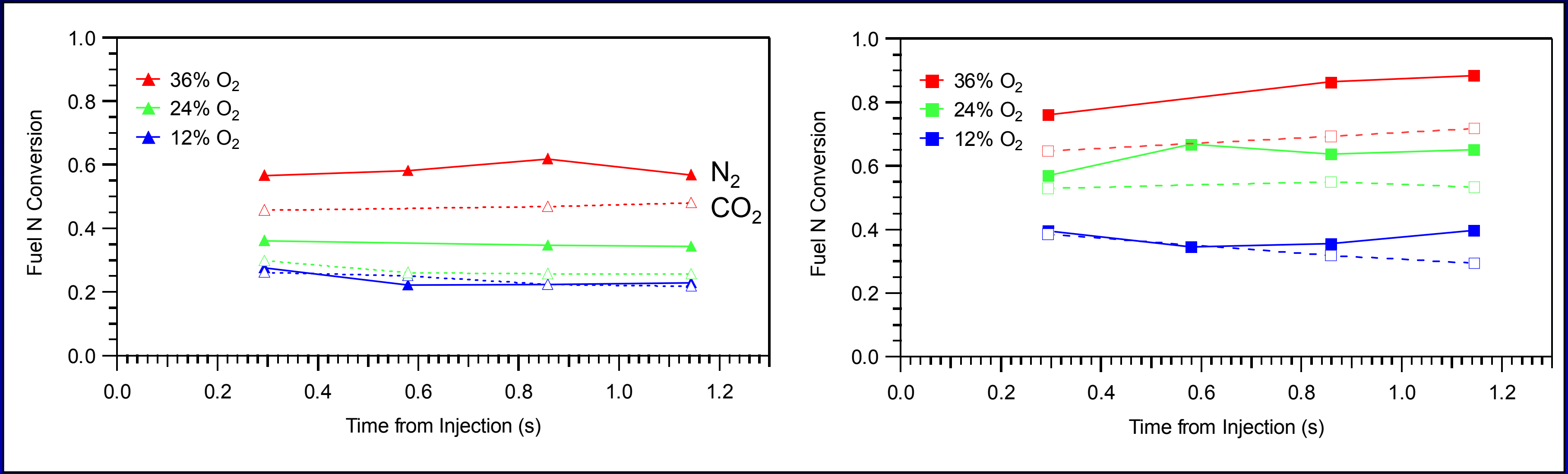
MFC Gas Compositions Investigated

Nominal Condition	Initial Concentration (vol-%)				Final Concentration (vol-%)			
	O_2	N_2	CO_2	H_2O	O_2	N_2	CO_2	H_2O
12% O_2 in N_2	12.6	75.9	3.9	7.6	10.7	75.7	5.4	8.2
24% O_2 in N_2	25.0	63.5	3.9	7.6	21.2	63.2	6.9	8.7
36% O_2 in N_2	37.6	50.9	3.9	7.6	31.9	50.5	8.3	9.3
12% O_2 in CO_2	13.3	1.1	73.9	11.7	11.3	2.3	74.3	12.1
24% O_2 in CO_2	26.0	1.1	61.2	11.7	22.2	1.2	63.8	12.8
36% O_2 in CO_2	38.7	1.1	48.6	11.7	32.9	1.1	52.6	13.4

- **Equivalence Ratio maintained at 0.15 for all experiments**
  - ✓ **low solids loading, little O_2 consumption (reactor as entrained flow reactor)**
- **Two levels of background NO investigated**
  - ✓ **30 ppm for 'low reburn'**
  - ✓ **530 ppm for 'high reburn'**

Fuel N Conversion to NOx: low reburn

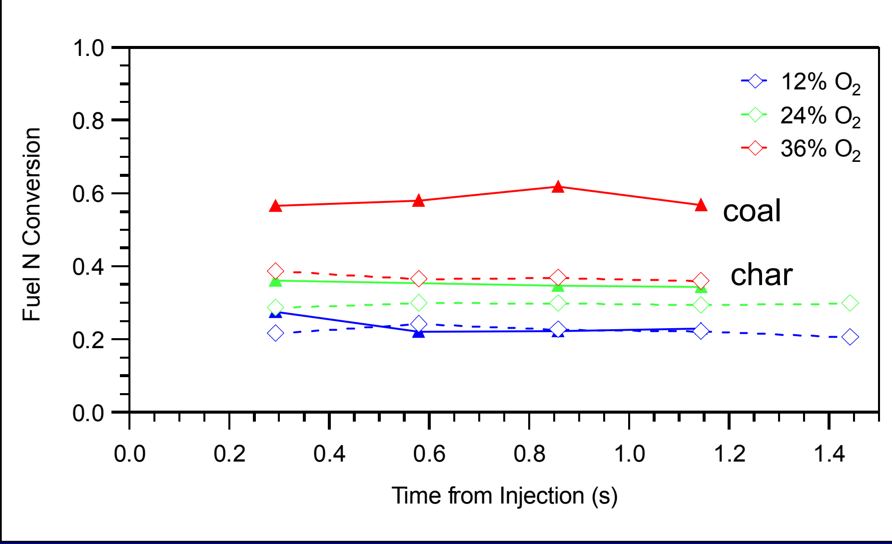
Pittsburgh coal / **Black Thunder coal**



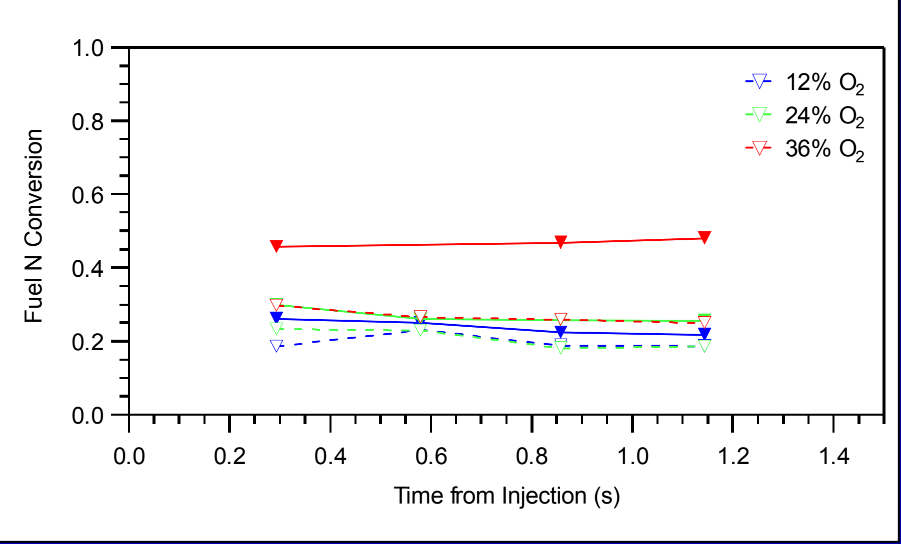
- **Fuel N conversion to NOx increases with higher O_2**
- **CO_2 diluent decreases fuel N conversion to NOx**
- **Black Thunder has substantially higher fuel N conversion to NOx**
  - ✓ **higher volatile content**
  - ✓ **higher char combustion temperature**

Coal vs. Char Fuel N Conversion to NOx

N_2 Environment



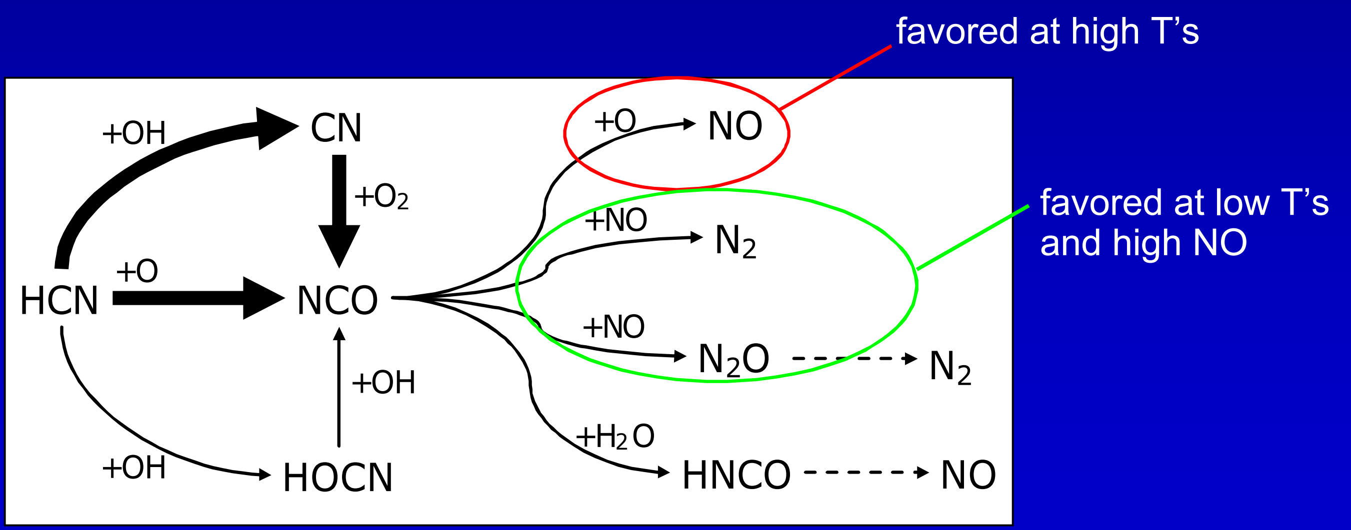
CO_2 Environment



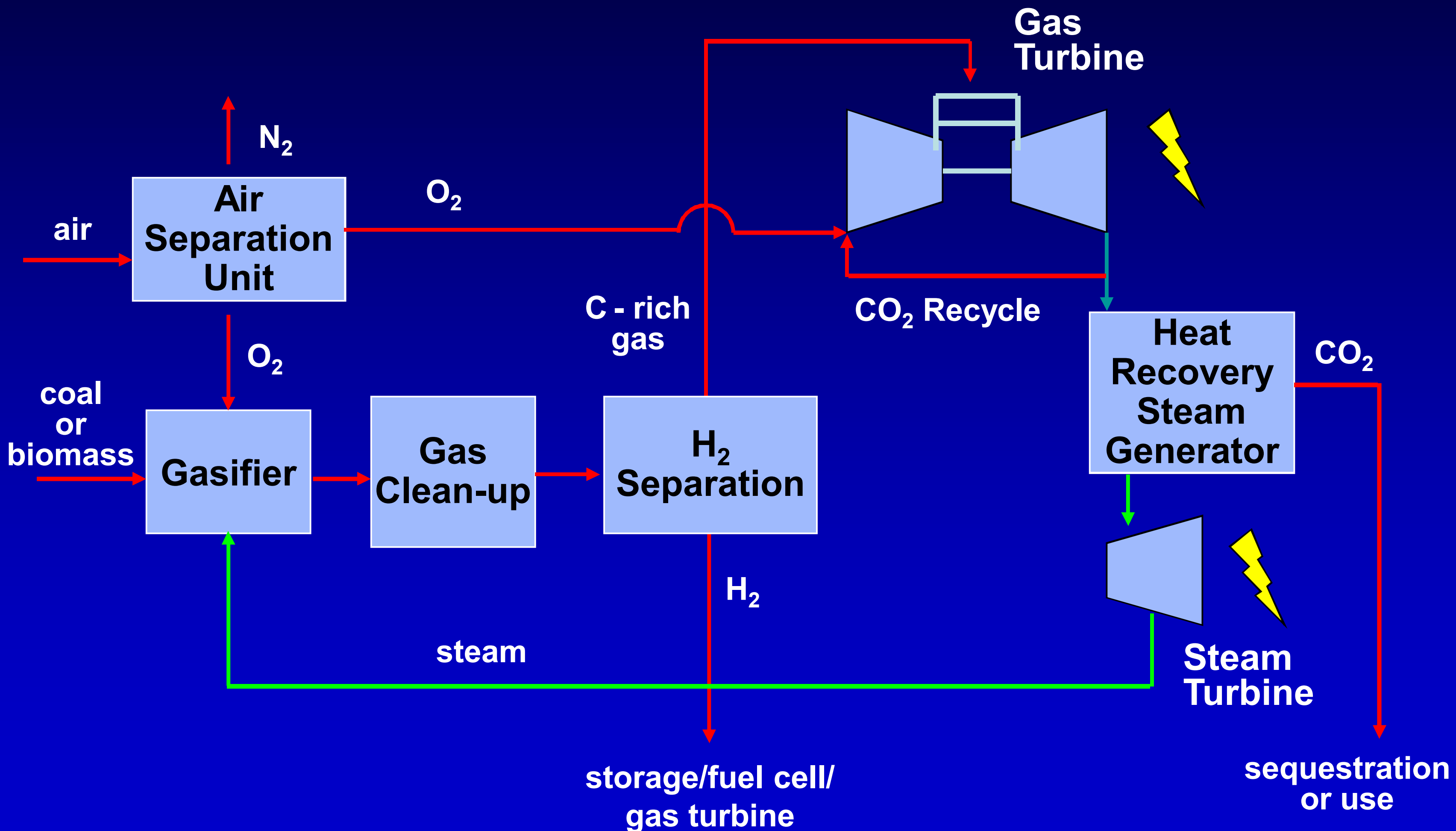
- Volatile-N preferentially produces NOx at elevated oxygen levels
  - ✓ higher volatile flame temperature
- Char-N produces more NOx at elevated oxygen levels
  - ✓ higher char comb. temperature with more O_2

Chemical Kinetic Interpretation of Measured Trends in NOx Production

- **Joint experiment/modeling study provides strong evidence for dominant route of N release from pc char as CN compound (here modeled as HCN)**
- **HCN is oxidized to NCO**
- **NCO is either oxidized to NO (favored at high temps), or reacts with NO to form N_2 (favored at low temps and for high background NO)**



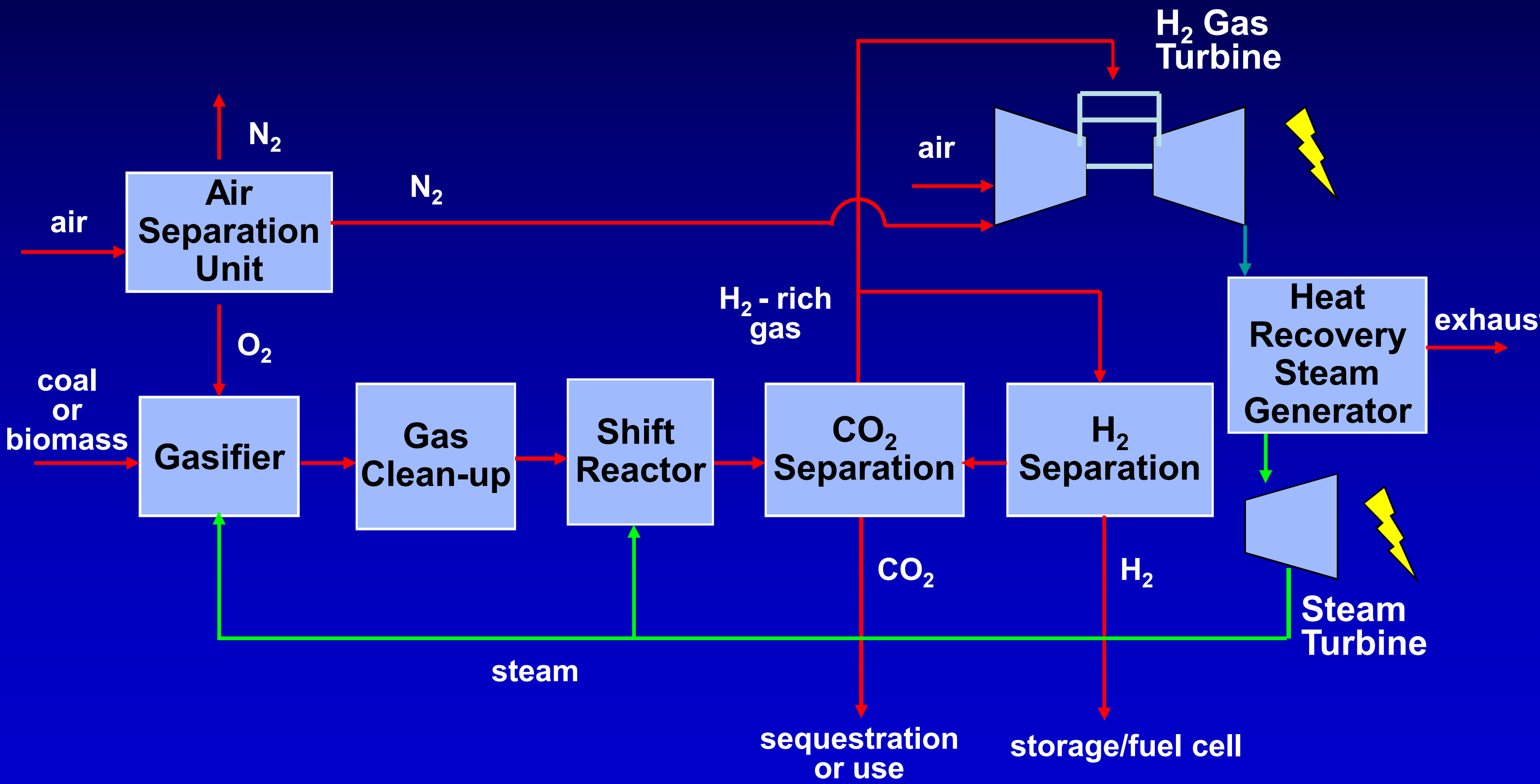
System Layout for Co-Production of Electricity and H_2 (with Oxy-Combustion of Syngas)



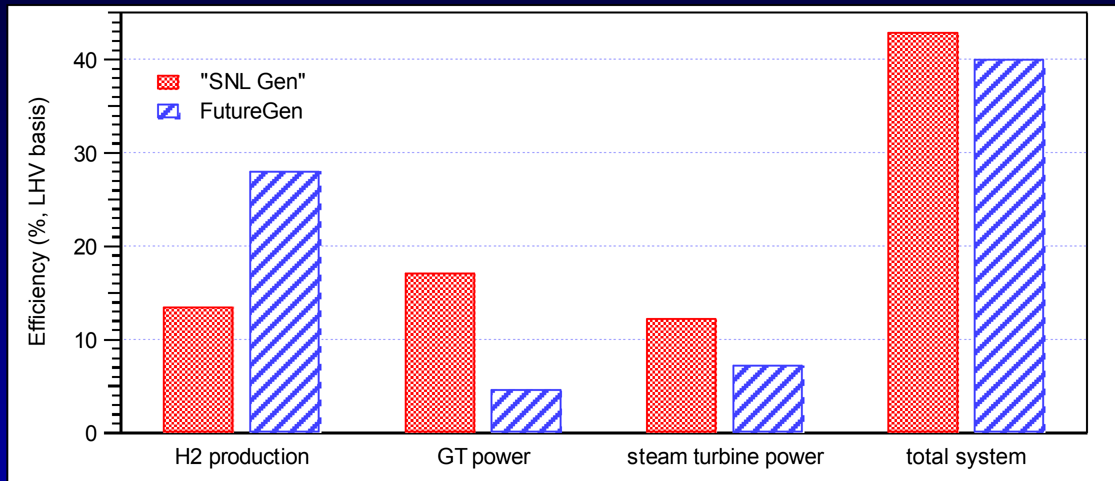
Oxy-Combustion of Syngas: Critical Questions

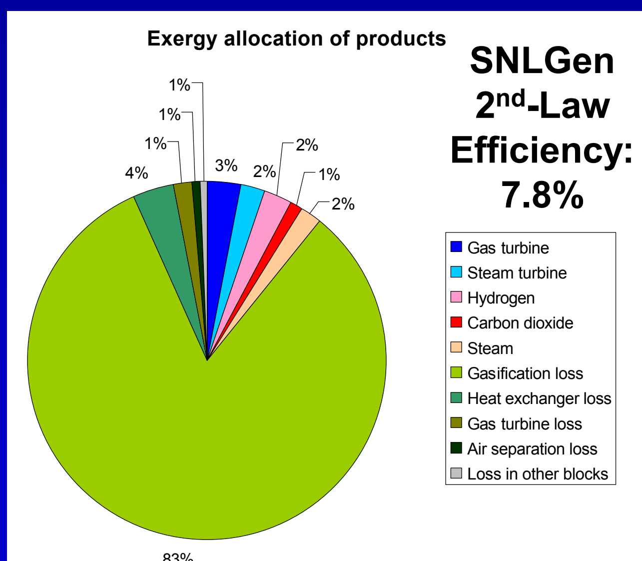
- Can a system with oxy-combustion of syngas be competitive with alternative H_2-based combustion system?
- Does oxy-combustion with CO_2 recycle have acceptable gas turbine flammability limits and emission characteristics?

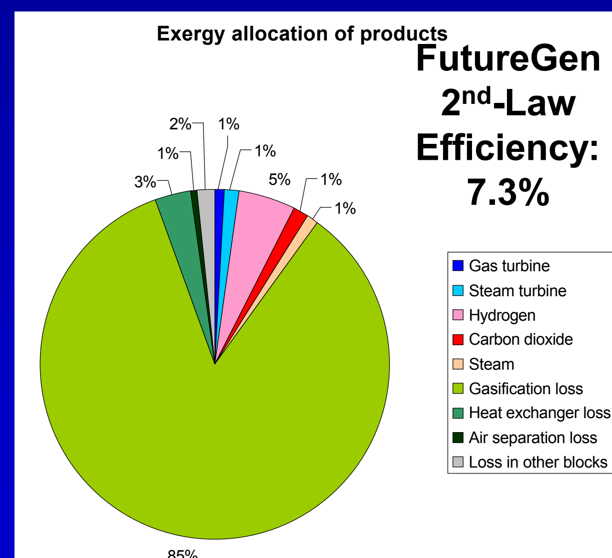
Traditional System Layout for Co-Production of Electricity and H_2 (FutureGen)



Co-Production System Comparison



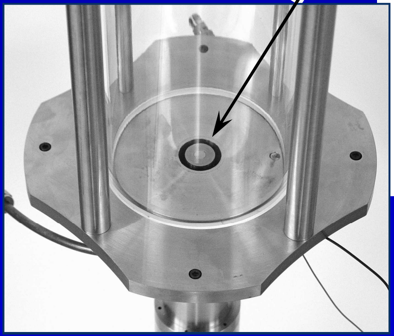


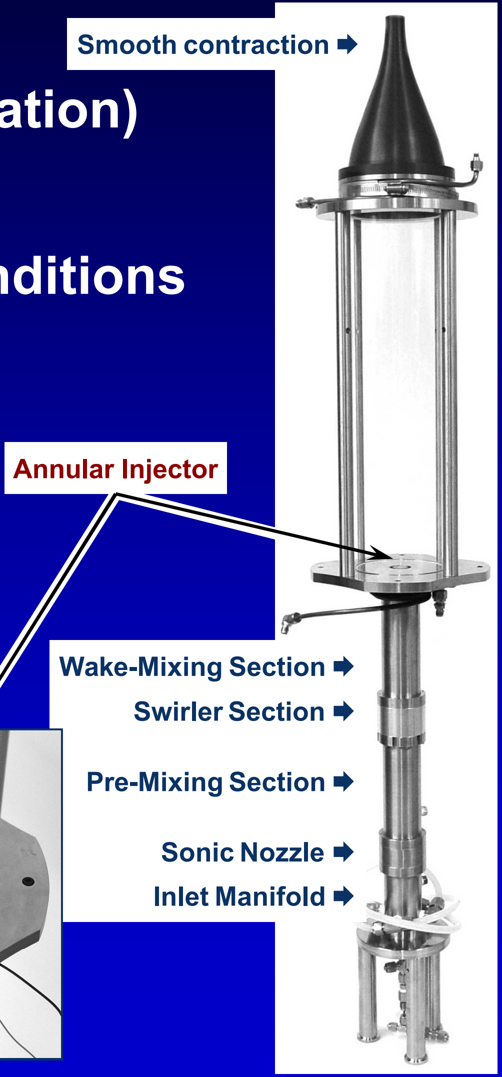


Experimental Setup: Dump Combustor

- Designed for high-fidelity (large eddy simulation) model validation
- Well-defined, non-ambiguous boundary conditions
- Operates at 1 atm
- Has full optical access for application of laser diagnostics
- Pressurized (30 atm) 'sister' burner is at DOE NETL in Morgantown, WV

Lean Premixed Methane Flame





Experiments on Oxy-Combustion of Syngas

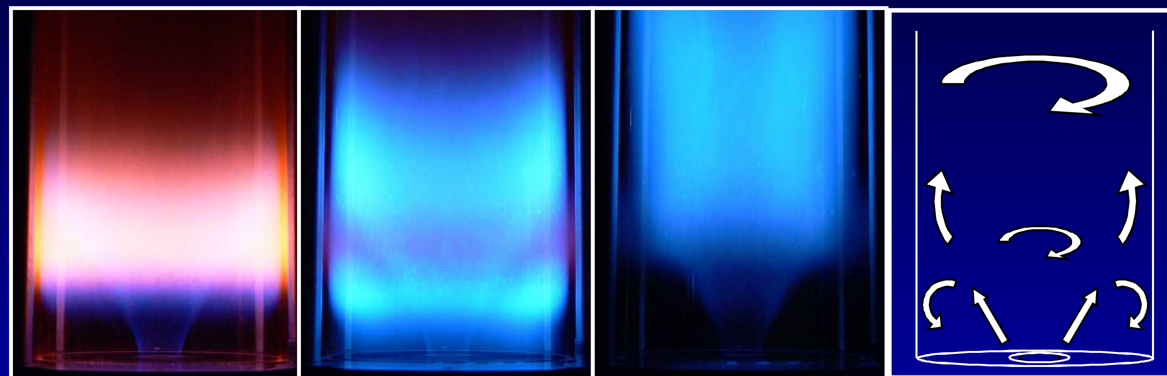
- Varied fuel gas mixture and oxidizer composition
  - ✓ oxidizers included air and O_2/CO_2 mixtures (O_2-enriched to O_2-depleted)
  - ✓ fuel composition chosen to match representative scenarios

Fuel	Fuel Composition					H_2/CO	LHV
	CH_4	H_2	CO	N_2	CO_2		MJ/Nm^3
Methane	100	-	-	-	-	-	32.8
Slurry feed syngas	-	35	50	1	14	0.70	9.2
Dry feed syngas	-	28	64	5	3	0.44	10.2
H_2-lean syngas	-	1	76	2	21	0.013	8.9
H_2-rich syngas	-	95	1	3	1	95	9.5

- Collected digital photographs to visualize changes in flame structure
- Measured lean blowout limit and NOx and CO emissions between blowout limit and $\phi = 1.05$
- Collected OH PLIF for canonical flame conditions

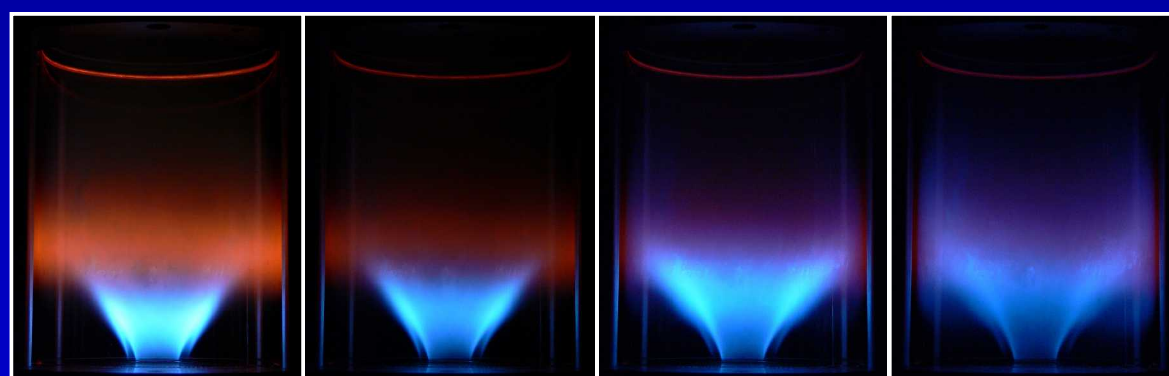
Photographs of Different Flame Structures

CH4/
30% O_2-
CO_2



φ = 0.7 [1 s]　φ = 0.65 [4 s]　φ = 0.58 [4 s]　Outline of combustion chamber and annulus

slurry-feed
syngas
$\phi = 0.95$



25% O_2-CO_2 [0.05 s]　20% O_2-CO_2 [0.05 s]　15% O_2-CO_2 [0.25 s]　13% O_2-CO_2 [0.25 s]

Emissions from Oxy-Combustion of Syngas

- Increasing H_2 content in syngas increases flame stability and intensity – leaner blowout limit, higher NOx emissions
- For oxy-fuel combustion, low levels of NOx are produced at all stoichiometries
- For all fuel and air mixtures investigated, CO emissions only become significant near lean blowout and for $\phi > 0.95$