SAND2010-6651P

Thermo-chemical Conversion of Biomass and Coal: Research Efforts at Sandia National Labs

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October 18, 2010

Presentation Outline

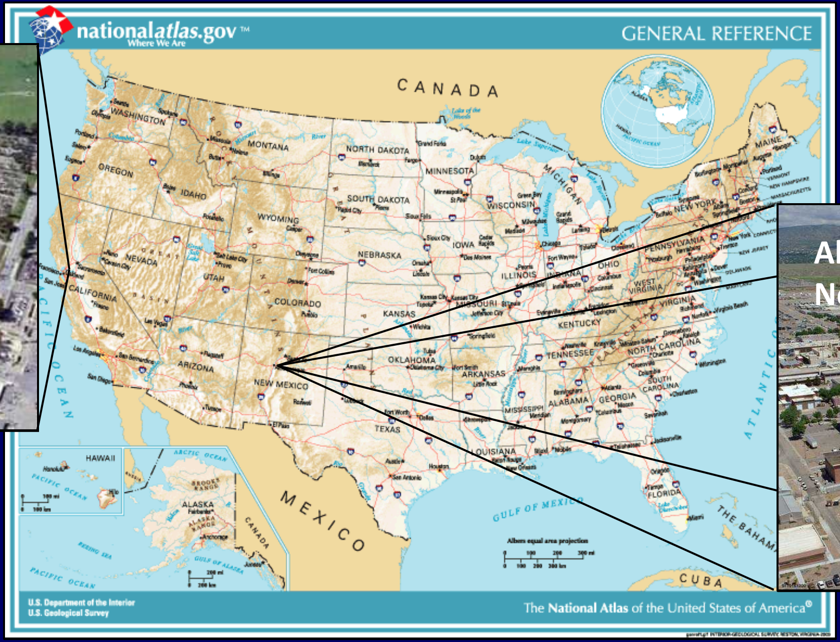
- Overview of Sandia Energy Research

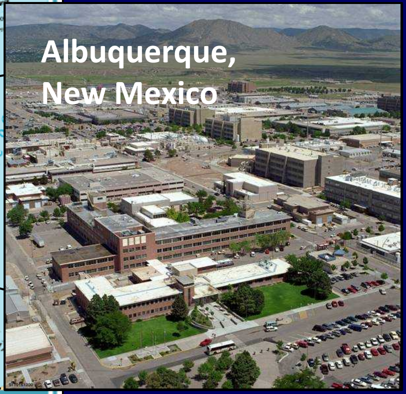
- Current Research on Thermo-chemical Conversion of Coal and Biomass
  - Oxy-combustion of coal
  - Gasification of coal
  - Combustion and gasification of lignin

- 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



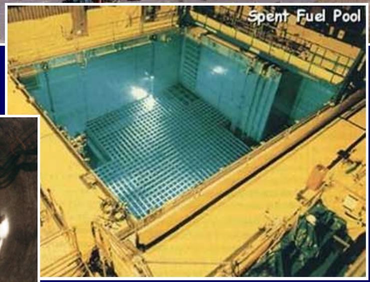


- Approx. one-half of Sandia's efforts are devoted to nuclear weapons issues and one-half to energy and environment and homeland security

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**

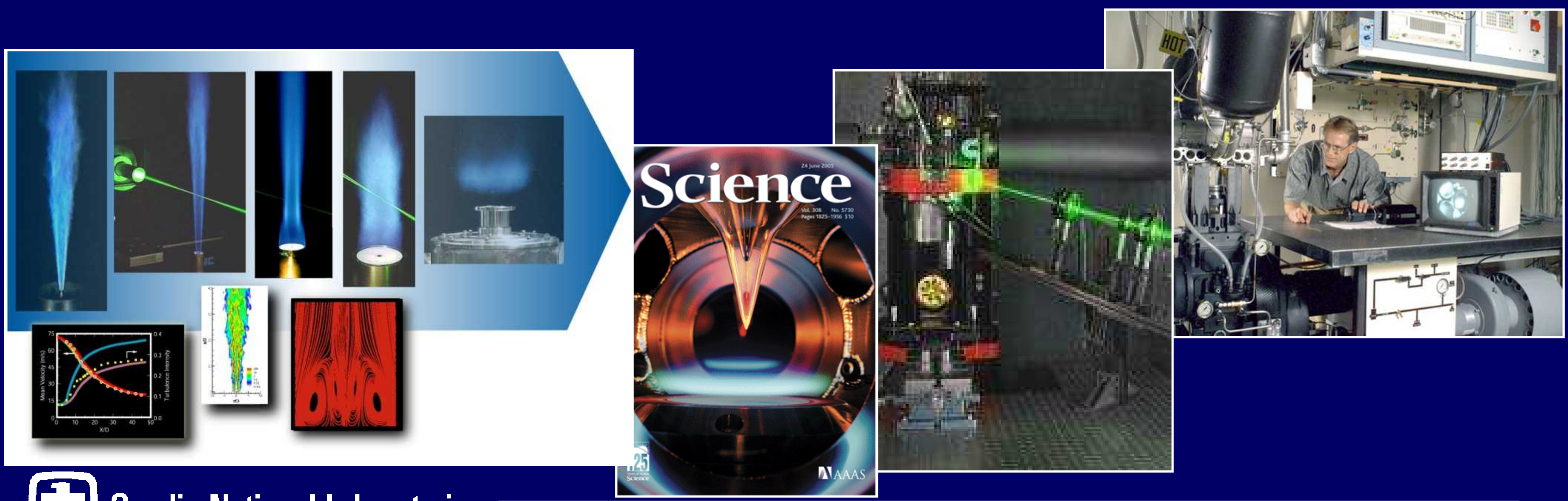
  - Advanced pretreatment and enzymatic hydrolysis of lignocellulosic biomass
  - Algal biodiesel

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 advance laser diagnostics**
  - **Computation work includes master equation solutions, direct numerical simulation (DNS), large eddy simulation (LES), and simplified description of turbulent mixing (LEM)**



Thermo-chemical Conversion of Coal and Biomass

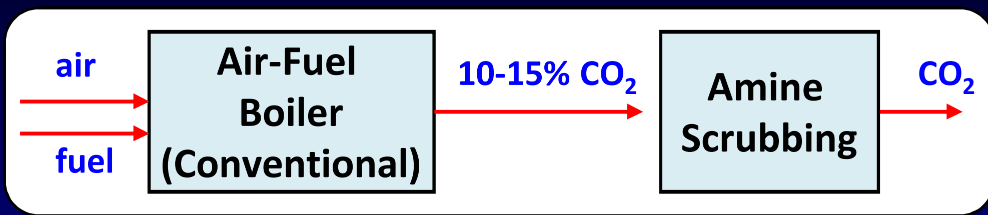
- Coal and biomass are two of the most abundant energy resources in the world
- Traditional conversion of these fuels to useful energy, by combustion in air to generate electricity, releases CO_2 and does not reduce need to import oil for use in the transportation sector
- Recent international assessments 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

In Response to this Motivation…

- The U.S. DOE, together with governments and research associations around the world, is supporting research on
  - determining the lowest cost method of generating electricity from coal and biomass while capturing CO_2 for sequestration (for example, in saline aquifers)
  - developing strategies for producing, from these raw materials, H_2 and other synthetic fuels for use in the transportation sector, while capturing CO_2

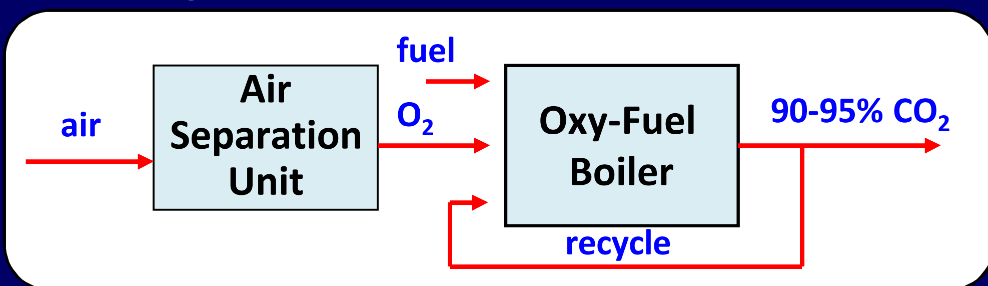
3 Routes to Carbon Capture

❑ Post-Combustion



- Simplest approach
- Existing technology
- Probably the most expensive option

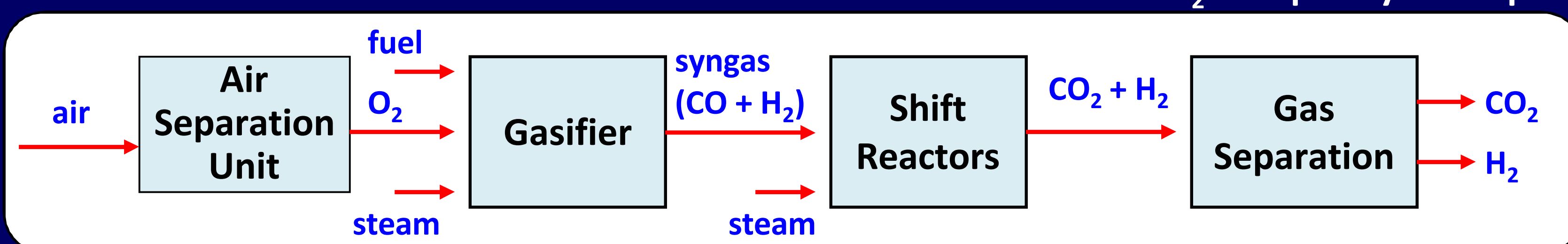
❑ Oxy-Combustion



- Can be retrofitted to existing boilers
- Modest modification of existing technology
- Concurrent emissions reductions

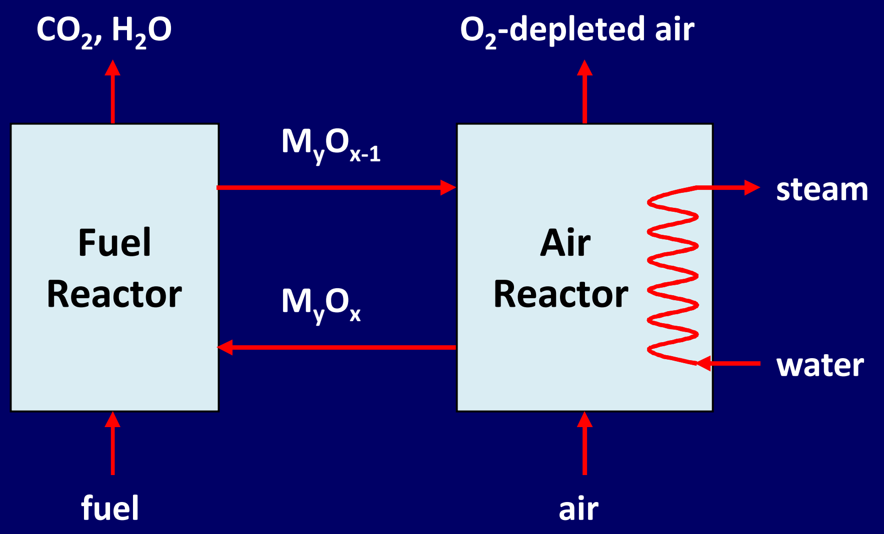
❑ Pre-Combustion

- Major shift from existing technology
- Very low emissions
- Route to H_2 or liquid synfuels production



Variant of Oxy-Combustion: Chemical Looping 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 is being developed worldwide

- 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

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

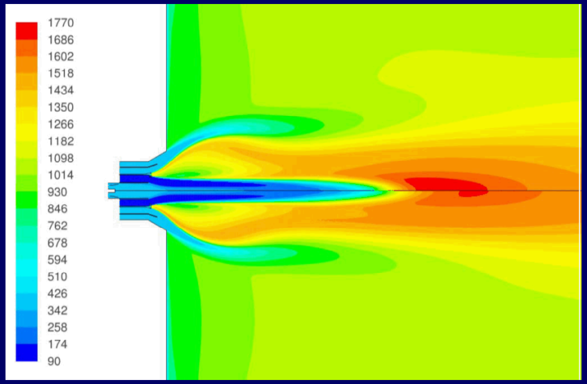
Schwarze Pumpe pilot plant

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
  - NO_x 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?

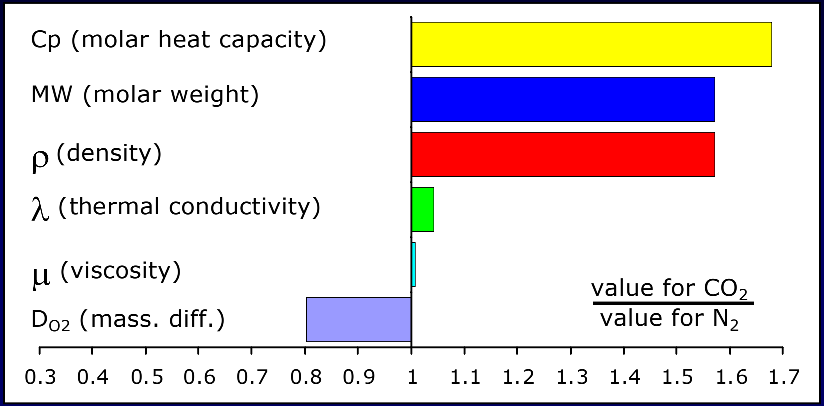
- Elimination of nitrogen diluent and its partial replacement with recycled CO_2 results in
  - Lower gas velocity
  - more concentrated product gases in the boiler
  - significant differences in gas transport properties
  - radiantly active gas medium (IR absorption and emission)
- Improved control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



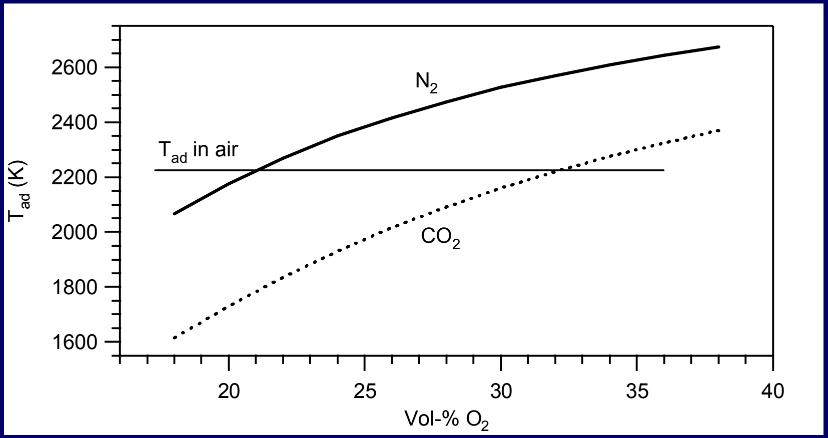
T field of simulated burner

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 post-flame) temperatures**



Adiabatic flame temperature for CH_4 combustion

Sandia Research on Oxy-Coal Combustion

❑ NO_x production

- experiments using large entrained flow reactor
- interpretation with plug flow particle combustion model and with single-particle combustion model

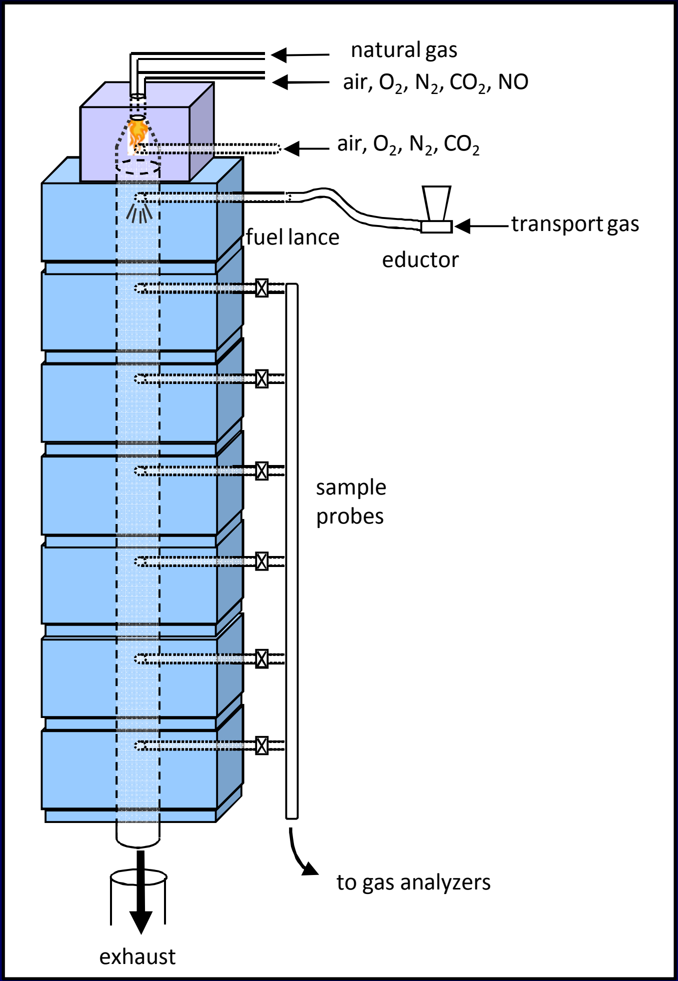
❑ Single particle ignition and devolatilization rates

- 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, single-particle combustion model and detailed numerical model of reactive porous particles

Experimental Setup: Multifuel Combustor

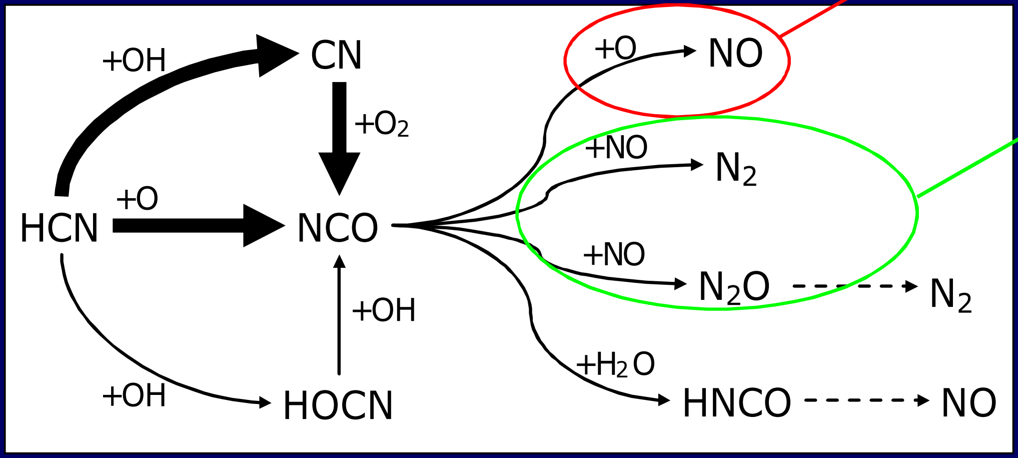


- 1 atm
- 150 mm dia, 4.2 m long SiC reaction tube with 7 independently controlled heater sections (up to 1350 °C)
- operates on air or specified mixtures of O_2 with N_2 or CO_2
- natural gas burner to preheat gases
- coal or char particles introduced at top of reactor
- Horiba CEM and micro-GC analysis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

Chemical Kinetic Interpretation of Measured Trends in NO_x Production

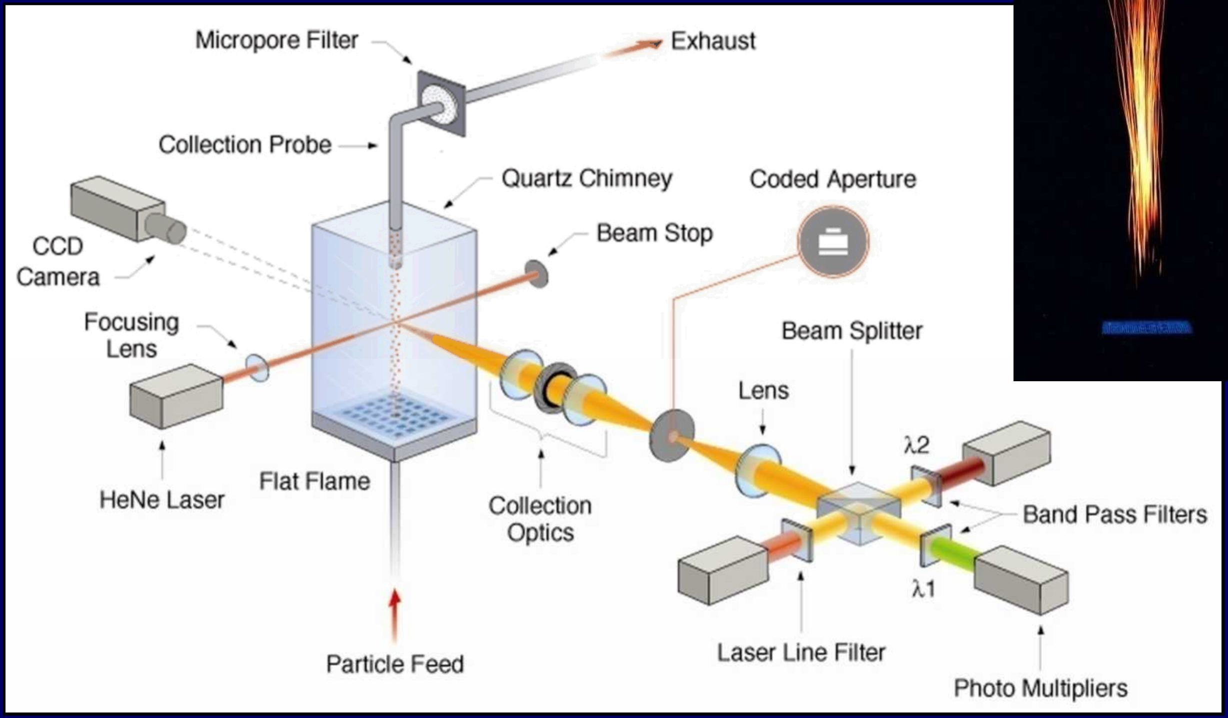
- Joint experiment/modeling study provides strong evidence for dominant route of N release from pc char as CN compound (here modeled as HCN)
- HCN is oxidized to NCO
- NCO is either oxidized to NO (favored at high temps), or reacts with NO to form N_2 (favored at low temps and for high background NO)

favored at high T's



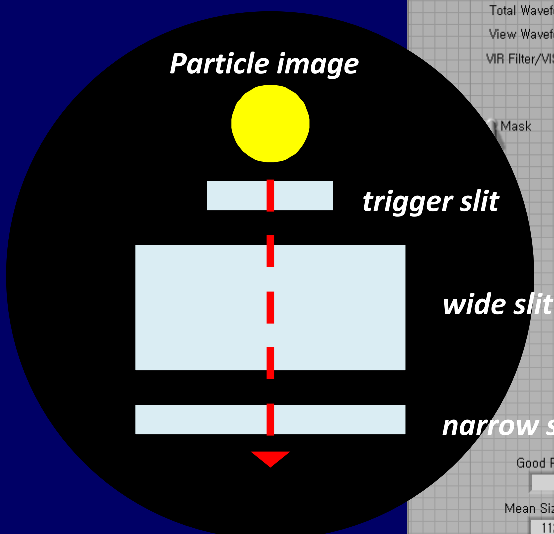
favored at low T's and high NO

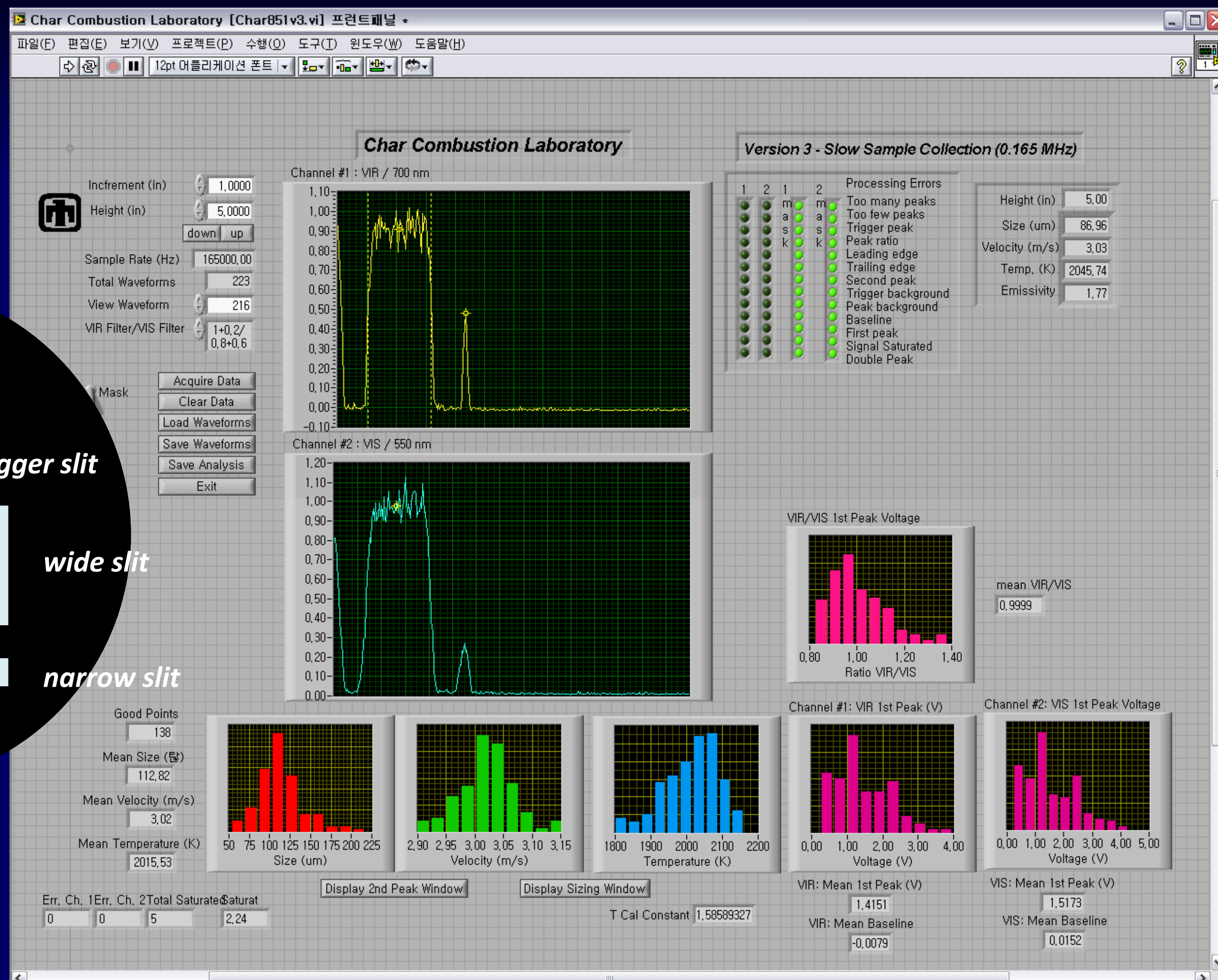
Experimental Setup: Combustion-Driven Optical Entrained Flow Reactor



- 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

Particle-sizing pyrometry in the laminar entrained flow reactor



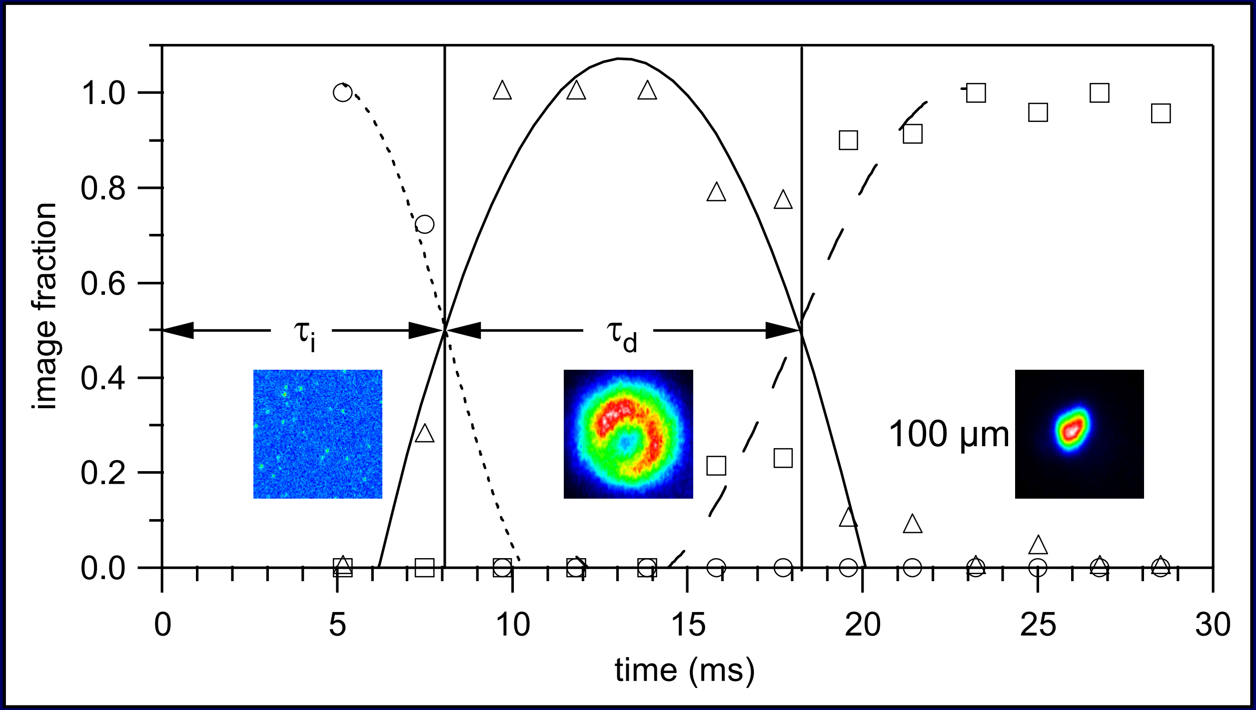


Conclusions from previous Oxy-combustion studies

- Ignition time and devolatilization rate are sensitive to local oxygen concentration
- CO_2 retards particle ignition (slightly) and decreases devolatilization rate (slightly)
- Results are consistent with theories of adiabatic thermal explosion and droplet combustion (CO_2 c_p and D_{fuel} effects)
- CO_2 reduces char particle combustion temperature, in amount consistent with reduction in O_2 diffusion through boundary layer
- Apparent single-film char kinetic rates are unaffected by CO_2

Characteristic Time Scales from Particle Imaging

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



Explanation of measured trends

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

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

– CO_2 increases local mixture c_v

– O_2 increases mixture reactivity

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

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

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

– D_{fuel} is 20% lower in CO_2

– $Y_{O,\infty}$ is part of Spalding B factor (increases diffusional flux of O_2)

Kinetics parameters are specific for chosen steady-state Single Film model

- **Particle temperature follows from instantaneous energy balance**

$$\frac{D_P \rho_P c v_P}{6}\frac{\mathrm{d}T_P}{\mathrm{d}z} = -\varepsilon\sigma\left(T_P^4 - T_W^4\right) - \frac{2\lambda}{D_P}\left[\frac{\kappa/2}{\exp(\kappa/2)}\right](T_P - T_G) + q\,\Delta h$$

  - *n*-th order Arrhenius oxidation kinetics

$$q = A\,p_{O_2,s}^n \exp\left(-\frac{E}{RT_P}\right)$$

  - $p_{O2,s}$ from solution of diffusion equation
  - CO_2/CO production ratio (Tognotti, 1990)

$$\frac{\dot{s}(CO_2)}{\dot{s}(CO)} = 0.02\,p_{O_2,s}^n \exp\left(\frac{3070}{T_P}\right)$$

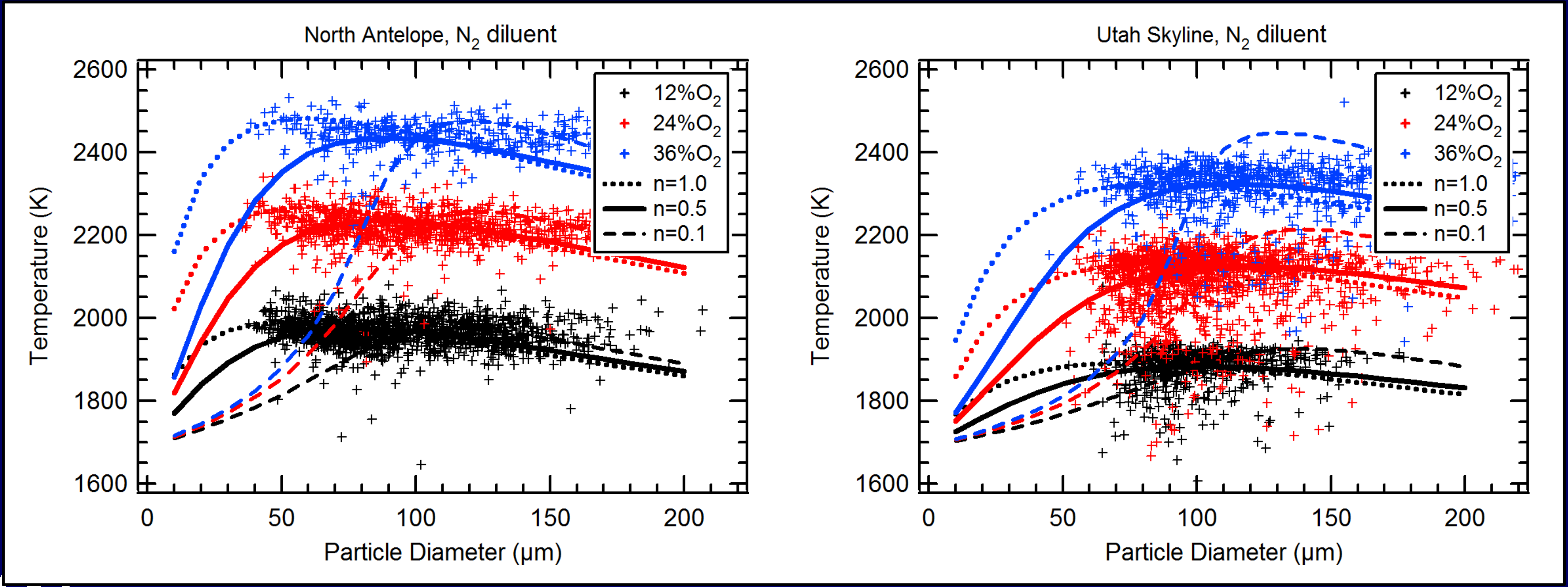
  - Film average temperature, diffusivities based on bulk composition
  - $dT_p/dz = 0$

- **Fit model to N_2 data**
  - Match temperatures of (100±3)μm particles with fixed reaction order *n*
  - Fitting parameters may have no physical relevance (e.g. *n* = 1 cases), implies model inadequacy

Fixed *n* =	*A* (kmol/m²·s)	E (kJ/mol)
	North Antelope:	
1	0.44	0.00
0.5	0.67	36.50
0.1	1.70	76.26
	Skyline:	
1	0.39	11.95
0.5	1.05	51.75
0.1	2.31	83.54

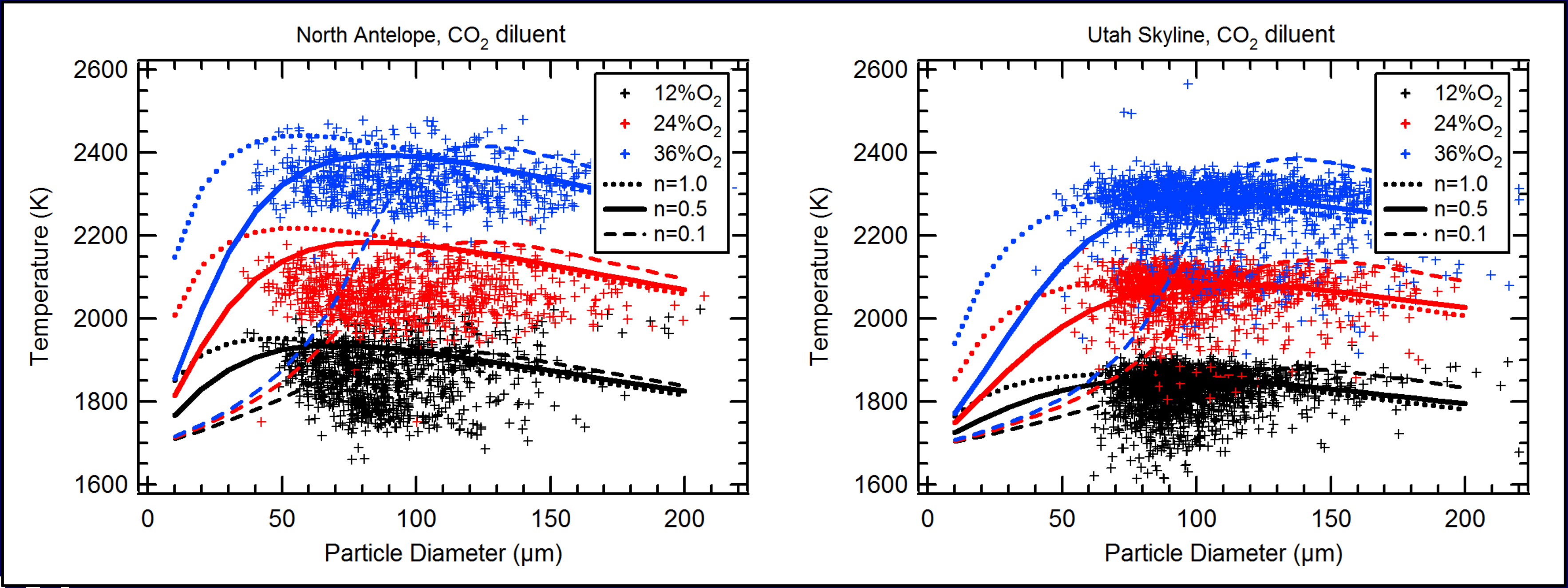
Simple Single-Film models produce good fits for N_2 environments

- Clear increase of temperatures with increasing O_2 concentration, higher temperatures for subbit. char
- Reaction orders between 0.5 and 1 give best agreement over wide size range, but best-fit activation energies unrealistically low
- Information for estimating reaction order requires data from wide size and O_2 concentration ranges



Single-Film models over-predicted particle temperatures for CO_2 environments

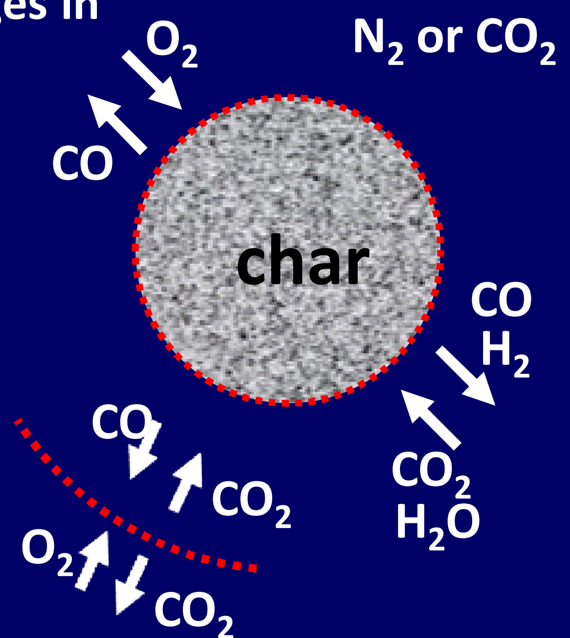
- Lower temperatures measured in CO_2 environment
- Good fit for US, but temperatures over-predicted for NA char
- Wider spread in measured temperature-size data than in N_2 diluent
- Model deficiencies shown more clearly for NA (wider overall measured range of temperatures, higher temperatures)



SKIPPY resolves species and temperature fields of reacting porous char particle

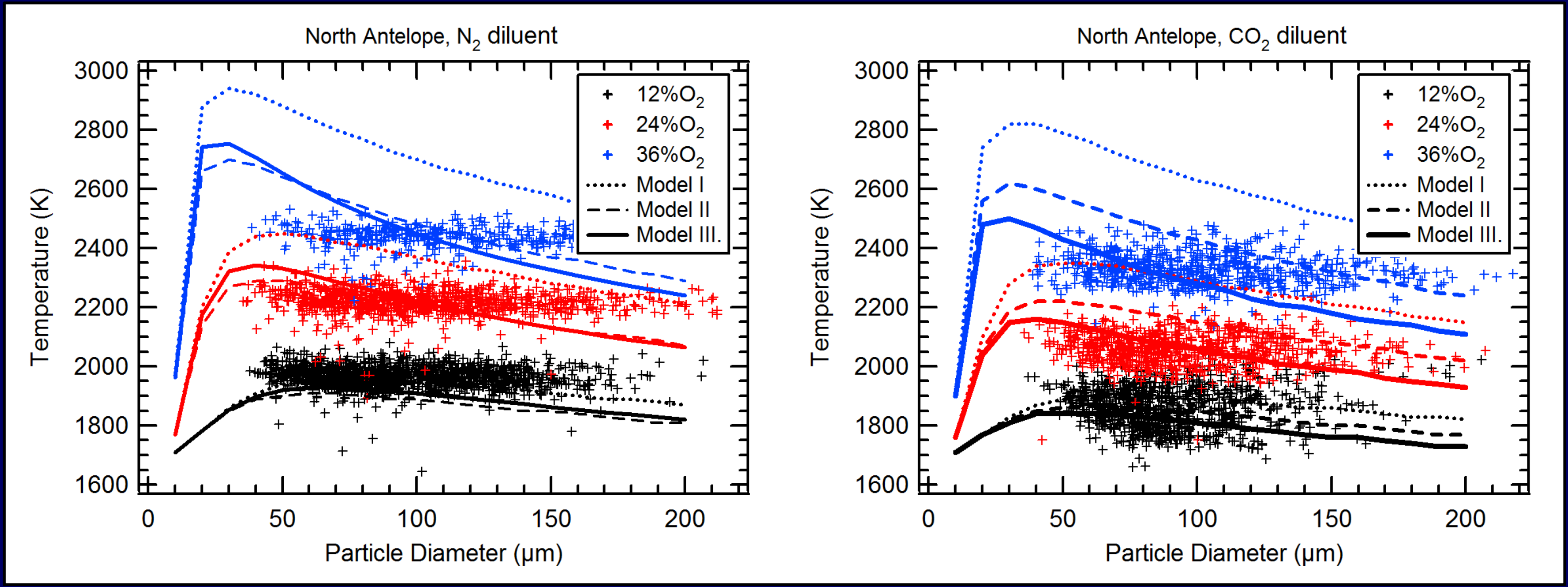
- SKIPPY (Surface Kinetics in Porous Particles)
  - Utilizes GRI-MECH 3.0 gas-phase kinetics (w/o nitrogen reactions) and CHEMKIN II surface kinetics, 1D steady-state model of spherical porous char particle
  - Heterogeneous mechanism, char properties and combustion environment specified by user
  - Useful tool in evaluation relative effects of changes in mechanism or kinetics rate parameters

Reaction	*A* (g/cm[2] s)	*E* (kJ/mol)
Heterogeneous oxidation:		
(R1) C_s + O_2 => CO + O_s	3.3E+15	167.4
(R2) O_s + 2C(b) => CO + C_s	1.0E+08	0.
(R3) C_s + O_2 => O_2_s+ C(b)	9.5E+13	142.3
(R4) O_2_s + 2C(b) => C_s + CO_2	1.0E+08	0.
CO_2 gasification reaction:		
(R5) C_s + CO_2 => CO + O_s + C(b)	3.60E+15	251.0
Steam gasification reaction:		
(R6) C_s + H_2O => H_2 + O_s + C(b)	4.35E+14	222.8



Including gasification reactions improves quality of SKIPPY predictions

- Fixed surface area 10m^2/g for all sizes, O_2 concentrations
- Model I: Oxidation only (R1 – R4)
- Model II: I + steam gasification (R6, w/ Ea = 251kJ/mol)
- Model III: I + steam and CO_2 gasification (R5, R6 w/ Ea = 223kJ/mol)



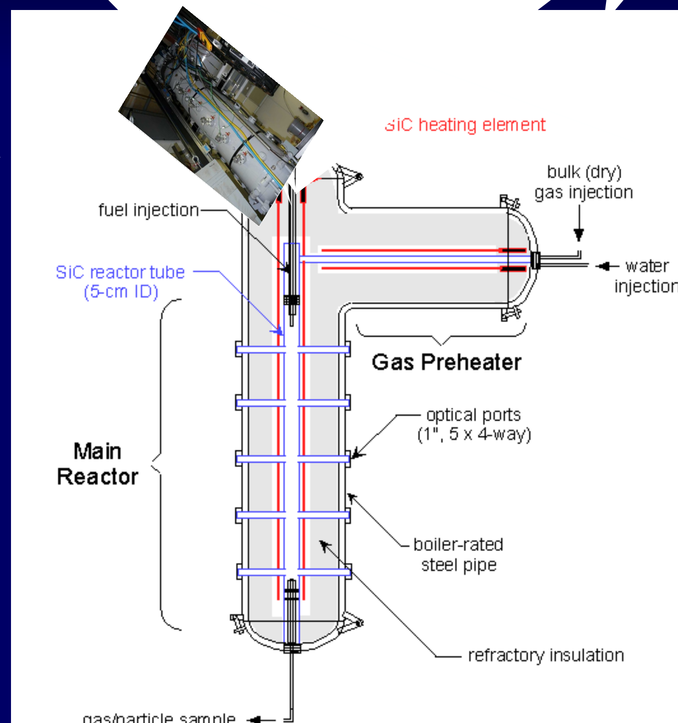
New Areas of Research at Sandia

- Char gasification rates and kinetics
  - Experiments using (small) atmospheric and (intermediate size) pressurized entrained flow reactors
- Group effects on ignition behavior
  - experiments using small entrained flow reactor
- Combustion and gasification of lignin extract from lignocellulosic ethanol production
  - Experiments using (small) atmospheric and (intermediate size) pressurized entrained flow reactors

Coal and Biomass Gasification

- Currently, gasifier designs largely based on empiricism and 'cut and try' approaches
- Refractory wear and carbon burnout are recurring problems in entrained flow gasifiers – are linked by gasifier operating T
- Need to be able to predict chemical reaction rates under relevant conditions so that CFD models can be effectively employed to improve gasifier design and operation
- Entrained flow gasifiers operate under pressure
  - slow gasification reactions require pressure to achieve conversion in reasonably-sized vessels
  - subsequent gas cleanup costs are reduced at pressure
  - allows coupling to gas turbine without additional compression step
- Existing kinetic data limited to TGAs with low heating rates and a few PDTF studies

Sandia's Pressur d En ained ow



Sandia Gasification Experim en

- ill establish volatilization of differe
  function of pressure and det
  acteristics
- Will implement optical pyrometer f
  of particle temperature (and possib
- Will measure rate of gasification of c
  environments, steam environ
  steam mixtures
- Will determine effect of gasification
  and H_2 through coupling of experime
  particle modeling

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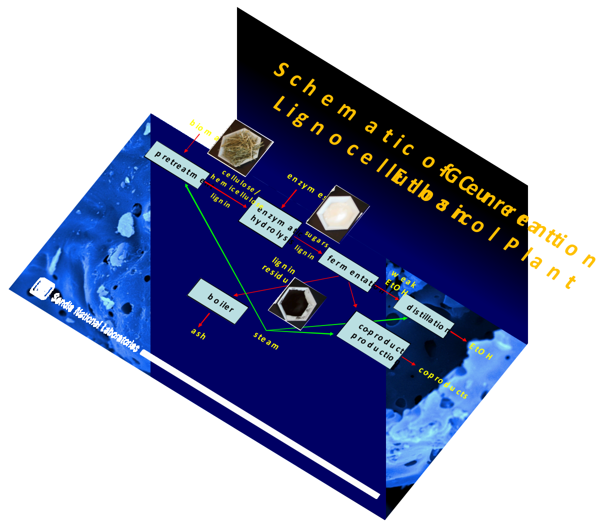
Schematic of Generic
Lignocellulosic Ethanol Plant
pretreatm
cellulose/
hemicellulose
lignin
enzyme
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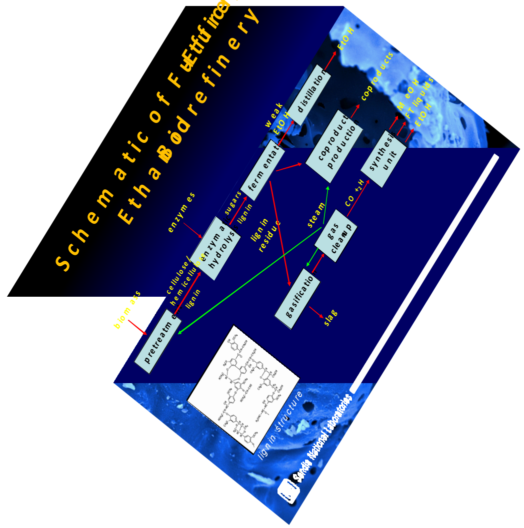
Schematic of Future High Efficiency Ethanol Biorefinery



Conclusions and Perspectives

he worldwide energy demand and far exc... fuels even when including biomass) su... derived fuels will need to be used fo...

...mbustion of coal and gasification of c... questration) are promising technolog... quantities of electricity and H_2 while CO_2 ... ions

- Co-combustion and co-gasification of coal and bioma... additional benefits while also addressing fuel... quality difficulties associated with biomass...
- Sandia, together with many research institu... is conducting both experimental research a... research on several of these key technolog... conversion of coal and bio-mass in a carbon-...
- Oxy-combustion would appear to involve a fa... of N_2 diluent with CO_2, but the substantially differen... CO_2 gas can have significant effects on combu...

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Acknowledgments

- …rof. M… Franz Holzleithn…
- …earch Funding
  - DOE Fossil Energy Power Systems Advanced R…
  - …anaged by … National Energy Technolo…
  - Laboratory
  - – Sandia Laboratory Directed Research and Devel…
- Research Collaborators
  - – Dr. Alejandro Molina, Universidad Nacional de Colombia, Colom…
  - – Dr. Jeffrey Murphy, The Aerospace Corporation
  - – Prof. Brian Haynes, University of Sydney, Austra…
  - – Mr. Ethan Hecht, Sandia National Labs
  - – Dr. Sang Min Lee, KIMM, South Korea
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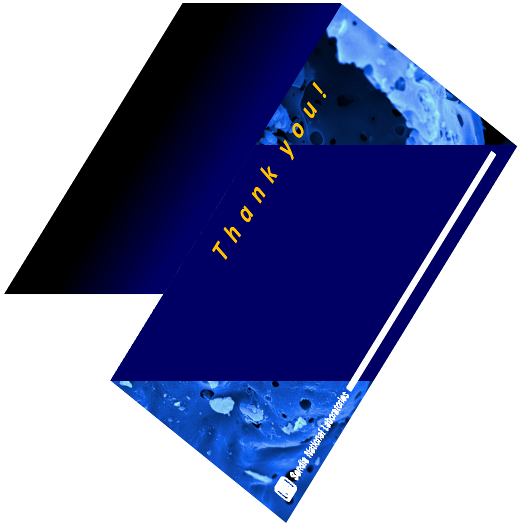
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