**DEVELOPMENT OF A VALIDATED MODEL FOR USE IN MINIMIZING NO_x
EMISSIONS AND MAXIMIZING CARBON UTILIZATION WHEN CO-FIRING
BIOMASS WITH COAL**

Quarterly Report

Reporting Period Start Date: 10/1/2001

Reporting Period End Date: 12/31/2001

Larry G. Felix, SoRI

P. Vann Bush, SoRI

January 31, 2002

DOE Cooperative Agreement No. DE-FC26-00NT40895

Southern Research Institute
2000 Ninth Avenue South
P. O. Box 55305
Birmingham, AL 35255-5305

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ABSTRACT

This is the fifth Quarterly Technical Report for DOE Cooperative Agreement No. DE-FC26-00NT40895. A statement of the project objectives is included in the Introduction of this report. One additional biomass co-firing test burn was conducted during this quarter. In this test (Test 9), up to 20% by weight dry hardwood sawdust and switchgrass was injected through the center of the single-register burner with Jacobs Ranch coal. Jacobs Ranch coal is a low-sulfur Powder River Basin coal (~ 0.5% S). The results from Test 9 as well as for Test 8 (conducted late last quarter) are presented in this quarterly report. Significant progress has been made in implementing a modeling approach to combine reaction times and temperature distributions from computational fluid dynamic models of the pilot-scale combustion furnace with char burnout and chemical reaction kinetics to predict NO_x emissions and unburned carbon levels in the furnace exhaust. Additional results of CFD modeling efforts have been received and preparations are under way for continued pilot-scale combustion experiments with the dual-register burner. Finally, a project review was held at NETL in Pittsburgh, on November 13, 2001.

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INTRODUCTION

The work to be conducted in this project received funding from the Department of Energy under Cooperative Agreement No. DE-FC26-00NT40895. This project has a period of performance that commenced September 20, 2000 and continues through September 19, 2002. A project Work Plan was submitted to DOE on October 18, 2000 as the first deliverable under the cooperative agreement. The Work Plan is not included in this report, but the objectives of the project are restated from the Work Plan in the following paragraphs.

Objectives

The project is designed to balance the development of a systematic and expansive database detailing the effects of co-firing parameters on nitrogen oxides (NO_x) formation with the complementary modeling effort that will yield a capability to predict, and therefore optimize, NO_x reductions by the selection of those parameters.

The database of biomass co-firing results will be developed through an extensive set of pilot-scale tests at the Southern Company/Southern Research Institute Combustion Research Facility. The testing in this program will monitor NO_x , Loss-on-Ignition (LOI), and other emissions over a broad domain of biomass composition, coal quality, and co-firing injection configurations to quantify the dependence of NO_x formation and LOI on these parameters. This database of co-firing cases will characterize an extensive suite of emissions and combustion properties for each of the combinations of fuel and injection configuration tested.

The complementary process modeling will expand the value of the raw test data by identifying the determining factors on NO_x emissions and LOI. Niksa Energy Associates (NEA) will develop and validate a detailed process model for predicting NO_x emissions and LOI from biomass co-firing that builds on a foundation of existing and proven fluid dynamics, reaction kinetics, and combustion products models. The fluid dynamics data will be produced from computer models developed by Reaction Engineering International (REI). The modeling process will resolve all major independent influences, including biomass composition, coal quality, chemical interactions among biomass-and coal-derived intermediate species, competitive O_2 consumption by biomass- and coal-derived intermediate species and chars, extent of biomass/coal mixing prior to combustion, and mixing intensity during biomass injection.

The overall goal of the project is to produce a validated tool or methodology to accurately and confidently design and optimize biomass co-firing systems for full-scale utility boilers to produce the lowest NO_x emissions and the least unburned carbon. Specific program objectives are:

- Develop an extensive data set under controlled test conditions that quantifies the relationships between NO_x emissions and biomass co-firing parameters.
- Provide a data set of the effects of biomass co-firing over a broad range of fuels and co-firing conditions on flame stability, carbon burnout, slagging and fouling, and particulate and gaseous emissions.
- Develop and validate a broadly applicable computer model that can be used to optimize NO_x reductions and minimize unburned carbon from biomass co-firing.

Once validated, the model provides a relatively inexpensive means to either (1) identify the most effective co-firing injection configuration for specified compositions of biomass and coal within a particular furnace environment, or (2) to forecast the emissions for a specified pair of fuels fired under an existing configuration. As such an important cost-saving tool, the modeling has the potential to accelerate widespread adoption of biomass co-firing as a NO_x control strategy in the electric utility industry.

RESULTS

Model Development

The three independent aspects of modeling for this project are (1) the mechanisms for fuel devolatilization and char burnout, and (2) the detailed chemical mechanism for combustion and fuel-N conversion in the gas phase, and (3) the equivalent reactor network. Niksa Energy Associates (NEA) has addressed all three aspects in a comprehensive annual report covering work from September, 2000 through August, 2001. This report was received shortly after the last Quarterly Progress Report was submitted and therefore, was not included in that report. In this annual report, NEA detailed the results of their work on each aspect of the modeling effort. This annual report is included here in Appendix A. The executive summary of this annual report is reproduced below to present a brief summary of NEA's activities. Subsequently, NEA has begun tests of the model with coal flames. Their first results are also presented below,

after the executive summary. Throughout the next quarter, NEA will focus on performing additional testing of the model, with and without biomass cofiring, for various biomass injection schemes.

Executive Summary of the NEA Annual Report This annual report was prepared under the research project from Southern Research Institute (SRI) to Niksa Energy Associates (NEA) entitled “Development of a Validated Model for Use in Minimizing NO_x Emissions and Maximizing Carbon Utilization When Cofiring Biomass with Coal.” Research objectives were defined in the proposal of the same name submitted to the U. S. DoE under Solicitation No. DE-PS26-00NT40775. NEA’s role is to develop a post-processing methodology for CFD simulations of the SRI pilot-scale pulverized fuel (p. f.) flame that accurately predicts NO_x and UBC emissions. The post-processor incorporates the most advanced models for coal combustion chemistry as well as elementary reaction mechanisms for gas phase chemistry, and is therefore expected to perform better than conventional approaches based on drastically simplified process chemistry. Simulations of all runs in SRI’s testing program will ultimately be used to identify the optimal co-firing configuration for various forms of biomass on various coal types, and to interpret the behavior in terms of the detailed reaction mechanisms. During the period from November, 2000 through August, 2001, the program objectives were advanced by the formulation of reaction mechanisms for all stages of combustion, including devolatilization, volatiles combustion, soot oxidation, and char burnout.

A multitude of fuel species – CO, H₂, CH₄, C₂H₂, HCN, soot, and char – compete for the available O₂ in a p. f. flame. This competition determines local heat release rates, which govern flame stability, combustion efficiency and LOI, and the local oxidizing potential of the gas phase, which governs N-species conversion. The central premise behind our modeling approach is that the crucial outcome this competition cannot be forecast from the burning rates of the individual fuels determined in isolation. Instead, realistic chemical kinetics for each distinctive combustion process must be incorporated into a comprehensive analysis. Our analysis incorporates the most comprehensive chemical reaction submodels available, and imposes no *a priori* assumptions whatsoever regarding the apportioning of O₂.

The devolatilization submodel, called FLASHCHAIN[®], distinguishes primary devolatilization, which relates fuel properties to the composition of volatiles, from secondary volatiles pyrolysis, which generates the volatiles that

actually burn in p. f. flames. FLASHCHAIN[®] determines the complete distribution of primary products from almost any p. f., and also predicts the yield and elemental composition of char. When combined with a swelling factor correlation and a correlation for the initial carbon density in char, it specifies all the necessary char properties for a char oxidation simulation. Hence, the complete distribution of volatiles, including gaseous fuels and soot, and all char properties are completely determined from the fuel's proximate and ultimate analyses.

The reaction mechanism for chemistry in the gas phase must describe the ignition and combustion of all secondary volatiles pyrolysis products, as well as the conversion of all N-species across the full range of stoichiometric ratio (S. R.) values in p. f. flames. Our homogeneous reaction mechanism contains 444 elementary reactions among 66 species, including all relevant radicals and N-species. It is implemented in the simulations without any approximations whatsoever. All rate parameters were assigned independently, so there are also no adjustable parameters in the submodel for gas phase chemistry.

Soot plays several important roles. As it burns, it directly competes for the available O₂ and also consumes O-atoms and OH that would otherwise sustain homogeneous chemistry. Soot also promotes recombinations of H-atoms and OH that could also sustain homogeneous chemistry. And soot reduces NO directly into N₂. Our soot chemistry submodel depicts all these effects in the form of a collection of elementary reactions that can be coupled to the homogeneous reaction mechanism within the CHEMKIN/SURFACE CHEMKIN framework.

Char burning rates are determined by thermal annealing, ash encapsulation (of low-rank chars), and a transition to chemical kinetic control. The Char Burnout Kinetics (CBK) Model includes all these effects, and depicts the impact of variation in gas temperature, O₂ level, and char particle size within useful quantitative tolerances. However, it is not yet possible to specify the initial char reactivity within useful tolerances from the standard coal properties. We must calibrate this value with LOI predictions or some other suitable index on combustion efficiency. The submodel for char-N conversion is subject to a similar calibration requirement (with NO emissions), compounded by its simplistic mechanistic premise; viz., that a fixed fraction of char-N is converted into NO at the overall burning rate throughout all stages of char oxidation.

To summarize the status of our reaction mechanisms, the initial char reactivity and the fraction of char-N converted to NO can only be specified from calibration procedures. Otherwise, all other model parameters can be assigned from the fuel's proximate and ultimate analyses within useful quantitative tolerances, or directly adopted from the literature. We believe that the submodels for devolatilization, homogeneous chemistry, and char burnout are complete, whereas those for soot/radical chemistry and for char-N conversion will probably be subject to revisions in the near term.

Simulations of a 1 MW tunnel furnace fired with various p. f. demonstrated several tangible benefits of all the mechanistic complexity. Based on a CFD simulation of a hvA bituminous coal flame, the flame structure in this furnace was resolved into four regions: a flame core, mixing layer, SOFA zone, and burnout zone. Parametric variations of the mixing intensity of the secondary air stream produced higher NO emissions for higher mixing rates, as expected. An evaluation of staged versus un-staged firing configurations was also qualitatively satisfied, but remains to be quantitatively validated. Predicted NO emissions increased in direct proportion to increases in the fraction of char-N converted into NO. Somewhat surprisingly, NO emissions were significantly lower for higher values of the initial char reactivity because there was more NO generated in the core and subsequently reduced before the mixing layer, and also less residual char-N to generate NO during succeeding stages of burnout.

Subbituminous flames had three times higher extents of char burnout in the core than bituminous flames. This factor, in conjunction with a lower coal-N level and a much higher coal-H level, explained the reduction in NO emission by a factor of two. Subbituminous flames also generated much higher CO concentrations in the flame core, and the ultimate extent of char burnout was higher by almost 2 %. Simulations with coal blends highlighted a new aspect of the competition for the available O₂. The most reactive char wins the competition at the expense of the least reactive char, so that unburned carbon becomes enriched in the least reactive char component. Simulations of biomass co-firing introduced yet another tradeoff in the char burnout profiles, because switchgrass has a much higher char reactivity but is usually fed at much larger sizes. The smaller switchgrass size cuts burned faster in the core. But once they were annealed, the largest size fractions of these chars burned slower than the smaller

bituminous chars. Consequently, unburned carbon became enriched in the largest size fractions of the switchgrass chars.

Recent Work

During December, NEA concentrated on finishing the simulations for coal-only baseline tests. All tests with the Pratt seam hvA bituminous coal were completed, including Test Series 1 with the co-milled injection configuration and Test Series 4 with the axial injection configuration. NEA needs to base the simulations on independent CFD simulations for each furnace exit O_2 (FEO) level, overfire air (OFA) level, and injector configuration. However, NEA had only received the baseline CFD simulation for 15 % OFA with 4 % excess O_2 and the co-milled injector configuration. To compensate, NEA developed the following calibration procedure:

Preliminary simulations indicated that a single mixing parameter was the most important influence on the exhaust NO_x emissions: the fraction of secondary air, which penetrated into the flame core at the inlet. NEA's analysis of the baseline CFD simulation assigned a value of 16 % to this parameter, but it had to be increased to 20 % to match the observed NO_x emission for this case. In fact, the parameter was assigned as 18% for 2.5% FEO, 20% for 4% FEO and 22% for 5% FEO. This same calibration curve was applied to the test cases with 0% OFA to obtain the results for Test Series 1 shown in Figures 1 and 2.

In their simulations, the reported flow rates of primary, secondary, and tertiary air for each individual run were imposed, while the coal feed rate was fixed. The nominal temperature profile along the furnace was reduced by 5% for runs with 2.5% FEO, and increased by 5 % for runs with 5% FEO. As seen in the plot evaluating the predicted NO_x emission for Test Series 1, the predictions are within experimental uncertainty across the complete range of FEO, except for the lowest values with 15% OFA and except, perhaps, for the highest values with 0% OFA.

To simulate tests with center-axial injection, 30 SCFM was added to the primary air, based on an assessment of the axial injection air obtained from Southern Research. The same calibration procedure was applied, except that the fraction of secondary air mixed into the core at the inlet had to be increased to 21, 23, and 25% for respective FEO levels of 2.5, 4, and 5%. Temperature

Figure 1. Predicted exhaust NO_x emissions for coal only, Test Series 1.

Figure 2. Predicted exhaust NO_x emissions for coal-only, with the single-register burner configured for center-axial biomass injection (Test 4).

profiles were adjusted for different O₂ levels, as before. As seen in Figure 2, for Test Series 4, the predictions are within experimental uncertainty for the entire range of FEO with 15 % OFA, and for all FEO levels except the highest values with 0% OFA.

Based on these encouraging results, NEA will move to the co-firing cases, as additional CFD simulations are delivered from REI.

Submitted Paper NEA has submitted a paper for presentation at the Twenty-Ninth International Symposium on Combustion in July, 2002 at Hokkaido University in Sapporo, Japan. The paper reports, in part, on the modeling effort NEA is engaged in on this project. The paper is entitled “Advanced CFD Post-Processing for Coal Flame Structure and Emissions,” and the paper acknowledges that support was provided through a subcontract from Southern Research Institute, under our current project with the U. S. Department of Energy (DE-FC26-00NT40895). The complete paper is included in Appendix B of this report. The abstract for this paper follows:

“The simulation strategy described in this paper provides an alternative to conventional CFD post-processing to estimate exhaust NO_x emissions. The method first analyzes a CFD furnace simulation to specify temperature histories and mixing rates. Then the bulk flow patterns are represented with an equivalent network of idealized reactor elements. Detailed reaction mechanisms are then applied over the reactor network, including the most fully validated reaction mechanisms for coal devolatilization and char oxidation and complete elementary reaction mechanisms for chemistry in the gas phase and in soot. The analysis predicted the NO_x emissions from a 1.7 MWt pilot-scale coal flame within experimental uncertainty, over a broad range of O₂ concentrations, with and without staging. The predicted unburned carbon emissions were qualitatively correct for all test conditions, but char reactivity parameters would need to be specified in a one-point calibration for quantitative predictions. The analysis also characterized distinctive chemistry within the flame core, a mixing layer for secondary air entrainment, an overfire air zone, and a char burnout zone. The main practical benefit of the mechanistic complexity is that simulations based on detailed mechanisms require far fewer parameter adjustments than conventional CFD simulations whenever different fuels are considered.”

CFD Simulations

Reaction Engineering International, Inc. (REI) has completed further simulations of the single-register burner used in the pilot-scale combustor. In particular, REI is nearly through with a simulation of side injection discussed in the last Quarterly Report (Test 4). Also, just after the first of the year, REI reported on the recalculation of a previous simulation of 20% hardwood sawdust comilled with 80% Pratt seam coal but with correct size distributions for the pulverized coal and biomass constituents. That report is presented in Appendix C. REI continues to work on their final deliverable, the standalone Configurable Fireside Simulator that will be used to generate temperature and flow fields and CO and O₂ mole fractions for model simulations to be carried out by NEA.

At the project review meeting on November 13 of last year, a question was asked about the particle size distribution of coal in comilled mixtures of sawdust and switchgrass. To provide an answer to the questions raised about coal fineness when biomass and coal are comilled, particle size distributions of archived samples of comilled coal and biomass were determined by a procedure described in the Project Review section, below. One of these size distributions (for 20% sawdust and Pratt seam coal) were then used by REI to recalculate furnace temperatures and CO, and O₂ mole fractions for a case that had been computed previously where the coal portion of particle size distribution was assumed to be 70% < 200 mesh. Then the results of the recalculation were compared with the original calculation. Only insignificant differences were found.

Pilot-Scale Combustor Testing

Project Review A project review was held on November 13, 2001 at the offices of the DOE National Energy Technology Laboratory, located in Pittsburgh, PA. The PowerPoint© slide presentation prepared for that meeting is reproduced in Appendix D of this report. At that meeting, all of the data processed to date were reviewed and the modeling effort was described in detail. An inspection of the data presented at this review, as well as the data presented below, indicates that the biomass cofiring tests conducted on this project have yielded sets of NO_x emissions data that reveal complex relationships among the coals, biomasses, and mixing intensities that have been tested. These relationships are clearly not straightforward; they serve to reinforce the importance of a comprehensive model that provides insights into understanding the experimental data as well as the ability to predict NO_x emissions resulting from an arbitrary choice of fuel, biomass, and injection geometry for biomass cofiring.

As indicated above, at that meeting, a question was asked about the particle size distribution of coal in comilled mixtures of sawdust and switchgrass. In comilling, a mixture of coal and biomass is typically ground to an overall fineness of 70% <200 mesh (74 μ m). Sieving such mixtures reveals that sieve fractions above 125 mesh are mostly biomass and sieve fractions below 125 mesh are predominantly coal. Thus, comilling results in a coal fraction that is more finely ground than when it is milled by itself. Because the combustion of very finely ground coal (~85% - 90% <200 mesh) may produce NO_x emissions that are different from those observed with more usual coal grinds (~ 70% < 200 mesh), coal fineness may be a parameter that could affect NO_x emissions when coal is comilled with biomass. Also, some of the benefits of comilling that have been attributed to the addition of biomass could be due to more finely ground coal.

To provide an answer to the questions raised about coal fineness when biomass and coal are comilled, particle size distributions of archived samples comilled coal and biomass were determined. At the Combustion Research Facility, all archived fuel and ash samples are preserved in tightly sealed metal cans. First, the various samples of comilled coal and biomass were located and sieved and the heat content of each sieve fraction was measured. Then, by comparing heat values of each sieve fraction (accounting for moisture) with separate heat values of dry coal and dry biomass, the actual portion of coal and biomass in each sieve fraction was determined. A number of sets of archived samples of comilled coal and biomass were tested. Table 1 summarizes the results of those measurements.

Table 1. Coal and Biomass Fractions of Comilled Samples

Coal		Biomass		% < 200 mesh (74 μ m)		
Name	(%)	Type	(%)	Sample	Coal	Biomass
Pratt Seam	80	Sawdust	20	69.4	89.8	11.7
Galatia	90	Switchgrass	10	69.3	84.7	0.0
Galatia	80	Switchgrass	20	70.5	91.4	9.7
Galatia	90	Sawdust	10	69.7	78.6	0.0
Galatia	80	Sawdust	20	68.4	83.4	0.0

It is clear from the results presented in Table 1 when coal is comilled with biomass, the result is distinctly different size distributions for each component: a finely divided distribution of coal and a somewhat coarse distribution of biomass.

Rosin-Rammler (Weibull) size distributions were fit to the coal and biomass fractions from each set of comilled samples. These distributions were then used by REI to recalculate furnace temperatures and CO, and O₂ mole fractions for a case that had been computed previously where the coal portion of particle size distribution was assumed to be 70% < 200 mesh. As discussed above, no significant differences were found in the two calculations. While this is a comforting result, in an upcoming combustor test it is planned to burn one coal ground normally (70% < 200 mesh) and to compare gaseous and particulate emissions for this coal with the same coal ground to approximately 90% < 200 mesh. Thus, in the absence of biomass, we will be able to measure only the effect of coal fineness on emissions.

Furnace Testing Nine furnace tests have been completed through the end of 2001. Tests 1 through 7 have been reviewed in previous quarterly progress reports. Test 8 (conducted late in the third quarter) and Test 9 (conducted in October) are reviewed below. Table 2 summarizes the tests that have been completed through the end of 2001.

As indicated above, in this Quarterly Progress Report we present and comment on the results obtained in Tests 8 and 9. In Test 8, up to 20% by weight dry hardwood sawdust and dry switchgrass and was comilled with Jacobs Ranch coal (a Powder River Basin low-sulfur coal, S ~ 0.5%). In Test 9, up to 15% by weight dry hardwood sawdust and up to 20% by weight switchgrass was injected through the center of the single-register burner with Jacobs Ranch coal.

As previously mentioned, all biomass (sawdust and switchgrass) was processed by MESA Reduction Engineering and Processing, Inc. in a collision mill of their design. When fitted to a Rosin-Rammler (Weibull) distribution, the D₅₀ of pulverized coal (nominally 70% less than 200 mesh) is 50 micrometers and the D₅₀ of MESA-processed sawdust is approximately 300 micrometers. Because of the fibrous nature of switchgrass, the D₅₀ of MESA-processed switchgrass can range as high as 600 micrometers. However, recently MESA has been able to tune their mill to produce switchgrass processed to the same fineness as the dry hardwood sawdust. Unfortunately, during Test 9, we determined that the most recent shipment of MESA-processed sawdust was not as finely milled as was typical for previous deliveries. As a result, during this test, 15% by weight sawdust was the maximum amount that could be injected. No problems were encountered with the MESA-processed switchgrass used in this test.

Table 2. Tests Completed Through 2001

- Test 1:** Pratt Seam Coal – Comilled Biomass, single register burner (Location 1), 15%, 20% Switchgrass, 10%, 20% Sawdust. 0%, 15%, 30% overfire air. 1/28-2/3/01
- Test 2:** Pratt Seam Coal – Biomass through center of burner (Location 2), single register burner, 10% Sawdust. 0%, 15% overfire air. Problems with biomass injection scheme and flame stability. 2/25-3/2/01
- Test 3:** Pratt Seam Coal – Biomass through center of burner (Location 2), single register burner, 10%, 20% Switchgrass, 10%, 20% Sawdust. 0%, 15% overfire air. Continued problems with flame stability. 4/8-14/01
- Test 4:** Pratt Seam Coal – no biomass, single register burner (Location 1), extensive characterization of coal-only firing at 0% and 15% overfire air. Corrected flame stability problem. 5/14-17/01
- Test 5:** Pratt Seam Coal – Biomass injection toward quarl (Location 3), single register burner, 10%, 20% Switchgrass, 10%, 20% Sawdust. 0%, 15% overfire air. 6/10-15/01
- Test 6:** Galatia Coal – Comilled Biomass, single register burner (Location 1), 10%, 20% Sawdust. 0%, 15%, overfire air. 7/8-7/13/01 (switchgrass not delivered in time for test)
- Test 7:** Galatia Coal – Comilled Biomass, single register burner (Location 1), 10%, 20% Switchgrass. 0%, 15%, overfire air. Pratt Seam Coal comilled with 20% sawdust. 8/5-10/01
- Test 8:** Jacobs Ranch Coal – Comilled Biomass, single register burner (Location 1), 10%, 20% Switchgrass, 10%, 20% Sawdust. 0%, 15% overfire air. 9/16-21/01
- Test 9:** Jacobs Ranch Coal – Biomass through center of burner (Location 2), single register burner, 10%, 20% Switchgrass, 10%, 20% Sawdust. 0%, 15% overfire air. 10/21-26/01

Figure 3. Locations for biomass injection in the SoRI/SCS furnace equipped with the single-register burner.

Test 8 For this test, from September 16 to 21, 2001, biomass was comilled with Jacobs Ranch Powder River Basin coal and injected into the furnace at injection location 1 as shown in Figure 3. The coal used in this test was Jacobs Ranch Powder River Basin (PRB) coal, reserved from a railway shipment delivered to a local Alabama Power steam plant. A typical proximate and ultimate analysis for this coal, and for the sawdust and switchgrass used in Tests 8 and 9 is presented in Table 3. Tables 4 and 5 present the results of proximate and ultimate analyses of pulverized (comilled) mixtures of coal and sawdust (Table 4) and coal and switchgrass (Table 5).

Testing was uneventful, and all comilled mixtures combusted well, with no appreciable slagging or fouling. Because this coal has a low ash content (~5.8%, comparable to Galatia, the Illinois Basin coal burned in Tests 6 and 7), the amount of fly ash and furnace bottom ash that was generated from the combustion of this coal (and with combustion of the mixtures of coal and biomass) was low. Three levels of furnace exit oxygen were tested (2.5%, 3.5%, and 4.5%) along with overfire air levels of 0% and 15%. Two levels of biomass addition were tested: 15% and 20% weight content for both sawdust and switchgrass.

Figures 4 and 5 present average NO_x emissions measured for 10% and 20% by weight sawdust (Figure 4) and switchgrass (Figure 5) comilled with Jacobs Ranch PRB coal. Figure 6 summarizes the NO_x reductions realized by the addition of biomass, with and without 15% overfire air, and Table 6 summarizes the data presented in Figure 6. Figures 4 through 6 and Table 6 show that with this coal, the addition of comilled biomass always decreases NO_x emissions. Some consistent trends appear. For example, for sawdust, NO_x emissions usually decrease with the addition of more biomass, with or without overfire air. On the other hand, for switchgrass, without overfire air, NO_x emissions usually decrease when the amount of comilled biomass is increased. However, when overfire air is added, NO_x emissions increase when the amount of comilled biomass is increased.

Finally, Figures 7 and 8 present the results of unburned carbon (UBC) measurements carried out on fly ash obtained by isokinetically sampling the furnace effluent at various values of furnace exit oxygen. Because Jacobs Ranch is a typical PRB coal, fly ash emissions were low (never exceeding 1.8 lb/10⁶Btu, for any test condition) and the levels of UBC in the fly ash never exceeded 0.7% and were usually lower than 0.3%. By comparison, for Pratt

Table 3. Typical Proximate and Ultimate analyses of Raw Fuel Samples from Tests 8 and 9.

Sample I.D. Fuel	J947-57-CC-1 Jacobs Ranch Coal		J-947-64-SDC-1 Sawdust		J947-57-SGC-1 Switchgrass	
Proximate Analysis	As Rec.	Dry Basis	As Rec.	Dry Basis	As Rec.	Dry Basis
Moisture, %	25.61	---	6.30	---	7.45	---
Ash, %	4.92	6.61	0.52	0.55	6.93	7.49
Volatile, %	48.68	65.44	68.21	72.80	63.12	68.20
Fixed Carbon, %	20.79	27.95	24.97	26.65	22.50	24.31
Sum	100.00	100.00	100.00	100.00	100.00	100.00
Heat Content, Btu/lb	8584	11539	7692	8209	7264	7849
Sulfur, %	0.25	0.34	0.02	0.02	0.08	0.09
MAF Btu/lb	---	12536	---	8254	---	8484
Ultimate Analysis	As Rec.	Dry Basis	As Rec.	Dry Basis	As Rec.	Dry Basis
Moisture, %	25.61	---	6.30	---	7.45	---
Carbon, %	52.15	70.10	46.47	49.59	42.69	46.13
Hydrogen, %	2.94	3.95	5.70	6.08	5.39	5.82
Nitrogen, %	0.94	1.27	0.12	0.13	1.19	1.29
Sulfur, %	0.25	0.34	0.02	0.02	0.08	0.09
Ash, %	4.92	6.61	0.52	0.55	6.93	7.49
Oxygen (diff.), %	13.19	17.73	40.57	46.43	36.27	39.18
Sum	100.00	100.00	100.00	100.00	100.00	100.00
Chlorine, %	0.01	0.01	0.02	0.02	0.24	0.26
Hardgrove Grindability	50		---		---	
Ash Fusion	Reducing	Oxidizing	Reducing	Oxidizing	Oxidizing	Oxidizing
Initial Deformation, °F	2090	2130	---	---	---	---
Softening, °F	2130	2185	---	---	---	---
Hemispherical, °F	2165	2225	---	---	---	---
Fluid, °F	2200	2265	---	---	---	---

Table 4. Proximate and Ultimate analyses of comilled mixtures of Jacobs Ranch coal and dry hardwood sawdust from Test 8.

Sample I.D. Fuel	J947-39-CFDC-1 10% Sawdust		J947-35-CFDC-1 20% Sawdust	
Proximate Analysis	As Rec.	Dry Basis	As Rec.	Dry Basis
Moisture, %	18.00	---	15.92	---
Ash, %	4.75	5.79	4.59	5.46
Volatile, %	49.82	60.76	48.47	57.65
Fixed Carbon, %	27.43	33.45	31.02	36.89
Sum	100.00	100.00	100.00	100.00
Heat Content, Btu/lb	9405	11469	9488	11284
Sulfur, %	0.25	0.30	0.24	0.29
MAF Btu/lb	---	12174	---	11936
Ultimate Analysis	As Rec.	Dry Basis	As Rec.	Dry Basis
Moisture, %	18.00	---	15.92	---
Carbon, %	55.51	67.70	56.12	66.75
Hydrogen, %	3.91	4.77	4.08	4.85
Nitrogen, %	0.66	0.81	0.63	0.75
Sulfur, %	0.25	0.30	0.24	0.29
Ash, %	4.75	5.79	4.59	5.46
Oxygen (diff.), %	16.92	20.63	18.42	21.90
Sum	100.00	100.00	100.00	100.00
Chlorine, %	0.01	0.01	0.02	0.02

Table 5. Proximate and Ultimate analyses of comilled mixtures of Jacobs Ranch coal and switchgrass from Test 8.

Sample I.D. Fuel	J947-22-CFDC-1 10% Switchgrass		J947-27-CFDC-1 20% Switchgrass	
Proximate Analysis	As Rec.	Dry Basis	As Rec.	Dry Basis
Moisture, %	17.72	---	15.19	---
Ash, %	5.26	6.39	4.89	5.76
Volatile, %	41.54	50.49	44.60	52.59
Fixed Carbon, %	35.48	43.12	35.32	41.65
Sum	100.00	100.00	100.00	100.00
Heat Content, Btu/lb	9442	11476	9316	10984
Sulfur, %	0.27	0.33	0.26	0.31
MAF Btu/lb	---	12259	---	11655
Ultimate Analysis	As Rec.	Dry Basis	As Rec.	Dry Basis
Moisture, %	17.72	---	15.19	---
Carbon, %	55.82	67.84	55.65	65.62
Hydrogen, %	3.87	4.70	4.15	4.89
Nitrogen, %	0.71	0.86	0.75	0.88
Sulfur, %	0.27	0.33	0.26	0.31
Ash, %	5.26	6.39	4.89	5.76
Oxygen (diff.), %	16.35	19.88	19.11	22.54
Sum	100.00	100.00	100.00	100.00
Chlorine, %	0.02	0.03	0.06	0.07

Jacobs Ranch Coal - Comilled Sawdust NO_x Performance in the Pilot-Scale Combustor Dependence on Furnace Exit Oxygen

Figure 4. NO_x emissions measured for sawdust comilled with Jacobs Ranch coal. Single register burner with and without overfire air.

Jacobs Ranch Coal - Comilled Switchgrass NO_x Performance in the Pilot-Scale Combustor Dependence on Furnace Exit Oxygen

Figure 5. NO_x emissions measured for switchgrass comilled with Jacobs Ranch coal. Single register burner with and without overfire air.

Jacobs Ranch Coal Comilling Injection Configuration NO_x Reduction from Biomass Addition Dependence on Furnace Exit Oxygen

Figure 6. NO_x reductions measured for sawdust and switchgrass comilled with Jacobs Ranch coal. Single register burner with and without overfire air.

Table 6. NO_x Emissions for Various Levels of Overfire Air at 3.5% Furnace Exit O₂, (wet) for Sawdust and for Switchgrass Comilled with Jacobs Ranch PRB coal with the Single Register Burner.

Biomass	Weight%	Overfire Air, %	NO _x Emissions at 3% O ₂ , dry ppmv	Reduction of NO _x Emissions, %
2.5% Furnace Exit Oxygen				
None	0	0	317	0
		15	177	0
Sawdust	10	0	285	9.9
		15	136	23.1
	20	0	275	13.3
		15	140	23.8
Switchgrass	10	0	274	20.8
		15	129	13.6
	20	0	284	10.2
		15	131	25.9
3.5% Furnace Exit Oxygen				
None	0	0	365	0
		15	215	0
Sawdust	10	0	331	9.4
		15	183	14.9
	20	0	320	17.5
		15	177	14.1
Switchgrass	10	0	316	13.6
		15	171	20.5
	20	0	310	15.2
		15	176	18.1
4.5% Furnace Exit Oxygen				
None	0	0	421	0
		15	262	0
Sawdust	10	0	384	8.8
		15	246	5.8
	20	0	374	11.2
		15	225	14.1
Switchgrass	10	0	364	13.5
		15	227	13.4
	20	0	338	19.8
		15	237	9.4

Jacobs Ranch PRB Coal Comilling with Sawdust and Switchgrass Unburned Carbon Performance in the Pilot-Scale Combustor

Figure 7. Unburned carbon emissions for the comilling of sawdust and switchgrass with Jacobs Ranch PRB coal. Single register burner with no overfire air.

Jacobs Ranch PRB Coal Comilling with Sawdust and Switchgrass Unburned Carbon Performance in the Pilot-Scale Combustor

Figure 8. Unburned carbon emissions for the comilling of sawdust and switchgrass with Jacobs Ranch PRB coal. Single register burner with 15% overfire air.

seam coal which can have up to 14% ash, UBC levels in the fly ash did not exceed 1.8%, but mass emissions ranged from 5.0 to 7.0 lb/10⁶Btu.

Test 9 For the ninth test, from October 21-26, 2001, the single register burner was kept in the axial injection configuration used for Tests 2, and 3 (location 2 in Figure 3). That is, a modified burner pipe was reinstalled that enables finely divided hardwood sawdust and switchgrass (prepared by MESA Reduction Engineering) to be injected through the center of the 3.5 inch (outer diameter, 0.125 inch wall thickness) burner. This modification was originally effected by enlarging the existing blast pilot tube to 1.5 inches outside diameter from the original 1-inch pipe (~1.3 inch outside diameter) and inserting a 1 inch outside diameter tube through the center of the enlarged blast pilot. Biomass is injected through this center tube and natural gas for ignition is directed through the 0.125 inch annular space between the inner and outer tubes. Thus, the blast pilot assembly can function either as a natural gas igniter or as a location for biomass injection.

Testing was uneventful and all mixtures combusted well, without slagging or fouling beyond what has been observed with raw Jacobs Ranch coal. However, because the hardwood sawdust processed for this test by MESA Reduction Engineering contained occasional large slivers of wood, we were not able to feed sawdust at a 20% level of addition. At this feed rate, the funnel into which the sawdust was delivered from the screw feeder suffered frequent plugging. After some experimentation, a feed rate of 15% by weight was found to be sustainable and that level of addition was used for testing. Problems were not encountered at the 10% level of addition for sawdust or with switchgrass for which a feed rate of 20%, by weight, was easily accommodated. Three levels of furnace exit oxygen were tested (2.5%, 3.5%, and 4.5%) along with overfire air levels of 0% and 15%.

One error was made in testing. For the baseline case, where no biomass is added, the air purge through the center of the burner was turned off. In previous testing with center-axial biomass injection, during baseline testing the air purge was turned on so that when biomass was added, the only difference between 100% coal and coal plus biomass would be the biomass. This error could be significant because a high air velocity (~90-100 ft/sec) is required to convey up to 60 lb of biomass per hour with a sufficient safety factor to prevent flashback through the axial biomass injection system. Thus, with baseline coal firing, when this purge air is flowing, a considerable quantity of cold (room temperature) air is injected into the center of the coal flame. When no biomass is injected, the

thermal environment at the root of the coal flame experiences even more cooling by this jet of air and, as might be expected, NO_x emissions had been previously observed to increase, compared to those measured for the nominal comilling configuration (location 1 in Figure 3). Figure 9 demonstrates this earlier observation with Pratt seam coal, showing that without overfire air, the effect of adding air to the root of the flame is to raise and flatten the NO_x versus furnace exit oxygen (FEO) curve. In this configuration, below FEO levels of about 4%, NO_x emissions are greater than those measured for the baseline (comilling) case. When overfire air is added, the shape of the NO_x versus FEO curve is maintained, but with axial injection of air (without biomass), NO_x emissions are always greater than those measured for the baseline (comilling) case.

For Test 9, perhaps because of the lack of biomass transport air, a different behavior was observed for coal-only baseline testing. As Figure 10 shows, with the core injection apparatus installed without transport air, NO_x emissions were reduced compared to those measured with the single-register burner set up for a standard (comilling) configuration. If this behavior results from a lack of transport air, a possible explanation is that first, the flame is not disturbed by a low-temperature jet of air exiting from the center tube and second, the flame may become elongated because of the somewhat higher exit velocity of the pulverized coal stream (because of the presence of the center pipe). Regardless, this will be an interesting case to use in Model verification.

Figures 11 and 12 present average NO_x emissions measured for 10% and 15% by weight sawdust (Figure 11) and 10% and 20% by weight switchgrass (Figure 12) co-injected with Jacobs Ranch PRB coal. Figure 13 summarizes the changes in NO_x emissions realized by the center-axial injection of biomass, with and without 15% overfire air, and Table 7 summarizes the data presented in Figure 13. Given that the 100% coal NO_x emissions data may have been reduced due to the lack of biomass transport air, Figures 11 through 13 and Table 7 show that with this injection scheme, the addition of biomass frequently increases NO_x emissions. With no overfire air, at a 10% level of addition, NO_x emissions are either unaffected (sawdust) or slightly improved (switchgrass, < 4% FEO). At higher levels of biomass addition, NO_x emissions either increase (sawdust, >3.5% FEO) or drastically increase (switchgrass). When 15% overfire air is added, a consistent trend appears: the addition of biomass increases NO_x emissions and adding more biomass further increases NO_x emissions. Other than the strong possibility that the lack of biomass transport air tends to lower NO_x emissions when 100% coal is burned with the center-axial injection system in place, no straightforward explanation appears to explain this behavior.

Pratt Seam Coal
Baseline and Axial Injection Configuration
NO_x Performance in the Pilot-Scale Combustor
Dependence on Furnace Exit Oxygen

Figure 9. Comparison of comilled (baseline) firing mode versus the burner configured for axial (center) biomass injection. Pratt Seam coal with the single register burner.

Jacobs Ranch Coal Baseline and Axial Injection Configuration NO_x Performance in the Pilot-Scale Combustor Dependence on Furnace Exit Oxygen

Figure 10. Comparison of comilled (baseline) firing mode versus the burner configured for axial (center) biomass injection. Jacobs Ranch coal with the single register burner.

Jacobs Ranch Coal - Core-Injected Sawdust NO_x Performance in the Pilot-Scale Combustor Dependence on Furnace Exit Oxygen

Figure 11. NO_x emissions measured for sawdust coinjected with Jacobs Ranch coal. Single register burner configured for center-axial biomass injection with and without overfire air.

Jacobs Ranch Coal - Core-Injected Switchgrass NO_x Performance in the Pilot-Scale Combustor Dependence on Furnace Exit Oxygen

Figure 12. NO_x emissions measured for switchgrass coinjected with Jacobs Ranch coal. Single register burner configured for center-axial biomass injection with and without overfire air.

Jacobs Ranch Coal Core Injection Configuration NO_x Reduction from Biomass Addition Dependence on Furnace Exit Oxygen

Figure 13. NO_x reductions measured for sawdust and switchgrass coijnnected with Jacobs Ranch coal. Single register burner configured for center-axial biomass injection with and without overfire air.

Table 7. NO_x Emissions for Various Levels of Overfire Air at 3.5% Furnace Exit O₂, (wet) for Sawdust and for Switchgrass Coinjected with Jacobs Ranch PRB coal with the Single Register Burner.

Biomass	Weight%	Overfire Air, %	NO _x Emissions at 3% O ₂ , dry ppmv	Reduction of NO _x Emissions, %
2.5% Furnace Exit Oxygen				
None	0	0	271	0
		15	137	0
Sawdust	10	0	267	1.5
		15	173	-26.2
	15	0	240	11.6
		15	209	-52.1
Switchgrass	10	0	234	13.7
		15	156	-13.8
	20	0	327	-20.6
		15	173	-25.9
3.5% Furnace Exit Oxygen				
None	0	0	305	0
		15	176	0
Sawdust	10	0	305	0
		15	219	-24.6
	15	0	308	-1.1
		15	252	-43.0
Switchgrass	10	0	288	5.7
		15	209	-18.6
	20	0	387	-27.0
		15	224	-27.4
4.5% Furnace Exit Oxygen				
None	0	0	343	0
		15	226	0
Sawdust	10	0	348	-1.5
		15	278	-23.0
	15	0	396	-15.6
		15	304	-34.4
Switchgrass	10	0	353	-3.2
		15	279	-23.5
	20	0	458	-33.7
		15	291	-28.8

Finally, Figures 14 and 15 present the results of unburned carbon (UBC) measurements carried out on fly ash obtained by isokinetically sampling the furnace effluent at various values of furnace exit oxygen. As with Test 8, fly ash emissions were low (in this case, never exceeding 1.9 lb/10⁶Btu, for any test condition) and the levels of UBC in the fly ash never exceeded 0.8% and were usually lower than 0.4%. The same comments made for Test 8 also apply here.

DISCUSSION

As test results become available, Southern Research has provided to REI the information necessary for the production of CFD models of the combustion research facility. To date, four cases have been simulated to include the single-register burner configured for testing with coal or co-milled biomass for a variety of biomass injection schemes. These simulations are a prerequisite to NO_x and carbon burnout modeling. REI's latest report on the simulation of 20% sawdust comilled with 80% Pratt seam coal with realistic size distributions for both coal and biomass is included in Appendix C.

NEA has continued to make progress in the development of an innovative approach for the construction of the process model that will yield predictions of NO_x emission rates and carbon burnout efficiency. This approach is being developed to help determine the system of reactors in which the CBK, Chemkin III[®] and bio-Flashchain[®] modules are used in the PC Coal Lab[®] calculations of NO_x and unburned carbon. NEA is close to completing the reactor simulation of the pilot-scale furnace. NEA's Annual Report is included in Appendix A of this quarterly narrative and a paper authored by NEA for presentation at the Twenty-Ninth International Symposium on Combustion in July, 2002 at Hokkaido University in Sapporo, Japan. The paper is entitled "Advanced CFD Post-Processing for Coal Flame Structure and Emissions," and the paper acknowledges that support was provided through a subcontract from Southern Research Institute, under our current project with the U. S. Department of Energy (DE-FC26-00NT40895). The complete text of the paper is included in Appendix B.

Recent pilot-scale tests have investigated the cofiring of sawdust and switchgrass, at two concentrations, with a Powder River Basin coal. Both comilling and the injection of biomass through the center of the single-register burner were tested. Mesa Reduction Engineering and Processing, Inc. continues

Jacobs Ranch Coal

Core Injection with Sawdust and Switchgrass

Unburned Carbon Performance in the Pilot-Scale Combustor

Figure 14. Unburned carbon emissions for the coinjection of sawdust and switchgrass with Jacobs Ranch PRB coal. Single register burner configured for center-axial biomass injection with and without overfire air.

Jacobs Ranch Coal Coal Core Injection with Sawdust and Switchgrass Unburned Carbon Performance in the Pilot-Scale Combustor

Figure 15. Unburned carbon emissions for the coinjection of sawdust and switchgrass with Jacobs Ranch PRB coal. Single register burner configured for center-axial biomass injection with and without overfire air.

to process all biomass that will be injected into the furnace. In January, we plan to conduct a test with the dual-register burner. In February, we plan a short test without biomass to document the effect of coal fineness on NO_x emissions. At this point, the results of our modeling efforts are expected to have substantial input to the direction of future furnace testing. Depending on that input, we may conduct additional tests to add data for other mixing intensities, coals, or biomasses. Once we are satisfied that the data we have acquired form a consistent set of results, we will continue testing with tests specifically designed to test the model.

SUMMARY AND CONCLUSIONS

Important progress has been made in model development and in pilot-scale furnace testing. In particular, software development for the modeling effort that incorporates an innovative approach toward defining reaction zones in a combustion system is being tested, and preliminary results are encouraging. This development is a generally applicable algorithm that, if proven successful, should benefit other process modeling efforts in which carbon consumption or conversion is a major component.

One additional pilot-scale furnace test was concluded in the fourth quarter and further testing is planned. In the eighth combustor run, sawdust and switchgrass were comilled with Powder River Basin coal. In the ninth combustor run, the same Powder River Basin coal burned in Test 8 (Jacobs Ranch) was fired and sawdust and switchgrass were injected through the center of the single-register burner.

Significance of Test Results

The results from Test 8 reinforce the conclusion that although the choice of coal can significantly reduce NO_x emissions, the addition of biomass, particularly through comilling, can affect NO_x emissions as strongly as the choice of coal. Likewise, the results from Tests 8 and 9, along with the results of previous tests, continue to support the conclusion that biomass, as a comilled or injected combustion additive, can be beneficial in reducing NO_x emissions for one coal but detrimental for another. Finally, for a given coal, Tests 1-9 have repeatedly demonstrated that the choice of biomass can significantly affect the levels of NO_x reduction that are realized. The complex interrelationships among coal, biomass, and combustion mixing that have been documented point to the ultimate utility of

a comprehensive model that predicts NO_x emissions for biomass and coal cofiring.

Based on testing completed to date, several general observations can be made:

- The results from Test 8, along with previously presented results, suggest that compared to all the methods that have been tested for biomass cofiring, NO_x reductions are greatest when biomass is comilled with coal.
- Regardless of the method by which biomass is added, increasing the amount of a particular biomass can increase the production of NO_x.
- For the same biomass, method of cofiring, and conditions of combustion, the choice of coal can significantly affect the level of NO_x reductions that are achieved.

Plans

Plans for the next quarter include continued CFD simulations by REI, Inc., delivery of the first version of the Configurable Fire-Side Simulator from REI (which can be used to generate CFD simulations for the Pilot-Scale Combustor at Southern Research), continued software testing and refinement by NEA, and continued combustor runs, as dictated by the modeling effort. A project review is also planned for late February, in Birmingham.

APPENDIX A

NEA Annual Report

September 2000 – August 2001

Niksa Energy Associates

1745 Terrace Drive, Belmont, CA 94002
Phone: (650) 654 3182 Fax: (650) 654 3179
e-mail: neasteve@pacbell.net

Annual Report • October 22,
2001

DEVELOPMENT OF A VALIDATED MODEL FOR USE IN MINIMIZING NO_x EMISSIONS AND MAXIMIZING CARBON UTILIZATION WHEN CO-FIRING BIOMASS WITH COAL

Prepared by:

Dr. Stephen Niksa
President

Prepared for:

P. Vann Bush
Southern Research Institute
P. O. Box 55305
Birmingham, AL 35255-5305

EXECUTIVE SUMMARY

This annual report was prepared under the research project from Southern Research Institute (SRI) to Niksa Energy Associates (NEA) entitled “Development of a Validated Model for Use in Minimizing NO_x Emissions and Maximizing Carbon Utilization When Cofiring Biomass with Coal.” Research objectives were defined in the proposal of the same name submitted to the U. S. DoE under Solicitation No. DE-PS26-00NT40775. NEA’s role is to develop a post-processing methodology for CFD simulations of the SRI pilot-scale pulverized fuel (p. f.) flame that accurately predicts NO_x and UBC emissions. The post-processor incorporates the most advanced models for coal combustion chemistry as well as elementary reaction mechanisms for gas phase chemistry, and is therefore expected to perform better than conventional approaches based on drastically simplified process chemistry. Simulations of all runs in SRI’s testing program will ultimately be used to identify the optimal co-firing configuration for various forms of biomass on various coal types, and to interpret the behavior in terms of the detailed reaction mechanisms. During the period from November, 2000 through August, 2001, the program objectives were advanced by the formulation of reaction mechanisms for all stages of combustion, including devolatilization, volatiles combustion, soot oxidation, and char burnout.

A multitude of fuel species – CO, H₂, CH₄, C₂H₂, HCN, soot, and char – compete for the available O₂ in a p. f. flame. This competition determines local heat release rates, which govern flame stability, combustion efficiency and LOI, and the local oxidizing potential of the gas phase, which governs N-species conversion. The central premise behind our modeling approach is that the crucial outcome this competition cannot be forecast from the burning rates of the individual fuels determined in isolation. Instead, realistic chemical kinetics for each distinctive combustion process must be incorporated into a comprehensive analysis. Our analysis incorporates the most comprehensive chemical reaction submodels available, and imposes no *a priori* assumptions whatsoever regarding the apportioning of O₂.

The devolatilization submodel, called FLASHCHAIN[®], distinguishes primary devolatilization, which relates fuel properties to the composition of volatiles, from secondary volatiles pyrolysis, which generates the volatiles that actually burn in p. f. flames. FLASHCHAIN[®] determines the complete distribution

of primary products from almost any p. f., and also predicts the yield and elemental composition of char. When combined with a swelling factor correlation and a correlation for the initial carbon density in char, it specifies all the necessary char properties for a char oxidation simulation. Hence, the complete distribution of volatiles, including gaseous fuels and soot, and all char properties are completely determined from the fuel's proximate and ultimate analyses.

The reaction mechanism for chemistry in the gas phase must describe the ignition and combustion of all secondary volatiles pyrolysis products, as well as the conversion of all N-species across the full range of stoichiometric ratio (S. R.) values in p. f. flames. Our homogeneous reaction mechanism contains 444 elementary reactions among 66 species, including all relevant radicals and N-species. It is implemented in the simulations without any approximations whatsoever. All rate parameters were assigned independently, so there are also no adjustable parameters in the submodel for gas phase chemistry.

Soot plays several important roles. As it burns, it directly competes for the available O_2 and also consumes O-atoms and OH that would otherwise sustain homogeneous chemistry. Soot also promotes recombinations of H-atoms and OH that could also sustain homogeneous chemistry. And soot reduces NO directly into N_2 . Our soot chemistry submodel depicts all these effects in the form of a collection of elementary reactions that can be coupled to the homogeneous reaction mechanism within the CHEMKIN/SURFACE CHEMKIN framework.

Char burning rates are determined by thermal annealing, ash encapsulation (of low-rank chars), and a transition to chemical kinetic control. The Char Burnout Kinetics (CBK) Model includes all these effects, and depicts the impact of variation in gas temperature, O_2 level, and char particle size within useful quantitative tolerances. However, it is not yet possible to specify the initial char reactivity within useful tolerances from the standard coal properties. We must calibrate this value with LOI predictions or some other suitable index on combustion efficiency. The submodel for char-N conversion is subject to a similar calibration requirement (with NO emissions), compounded by its simplistic mechanistic premise; viz., that a fixed fraction of char-N is converted into NO at the overall burning rate throughout all stages of char oxidation.

To summarize the status of our reaction mechanisms, the initial char reactivity and the fraction of char-N converted to NO can only be specified from

calibration procedures. Otherwise, all other model parameters can be assigned from the fuel's proximate and ultimate analyses within useful quantitative tolerances, or directly adopted from the literature. We believe that the submodels for devolatilization, homogeneous chemistry, and char burnout are complete, whereas those for soot/radical chemistry and for char-N conversion will probably be subject to revisions in the near term.

Simulations of a 1 MW tunnel furnace fired with various p. f. demonstrated several tangible benefits of all the mechanistic complexity. Based on a CFD simulation of a hvA bituminous coal flame, the flame structure in this furnace was resolved into four regions: a flame core, mixing layer, SOFA zone, and burnout zone. Parametric variations of the mixing intensity of the secondary air stream produced higher NO emissions for higher mixing rates, as expected. An evaluation of staged versus un-staged firing configurations was also qualitatively satisfied, but remains to be quantitatively validated. Predicted NO emissions increased in direct proportion to increases in the fraction of char-N converted into NO. Somewhat surprisingly, NO emissions were significantly lower for higher values of the initial char reactivity because there was more NO generated in the core and subsequently reduced before the mixing layer, and also less residual char-N to generate NO during succeeding stages of burnout.

Subbituminous flames had three times higher extents of char burnout in the core than bituminous flames. This factor, in conjunction with a lower coal-N level and a much higher coal-H level, explained the reduction in NO emission by a factor of two. Subbituminous flames also generated much higher CO concentrations in the flame core, and the ultimate extent of char burnout was higher by almost 2 %. Simulations with coal blends highlighted a new aspect of the competition for the available O₂. The most reactive char wins the competition at the expense of the least reactive char, so that unburned carbon becomes enriched in the least reactive char component. Simulations of biomass co-firing introduced yet another tradeoff in the char burnout profiles, because switchgrass has a much higher char reactivity but is usually fed at much larger sizes. The smaller switchgrass size cuts burned faster in the core. But once they were annealed, the largest size fractions of these chars burned slower than the smaller bituminous chars. Consequently, unburned carbon became enriched in the largest size fractions of the switchgrass chars.

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1.0 SCOPE AND OBJECTIVES

This annual report was prepared under the research project from Southern Research Institute (SRI) to Niksa Energy Associates (NEA) entitled “Development of a Validated Model for Use in Minimizing NO_x Emissions and Maximizing Carbon Utilization When Cofiring Biomass with Coal.” Research objectives were defined in the proposal of the same name submitted to the U. S. DoE under Solicitation No. DE-PS26-00NT40775.

NEA’s role in the project is to develop a post-processing methodology for CFD simulations of the SRI pilot-scale pulverized fuel (p. f.) flame that accurately predicts NO_x and UBC emissions. The post-processor incorporates the most advanced models for coal combustion chemistry as well as elementary reaction mechanisms for gas phase chemistry, and is therefore expected to perform better than conventional approaches based on drastically simplified process chemistry. Simulations of all runs in SRI’s testing program will ultimately be used to identify the optimal co-firing configuration for various forms of biomass on various coal types, and to interpret the behavior in terms of the detailed reaction mechanisms.

This report describes the reaction mechanisms that have been incorporated into NEA’s calculations during the period from November, 2000 through August, 2001. The program objectives were advanced by the formulation of reaction mechanisms for all stages of combustion, including devolatilization, volatiles combustion, soot oxidation, and char burnout. Chapter 2 describes each mechanism in detail, ending with a summary of all the fuel quality impacts that have been incorporated into the modeling. Chapter 3 first introduces some simple mixing mechanisms within the framework of an equivalent network of idealized reactors, then applies the mixing models and reaction mechanisms to the SRI tunnel furnace. The summary in Ch. 4 emphasizes the input data requirements and schemes to specify values for all modeling parameters.

2.0 CHEMICAL REACTION MECHANISMS

2.1 Overview

The means to exploit the advantages of realistic chemical reaction mechanisms in coal combustor simulations are now evident in the literature: Ignore the turbulence/chemistry interactions and use equivalent networks of idealized reactor elements to depict only the bulk flow patterns. This single premise enables the most advanced coal reaction submodels and elementary reaction mechanisms for gas phase chemistry to be used in furnace simulations, without any approximations. One immediate advantage is that all reaction rate parameters can be specified from the coal properties or independently assigned from fundamental kinetics work. So coal quality impacts will be apparent in the simulations. Another advantage is that earlier approaches that accurately predicted coal quality impacts on NO_x and unburned carbon (UBC) emissions with statistical regressions based on advanced coal decomposition models can be carried into the realm of CFD. And realistic chemistry may very well provide the means to supercede the dismal performance of simplified chemistry in predicting CO emissions.

Somewhat arbitrarily, the fuel combustion process will be subdivided into four distinct stages, as follows:

- (1) **Devolatilization** is the thermal decomposition of solid fuels into gaseous products, soot, and char. Volatiles contain fuel compounds which ignite and stabilize flames, nitrogen-bearing precursors to NO_x , and soot. Properties of the solid char residue are also determined by devolatilization reaction mechanisms.
- (2) **Volatiles Combustion** is the homogeneous conversion of gaseous volatiles into combustion products, including volatile-N species.
- (3) **Soot Oxidation** may compete effectively with gaseous volatiles for the available O_2 , and also attenuates radical concentrations in the gas phase by sustaining recombination chemistry. Soot also reduces NO.

- (4) **Char Oxidation** may also compete for the available O_2 , especially with the reactive chars from low rank coals. It also determines LOI levels and contributes significant portions of NO_x emissions via the conversion of char-N species.

At the outset, it is important to realize that we tend to discuss these reaction mechanisms as distinct stages in the combustion process whereas, in actuality, they occur simultaneously in pulverized fuel (p. f.) flames. Even though the intrinsic burning rates of gaseous fuels are faster than those of soot and char, the very small sizes of soot and in the low end of the char particle size distribution (PSD) enable the solid fuels to effectively compete for O_2 with the slowest burning gaseous fuels, particularly CO. The outcome of this competition is determined by the kinetics for conversion of the various fuels in this system. Our modeling approach fully incorporates this crucial competition. Along with only one recent approach (Pedersen et al., 1998a) and, perhaps, a second (Benedetto et al., 2000), our modeling framework accommodates detailed distributions of all fuel-derived compounds without imposing any a priori assumptions regarding the relative burning rates of the various fuel species.

2.2 Reaction Mechanisms for Pulverized Fuel Combustion

2.2.1 Devolatilization

During combustion, coal particles ground into the p. f. size grade are entrained in air into a very hot, intense mixing field. Swirling flows are used to mix the coal with the hot process gases as fast as possible. Temperatures near the coal injectors can exceed 1500°C .

Devolatilization in such systems is responsible for generating the gaseous fuels that ignite and stabilize flames onto the coal injectors or, at least, within the vortical mixing region. Since the coal particles are so finely pulverized and the process temperatures are so high, the coal devolatilizes while it is being heated at rates approaching $10^5\ ^\circ\text{C/s}$. Under such conditions, devolatilization begins at 400 to 600°C , and is complete long before the char reaches the reactor temperature, in only several milliseconds. Even so, the exposure to such high process temperatures is definitely important for the char's subsequent reactivity during char oxidation.

We describe devolatilization in terms of two separate chemical reaction mechanisms: (1) Primary devolatilization denotes chemistry within the condensed fuel phase that releases gaseous species from the coal matrix; and (2) Secondary volatiles pyrolysis converts the primary volatiles into the fuels that actually burn during combustion.

2.2.1.1 Primary Devolatilization

NEA distributes reaction mechanisms for the devolatilization of a wide variety of solid fuels. FLASHCHAIN[®] predicts the devolatilization behavior of any coal or

petroleum coke at any operating conditions. Well over 1000 coals from all geographical regions worldwide have been analyzed to date. *Bio-*FLASHCHAIN[®] predicts the devolatilization behavior of biomass, including woods, paper, grasses, and various agricultural residues. Recent publications describe the theory's mechanisms to predict the yields of the major volatile products, tar and gas, plus the yields of the gases containing oxygen and nitrogen (Niksa, 1995a; Niksa, 2001), and detailed mathematical formulations are also available (Niksa and Kerstein, 1991). The qualitative behavior is emphasized in the following brief overview.

The phenomenology in these models is based on the "flash distillation analogy," as follows: When steam is bubbled through a barrel of crude oil, the lightest fractions pass into the vapor and are transported away with bubbles breaking through the surface of the petroleum. But the material with high molecular weight remains in the liquid phase and condenses into coke if the temperature exceeds a certain threshold value. According to FLASHCHAIN[®], devolatilization follows this same sequence of steps once depolymerization chemistry has disintegrated a fuel's original three-dimensional macromolecular structure into a mixture of fragments that has a broad molecular weight distribution. The role of the steam is played by the noncondensable gases produced whenever aliphatic components are partially converted into refractory char links. Tar is generated when the depolymerization fragments become small enough to vaporize into the escaping noncondensable gases. (Fragments that vaporize at processing temperatures are still heavy enough to condense into viscous liquids at room temperature.) Char forms by crosslinking among heavier fragments in the condensed phase, whose further depolymerization is

suppressed whenever labile connections are converted into refractory char links. Noncondensable gases are produced as a by-product of charring.

According to this mechanism, the influences of thermal history, pressure, and particle size can be understood in terms of only four mechanisms: (1) Coal macromolecules depolymerize into fragments with a broad size distribution; (2) A phase equilibrium establishes the mole fraction of tar fragments in a gas stream that is convected out of the particle with no transport resistance; (3) The conversion of labile bridges in the fragments into char links suppresses depolymerization and simultaneously generates noncondensable gases; and (4) Fragments also crosslink in the condensed phase to form nonvolatile components of char.

According to the flash distillation analogy (Niksa, 1988a), the phase equilibrium shifts to retain a larger portion of the lighter fragments in the condensed phase as the pressure is increased. These fragments would constitute the heavy end of the tar molecular weight distribution (MWD) at low pressures, but remain in the coal at elevated pressures. Consequently, tar prepared at higher pressures becomes lighter and the tar yield diminishes. The fragments retained in the char also contain precursors to noncondensable gases which are eventually released, so gas yields increase as the pressure is elevated, but not by enough to compensate for the retention of tar precursors. Finite-rate transport mechanisms are not needed to explain the pressure effect. In fact, the scaling for negligible transport resistances in FLASHCHAIN[®] is consistent with the lack of a particle size effect for devolatilization of pulverized coal, which presents problems for earlier transport-based models that were never reconciled.

Thermal history effects are rooted in the chemical heterogeneity of a fuel's key reaction centers. A distribution of activation energies for the depolymerization chemistry represents the very broad thermal response of this reaction system, and explains why asymptotic volatiles yields are observed to depend on the pyrolysis temperature. But competitive char formation chemistry is needed to explain the proportions of tar and gas from coals of different rank. Heating rate affects the rate, yields, and composition of volatiles. As the heating rate is increased, the onset of devolatilization moves to higher temperatures and the devolatilization rate increases in rough proportion to the heating rate. Rapid heating enhances the volatile yields from coal by delaying the generation of

primary fragments until higher temperatures are achieved, where more of the heavier fragments are expelled as tar. Consequently, tar becomes more abundant and heavier as heating rates are accelerated. And gas yields decrease because the additional tar shuttles away precursors to noncondensibles. But the volatiles yields from biomass are independent of heating rate, primarily because the competition between bridge scission and charring is essentially independent of temperature.

All the above effects have been illustrated with laboratory measurements (Niksa, 1991b; 1994b& c). Additional implications for gas compositions and nitrogen-species have also been described at length (Niksa, 1994a; 1995a&b; 1996). From an operational standpoint, FLASHCHAIN[®] predicts the following properties of the distribution of volatile products from a solid fuel: the yields of char, tar, CH₄, C₂H₆, C₂H₄, C₃H₈, C₃H₆, HCN, H₂S, H₂, H₂O, CO, CO₂, plus the C/H/N/O/S compositions of tar and char and the MWD of tar. Specialized versions have also been prepared to predict the release of alkali (Na, K) and chlorine (HCl) species. Extensions to describe the release of various trace metals (Hg, Se, B, As) are now underway. The only sample-specific information needed to predict these product distributions are the proximate and ultimate analyses of the fuel (and the associated inorganic species loadings).

In addition, the pressure, fuel PSD, and the thermal history – which is particle temperature as a function of time – must be specified. In most practical applications (including SRI's simulations), the thermal histories are assigned from an energy balance. The energy conservation equation balances the particle's thermal capacitance against the net heat transfer rate, which includes contributions from enthalpy changes during moisture loss and devolatilization, convection, and radiation, according to

$$m_p C_p \frac{dT_p}{dt} = A_p (q_M \Delta H_M + q_v \Delta H_V) - h A_p (T_p - T_G) - \sigma \epsilon_p A_p (T_p^4 - T_W^4)$$

2.1

where

$$q_v = \frac{(\rho_0 d_p)}{6} \left(\frac{dY_{TAR}}{dt} + \frac{dY_{GAS}}{dt} \right)_{FLASHCHAIN}$$

$$q_M = \frac{h}{C_{p,H_2O}} \ln(1 + B_M) \quad \text{with} \quad B_m = \frac{C_{p,H_2O}(T_G - T_V)}{L + C_{p,H_2O}^L(T_V - T_O)}$$

$$h = \frac{Nu \lambda_g}{d_p} \frac{B_V}{1 - e^{-B_V}} \quad \text{with} \quad B_V = d_p \sum \frac{C_{p,i} q_i}{\lambda_i}$$

In these relations, the particle characteristics are denoted by m_p for mass; A_p for external surface area; d_p for diameter; ρ for bulk density; C_p for specific heat; and ε_p for total hemispherical emittance. The temperatures are T_p for the particle; T_G for the local gas temperature; T_W for the combustor wall temperature; and T_V for the boiling point of H₂O. The reaction enthalpies are denoted by ΔH_M for moisture loss and by ΔH_V for devolatilization. The volatiles flux is determined by the sum of the release rates for gases and tars from FLASHCHAIN[®], dY_{TAR}/dt and dY_{GAS}/dt . The gas production rate, dY_{GAS}/dt , represents the sum of the release of all primary devolatilization products from FLASHCHAIN[®] (H₂, CH₄, C₂H₄, C₂H₆, C₃H₆, C₃H₈, CO, CO₂, H₂O, HCN, and H₂S). The moisture evaporation flux is based on a conventional transport number that depends on the heat capacities of water, both liquid and vapor, and the latent heat of vaporization, L . The convective heat transfer coefficient, h , accounts for the flow regime and particle size of interest through the Nusselt number, Nu , which is evaluated with the Ranz and Marshall correlation. The convective coefficient is also proportional to the average thermal conductivity of the gas stream, λ_g . The factor involving B_V accounts for the reduction in heat transfer due to the outward flow of volatiles.

Given values for the local ambient conditions (T_G and T_W), eq. 2.1 can be used to assign the thermal histories to be imposed on the devolatilization reaction mechanism. In SRI's simulations, NEA's PC Coal Lab[®] simultaneously solves the energy balance and the FLASHCHAIN[®] equations, as explained in Ch. 3.

The predicted devolatilization behavior is illustrated in Table 2.1. These calculations are for primary devolatilization only, and therefore represent the distribution of volatiles that passes through the particle surface before secondary chemistry has come into play. The three samples represent an Eastern hvA bituminous coal, a Western subbituminous coal, and switchgrass; their proximate and ultimate analyses are tabulated. The thermal histories are based on injection into a gas stream at 1325°C within a furnace at 725°C. The nominal size was 55 μm for both coals and 260 μm for the switchgrass.

Table 2.1. Primary Devolatilization Products from PC Coal Lab®.

	hVA Bit.	W. Subbit.	Switchgrass
Properties			
Volatiles	33.2	45.2	47.6
Fixed Carbon	49.9	35.8	7.7
Moisture	1.9	6.1	15.2
Ash	15.1	12.8	29.5
%C, daf wt. %	83.4	78.0	56.1
%H	5.5	6.4	5.4
%O	7.5	14.5	35.6
%N	1.8	1.2	2.4
%S	1.8	0.1	0.4
Volatiles, daf wt. %			
Wt. Loss	61.9	72.8	85.7
Tar	48.6	46.5	42.5
CO	0.8	3.1	22.1
CO ₂	1.5	3.5	3.5
H ₂ O	4.1	5.9	6.8
CH ₄	2.4	5.6	2.1
C ₂ H ₄	1.0	2.1	0.8
C ₂ H ₆	0.6	2.3	0.2
C ₃ H ₆	0.9	2.3	0.4
Alcohols	-	-	3.3
H ₂	0.5	0.2	0.8
HCN	0.1	0.2	-
NH ₃	-	-	1.8
H ₂ S	1.3	0.1	0.3
Char Properties			
% C	97.4	97.6	97.3
% H	0.4	0.5	2.5
% N	2.2	1.7	0.0
d/d ₀	1.16	1.12	0.68
ρ, g/cm ³	0.37	0.24	0.71

The coals have comparable ultimate and tar yields, but the subbituminous releases much more of the oxygenated gases and hydrocarbons. Their distributions of nitrogen species are similar, but the Eastern bituminous releases

much more H_2S . Their chars have similar compositions and bulk densities, whereas the subbituminous char is somewhat less swollen. The volatiles from the switchgrass are grossly different from both coals'. Even though the tar yields are comparable, the total weight loss is much greater. Carbon monoxide accounts for most of the difference, although switchgrass also releases oxygenated alcohols, ethers, and ketones, which were not seen in the distributions of coal volatiles. There is also significantly more H_2 . Ammonia is the main volatile-N species with switchgrass, not HCN. The switchgrass char composition has a similar carbon level, but much more H and no N, compared to the coal chars. Switchgrass chars contract during devolatilization, so their bulk densities are higher. Obviously, the different product compositions will affect the simulated combustion behavior, especially in near-burner regions.

The gases in near-burner regions of coal combustors are generally much hotter than the entrained fuel particles. Since primary devolatilization occurs while the fuel is being rapidly heated, the primary volatiles are expelled into gases that are hotter than their parent fuel particles. Consequently, the products of primary devolatilization are rapidly transformed by secondary volatiles pyrolysis once they have been expelled into these hot gases. The very complex distributions of chain and condensed polynuclear aromatic hydrocarbons, carbon oxides, water and hydrogen that are released initially - and would appear to burn very rapidly - are converted into much simpler mixtures of soot, carbon oxides, H_2O , and H_2 with small amounts of CH_4 and C_2H_2 (Bruinsma, 1988; Nelson, 1986; Chen, 1992). The abundance of soot, CO, and combustion products in the secondary products ensures that they will burn relatively slowly (Marlow et al., 1992; Cho et al., 1995). Soot and CO may not even compete effectively for the available O_2 with the reactive chars from low-rank coals (Niksa and Cho, 1998).

2.2.1.2 Secondary Volatiles Pyrolysis

The primary product distributions from FLASHCHAIN[®] are converted to secondary pyrolysis products by applying pseudo-mechanisms based on the study of Chen et al. (1992). The distributions incorporate an extent of secondary pyrolysis, but not finite-rate kinetics. The extent of secondary pyrolysis is assigned as the soot fraction, which is the ratio of the yield of soot to the sum of the yields of tar, oils, and soot.

The soot composition is based on a constant value of H/C for all soots from all fuel types. All heteroatoms in tar are expelled as noncondensibles. Tar-O is released as CO in exchange for incorporation of C₂H₂ into soot. Tar-N is released as HCN and tar-S is released as H₂S. The bulk of tar-H is released as H₂. Consequently, with bituminous coals the sum of the yields of tar, soot, and oils remains nearly invariant throughout secondary pyrolysis, even though the yields of CO, C₂H₂, H₂ and HCN surge throughout. Non-condensable hydrocarbons are converted into CH₄ and C₂H₂, although CH₄ is also converted into C₂H₂ during the last half of secondary pyrolysis.

Product distributions based on this phenomenological mechanism for the three fuels considered in the previous section appear in Table 2.2. Total weight loss from the coals was not affected by secondary pyrolysis, but tars were converted into almost the same amount of soot. Methane and acetylene are the only hydrocarbons that survive, but their total yield is much lower than the primary hydrocarbon yield. There is much more H₂, CO, and HCN due to release of tar-H, tar-O, and tar-N, respectively. Due to the abundance of oxygen in biomass-derived tars, there is much less soot with switchgrass. The abundance of hydrocarbons and light oxygenated gases persists through secondary pyrolysis, but switchgrass generates much less H₂ than the coals. Since the fuels that actually burn during combustion are the secondary volatiles pyrolysis products, it is worth noting the relative abundance of CO and hydrocarbons and the depletion of soot and H₂ in the volatiles from switchgrass, compared to the coal products.

Table 2.2. Secondary Pyrolysis Products from PC Cal Lab[®].

Yield, daf wt. %	hvA Bit.	W. Subbit.	Switchgrass
Wt. Loss	61.9	72.8	85.7
Soot	43.4	41.8	13.1
CH ₄	0.3	0.9	7.4
C ₂ H ₂	0.3	2.0	1.2
C ₂ H ₄	-	-	1.5
H ₂	4.2	4.9	1.7
CO	4.8	11.6	41.4
CO ₂	1.5	3.5	8.1
H ₂ O	4.1	5.9	7.7

HCN	1.3	1.0	-
NH ₃	-	-	2.9
H ₂ S	1.3	0.1	0.3

2.2.1.3 Char Properties

Char oxidation rates are determined by several physical and chemical properties of the char. The oxidation mechanism that is implemented in PC Coal Lab[®] (which is called CBK and described in Sec. 2.2.4) requires the char yield, an elemental composition, the char PSD, and the initial density of carbon. Internal surface areas are often incorporated into char oxidation kinetics, but not in our mechanism.

FLASHCHAIN[®] predicts the yield of char from devolatilization, and also the C/H/O/N/S composition. Swelling during devolatilization is described with a correlation for the size swelling factor prepared by Hurt for use with CBK in terms of the carbon and hydrogen contents of the parent coal. This correlation explicitly accounts for the peculiar swelling behavior of South African and some South American coals. Given a swelling factor, the coal PSD can be converted into the char PSD. We use a Rosin-Rammler PSD for the original fuel, which is

$$\Phi(d) = \exp[-RR2(d)^{RR1}]$$

2.2

where $\Phi(d)$ is the fractional mass of the feed with diameter greater than d , and $RR1$ and $RR2$ are empirical parameters. It can be shown that the parameter $RR1$ is unaffected by swelling, so once a swelling factor has been specified, the parameter $RR2$ can be evaluated to determine the Rosin-Rammler distribution for the char PSD, according to the following expression:

$$(RR2)_{CHAR} = \frac{\ln\left(\frac{100}{\%Over}\right)}{d_{Over}^{RR1}}$$

2.3

where %Over is the mass percentage over a specified size in the coal PSD, and d_{Over} is the product of the swelling factor and that specified size.

Bulk particle densities of chars are evaluated from the mean char size and the char yield. Carbon densities within the chars are evaluated from a correlation prepared by Hurt for use with CBK in terms of the coal carbon content.

2.2.2 Homogeneous Chemical Reaction Mechanisms

The reaction mechanism used for all homogeneous chemistry in the gas phase was assembled by Glarborg and coworkers (1998) for applications involving reburning and other interactions among nitrogen- and hydrocarbon species. It is, by far, the most suitable mechanism in the combustion literature for this application because it is based on a laboratory database compiled with a flow reactor at temperatures from 525 to 1225°C. The complete mechanism of 444 elementary reactions is collected in Appendix A. The mechanism is subdivided into two subsets. The H₂/O₂ subset includes the familiar shuffle reactions among the oxyhydroxyl radicals (H/O/OH) as well as conversion channels for HO₂, which becomes a major chain carrier at lower temperatures. The H/N/O subset contains steps involving HNO, which are the main NO production channels at high temperatures, as well as steps involving NH₂, which are the main DeNO_x channels involving ammonia at moderate temperatures.

In addition to the frequency factors, power law exponents, and activation energies in the reaction mechanism, the reactions involving generic collision partners (denoted by M) usually have different collision efficiencies assigned for different collision partners (which are not indicated in the tabulation but are implemented in our calculations). Also, several steps, for example No. 281, appear with two sets of parameters. These are duplicate reactions that may proceed according to two independent channels involving the same reactant species. Finally, this mechanism was also distributed with a set of thermochemical equilibrium parameters, which were used in all calculations.

The most important features of homogeneous N-species conversion are illustrated in Fig. 2-1. These calculations are based on the simplified mechanism for coal volatiles combustion developed by Pedersen et al. (1998b) from a reduced version of the complete reburning mechanism in Appendix A. This

mechanism omits all C_1/C_2 chemistry and regards volatiles as H_2/CO mixtures, but otherwise retains realistic submechanisms for the fuel oxidation and nitrogen chemistry. Qualitatively, the behavior is the same as the full mechanism. The model also featured a detailed submechanism for soot oxidation that accounts for radical recombinations, oxidation by O and OH, and NO reduction on soot but, in this section, we focus on the case without soot oxidation. (Our soot chemistry submodel is described in Sec. 2.2.3.)

Figure 2-1. Model predictions for the complete mechanism (left) and without soot/radical reactions (right) (Pedersen et al. 1998).

The simulation results for the near-burner zone appear in Figs. 2-1, where the left case is for the complete model and the right case omits radical recombinations on soot. As the stoichiometric ratio (S. R.) is progressively increased from rich to lean mixture compositions, both the dominant radical chain carriers and N-species change. H-atoms are the main chain carriers in rich mixtures, but give way to OH radicals beyond the stoichiometric point. O-atoms are important only in the leanest mixtures. Among the N-species, HCN is important in all rich mixtures, whereas NH_3 appears only within a relatively

narrow range of rich S. R. values. An abrupt transition coincident with the shift to OH leaves NO as the only appreciable fixed nitrogen species.

It is interesting that the major features among the N-species in these simulations have been observed under conditions that closely simulate the chemical environments in near-burner zones (Niksa and Cho 1996). In Fig. 2-2, the distribution of hydrocarbon volatiles and nitrogen species from an hv bituminous coal for progressively leaner conditions shows that no NO appears

Figure 2-2. Measured distributions of fuel components and N-species from a one-dimensional coal flame at various O₂ levels (Niksa and Cho 1996).

until the hydrocarbons, H₂, CO, and most of the soot are burned away. Consequently, the character of TFN undergoes an abrupt transition from almost total HCN to almost total NO as the oxygen level is progressively increased. Hence, our homogeneous reaction mechanism is able to represent the main features in the fuel-N conversion mechanisms in near-burner zones.

2.2.3 Soot-Related Chemistry

Returning to Fig. 2-2, by comparing the cases with and without soot chemistry, we see that reactions on soot shift the S. R. transition toward leaner mixtures. The effect occurs for two reasons: (1) Soot oxidation consumes O_2 which would otherwise participate in the homogeneous reaction mechanisms; and (2) H-atoms and OH-radicals recombine on soot, thereby lowering the burning rates in the gas phase, like any other termination reaction. In addition, NO may be reduced on the carbon in soot. Submodels for each of these three processes are developed in the following sections.

2.2.3.1 Soot Oxidation by O_2

The rates of soot oxidation in the presence of O_2 for temperatures to 3000 K and pressures to 30 atm are well-described by so-called Nagle-Strickland-Constable (NSC) kinetics, which are

$$\omega_{NSC} = \frac{k_A p_{O_2}}{1 + k_Z p_{O_2}} \chi + k_B p_{O_2} (1 - \chi) \quad \text{where} \quad \chi = \frac{1}{1 + \frac{k_T}{k_B p_{O_2}}}$$

2.4

The soot oxidation rate, ω_{NSC} , has units of $g/cm^2 \cdot s$. It is determined by four rate constants of Arrhenius form, k_A , k_B , k_T , and k_Z , and the local free-stream partial pressure of O_2 , p_{O_2} . This expression is semi-empirical, in so far as the authors interpreted the rate constants in terms of elementary reaction processes but did not propose a complete reaction mechanism that determines the oxidation rate according to eq. 2.4.

NSC-kinetics are certainly robust enough for application in coal flame simulations. But they are very difficult to implement with detailed chemical reaction mechanisms. The reason is that a commercial software package called CHEMKIN III is available to solve the ordinary differential equations (ODEs) associated with the homogeneous chemical reaction mechanisms. However, CHEMKIN only accepts rate expressions in certain prescribed forms, and NSC-kinetics do not qualify. We would need to develop a customized in-house ODE solver to handle both the chemistry-derived ODEs and the NSC reaction rate

expression in eq. 2-4. Due to the stiffness of chemistry-derived ODEs, this is by no means a simple task.

We pursued an alternative strategy which first expresses the oxidation rate of soot by O_2 in terms of an elementary surface reaction mechanism. Then another commercial package, called SURFACE CHEMKIN, is used to simultaneously solve the ODEs associated with surface and homogeneous chemistry. So the elementary soot oxidation mechanism can be directly coupled with the homogeneous reaction mechanism, and solved with the commercial packages.

NEA's elementary soot oxidation mechanism is developed in terms of three distinct surface sites, plus bulk carbon, C_B , which replenishes surface sites: (1) C_A denotes a reactive free site; C_D denotes nearly unreactive free site; and C_O denotes a site with adsorbed O. There are four elementary reactions, as follows:

Reactions A and B describe dissociative- and oxidative-chemisorption of O_2 on the carbon sites, respectively. Oxidative chemisorption on unreactive sites directly produces CO whereas oxidative-chemisorption on reactive sites feeds into the desorption in Reaction C. Reactive sites are converted into nearly unreactive sites in Reaction D.

If the fractional surface coverages, χ_i , of all sites are in steady state, then the total conversion is given by

$$\begin{aligned}\frac{dC_B}{dt} &= k_B p_{O_2} (1 - \chi_A - \chi_O) + k_P \chi_O \\ &= k_B p_{O_2} (1 - \chi_A - \chi_O) + k_A p_{O_2} \chi_A\end{aligned}$$

2.6

where the second form follows from the steady state assumption for χ_O . The surface coverages are defined by

$$\chi_A = \frac{(1 - \chi_O)}{1 + \frac{k_T}{k_B p_{O_2}}} \quad \text{and} \quad \chi_O = \frac{\frac{k_A}{k_P} p_{O_2}}{1 + \frac{k_A}{k_P} p_{O_2} + \frac{k_T}{k_B p_{O_2}}}$$

2.7

If $k_A p_{O_2}/k_P \gg k_T/k_B p_{O_2}$ and $\chi_O \ll 1$, then the total conversion rate for NEA's elementary reaction mechanism reduces to the NSC-kinetics in eq. 2.4, as follows:

$$\omega_{NEA} = \frac{k_A p_{O_2}}{1 + k_Z p_{O_2}} \chi_A + k_B p_{O_2} (1 - \chi_A) \quad \text{where} \quad \chi_A = \frac{1}{1 + \frac{k_T}{k_B p_{O_2}}} \quad \text{and} \quad k_Z = \frac{k_A}{k_P}$$

2.8

Since the overall oxidation rate for NEA's elementary reaction mechanism has the

same form as the NSC rate expression, it is possible to reproduce NSC kinetics with NEA's reaction mechanism. The values of the rate constants to achieve this in practice were specified by fitting the soot oxidation rates reported by Park and Appleton (1973) for shock tube tests. As seen in Fig. 2-3, the agreement is nearly exact for the conditions relevant to p. f. combustion. The dashed lines in Fig. 2-3 are based on NSC kinetics, which generally agree with the shock tube measurements within experimental uncertainty. The solid curves are based on NEA's reaction mechanism. The agreement is also generally within experimental uncertainties for temperatures to 2000 K and O_2 concentrations up to 25 %, which covers the relevant domain of operating conditions in p. f. flames. For higher temperatures, the predicted soot oxidation rates are generally higher than

NSC-based values, although they are actually in better agreement with the measurements for some of the O_2 concentrations in this evaluation. Rate constants specified in this evaluation are reported in the next section.

2.2.3.2 Soot-Radical Chemistry

In addition to oxidation by O_2 , soot also burns with O and OH ; in fact, OH is often the primary soot oxidizer under rich-flame conditions (Neoh et al., 1981). These reactions were analyzed by Pedersen et al. (1998b), according to the following elementary reactions:

Figure 2-3. Soot oxidation rates from NEA's elementary soot oxidation mechanism for O₂ (solid curves) compared with rates from NSC-kinetics (dashed curves) that were assigned from measured values from shock tube tests (Park and Appleton, 1973).

where C_H is the site of an adsorbed H-atom. In addition to these oxidation reactions, there are the following radical recombinations:

The final soot reaction is the reduction of NO, according to

This reaction is obviously not an elementary step due to the fractional stoichiometric coefficient for N₂. But it is in a form that can be handled with SURFACE CHEMKIN.

2.2.3.3 Implementation in SURFACE CHEMKIN

Our complete soot chemistry submodel combines the elementary reaction mechanism for oxidation by O₂ with the radical oxidation steps plus the recombination and NO reduction reactions. In combining NEA's elementary soot

oxidation mechanism with Pedersen et al.'s recombination and NO reduction chemistry, we assumed that reactive (SA) and nearly unreactive (SD) sites were equivalent sites for recombinations and NO reduction. The complete soot chemistry submodel is collected in Table 2.3, including the values of all rate constants. Two forms of rate constants are implemented. The ones denoted as "Arrh." have a conventional Arrhenius form: $ATn\exp(-E_a/RT)$. The three parameters in the table are the A-factor, the power-law exponent, n, and the apparent activation energy, E_a . Rate constants denoted by "Stck." are based on sticking coefficients, which multiply the collisional frequency. Most of the sticking coefficients are simple multiplicative constants, although three include apparent activation energies which appear in conventional Boltzmann factors that multiply the collisional frequencies. All the rate constants in Table 2.3 are suitable for SURFACE CHEMKIN.

Table 2.3. NEA's Soot Chemistry Submodel.

	Form	A-Factor	T-Exp.	E_a , cal/mole
Oxidation				
$S_A + O_2(g) \Rightarrow O(g) + S_O$	Arrh.	3.00E+11	1	29000
$S_B + S_D + O_2(g) \Rightarrow CO(g) + O(g) + S_A$	Arrh.	4.00E+03	1	25180
$S_B + S_O \Rightarrow S_A + CO(g)$	Arrh.	3.00E+08	0	35000
$S_A \Rightarrow S_D$	Arrh.	3.10E+08	0	105000
$S_B + S_A + O(g) \Rightarrow CO(g) + S_A$	Stck.	0.23	0	0
$S_B + S_D + O(g) \Rightarrow CO(g) + S_A$	Stck.	0.23	0	0
$S_B + 2S_A + OH(g) \Rightarrow CO(g) + S_A + S_H$	Stck.	0.28	0	0
$S_B + 2S_D + OH(g) \Rightarrow CO(g) + S_A + S_H$	Stck.	0.28	0	0
$S_B + S_A + S_D + OH(g) \Rightarrow CO(g) + S_A + S_H$	Stck.	0.28	0	0
Recombination				
$S_A + H(g) \Rightarrow S_H$	Stck.	0.90	0	0
$S_D + H(g) \Rightarrow S_H$	Stck.	0.90	0	0
$S_H + H(g) \Rightarrow H_2(g)$	Stck.	0.19	0	2310
$S_H + OH(g) \Rightarrow S_A + H_2O(g)$	Stck.	0.65	0	0
NO Reduction				
$S_B + S_A + NO(g) \Rightarrow CO(g) + 1/2N_2(g) + S_A$	Stck.	1.82	0	29800
$S_B + S_D + NO(g) \Rightarrow CO(g) + 1/2N_2(g) + S_A$	Stck.	1.82	0	29800

Whereas the mechanism in Table 2.3 works with SURFACE CHEMKIN, there is one additional complication. SURFACE CHEMKIN is normally used for catalytic reaction systems, in which the surface properties are fixed throughout the simulation. It also includes an etching simulation mode, in which the surface may either react away or grow by deposition. However, the assumption that the surface area and all other surface properties undergo negligible changes is embedded in this operating mode. This assumption fails to apply in coal flame simulations whenever the extent of soot oxidation is significant across a particular reactor in the equivalent network.

We circumvented this limitation with the following iterative calculation scheme: The total surface area of the soot in a reactor, A_{SOOT} , was first expressed in terms of a uniform specific soot surface area, a_{SOOT} , according to

$$A_{SOOT} = y_{P,SOOT}^{J+1} \rho_{TOTAL} V_{REACTOR} a_{SOOT} \quad 2.12$$

where $y_{P,SOOT}^{J+1}$ is the mass fraction of soot in the product stream leaving the reactor; ρ_{TOTAL} is the total density of material within the reactor; and $V_{REACTOR}$ is the reactor volume. The specific surface area was evaluated as $10 \text{ m}^2/\text{g}$ based on reported values for soots extracted from rich flames (Roessler et al., 1981), and fixed throughout the reactor simulation. The reactor volume is also fixed. The total density is only affected by the soot mass fraction, because purely homogeneous chemistry would not affect it under constant temperature and pressure. Consequently, A_{SOOT} from eq. 2.12 can only be determined after $y_{P,SOOT}^{J+1}$ has been specified. With continuously stirred tank reactors (CSTRs), the contents of the reactor have a uniform composition that equals the product stream composition. So $y_{P,SOOT}^{J+1}$ is the primary iteration variable, and A_{SOOT} is assigned from its current value. The initial trial for A_{SOOT} is based on the inlet composition, then successive iterations refine the trial with the calculated value for $y_{P,SOOT}^{J+1}$, until a convergence tolerance is satisfied. We use Brent's algorithm to expedite the convergence.

At each iteration the amount of soot that has been oxidized into combustion products is determined from the calculated product gas composition, in terms of the atomic (C/O)-ratio of the mixtures. The ratio in the product stream is related to that in the reactant stream as follows:

$$\left(\frac{C}{O}\right)^{J+1} = \left(\frac{C}{O}\right)^J + \frac{X_{SOOT} F_{SOOT}^J / 12}{y_O^J F_P^J / 16}$$

2.13

where superscripts J and $J+1$ denote inlet and outlet conditions, respectively; X_{SOOT} is the fractional soot burnout across the reactor; F_{SOOT} is the inlet mass flowrate of soot; F_P is the inlet mass flowrate of gases; and y_O is the mass fraction of oxygen in the inlet stream. Equation 2.13 can be rearranged into the following explicit definition for X_{SOOT} :

$$X_{SOOT} = \left[\left(\frac{C}{O}\right)^{J+1} - \left(\frac{C}{O}\right)^J \right] \frac{y_O^J F_P^J / 16}{F_{SOOT}^J / 12}$$

2.14

In the calculation sequence, the (C/O)-ratios are evaluated from the gas compositions from CHEMKIN, then inserted into eq. 2.14 to specify the extent of soot burnout. Then the burnout value is used to calculate the mass flowrate of soot leaving the furnace, which factors into the suspension loading of soot and the soot mass fraction within the reactor. The soot mass fraction enters into the updated estimate for the total area of soot within the reactor, according to eq. 2.12. When the procedure has converged, the assigned total soot area is consistent with the conversion and product composition, including soot conversion effects on both the total area within the reactor and the addition of carbon products to the gas phase.

2.2.4 Char Oxidation Mechanisms

Char burnout largely determines two of the most important emissions levels: LOI, through the efficiency of char oxidation, and NO_x , through the conversion of char-N. Each topic is described separately in the sections that follow, beginning with combustion efficiency.

2.2.4.1 CBK8

NEA's char oxidation submodel is the Carbon Burnout Kinetic (CBK) Model, which is a kinetics package that describes char oxidation under conditions relevant to pulverized fuel combustion processes. It has been developed by Prof. Robert Hurt both at Sandia National Laboratories, Livermore and, currently,

at Brown University. Detailed publications on the earlier versions of CBK are available (Hurt et al. 1995; Hurt et al. 1996; Hurt et al. 1997; Sun and Hurt 1997), although nothing in the literature describes CBK8, the latest version. The mechanism predicts the rate of burning, the char particle temperature, and the changes in the particle diameter and bulk density as combustion proceeds, given a complete description of the combustion environment; namely, gas temperature, radiative exchange temperature, and oxygen partial pressure. It is specially designed for carbon burnout applications, because it treats the late stages of char combustion in detail.

Within the theory, char reactivity is a dynamic function of heat treatment severity, based on a distributed activation energy model of thermal annealing. The theory uses mass-specific intrinsic kinetics, and earlier versions emphasized the statistical variability of intrinsic char oxidation reactivity. There is a standard model of the reaction/diffusion process within porous char particles, and the "one-film" description of the boundary layer processes to predict burning rates over a wide range of conditions, including Zone I, Zone II, and Zone III and their transitional regimes. The code also includes a model of the effect of ash inhibition in the late stages of combustion. Together, these mechanisms act to significantly reduce char conversion rates during the later stages of combustion, in accord with observations of very long reaction times for conversion of the last few percentage points of the char mass.

The reduction in char burning rates is seen clearly in Fig. 2-4. These curves show the radiant emission monitored from individual levitated char particles throughout their combustion histories. The hv bituminous coal and low volatility coal in the top panel exhibit near-extinction at 50 to 70 % burnout, when the burning rates and the particle temperature diminish continuously. This phenomenon is responsible for the characteristic "tail" of char combustion, which is a physical manifestation of the dramatically expanded times to convert the last portions of these chars. However, near-extinction is not observed with subbituminous or lignite chars or with various forms of biomass.

The transport rate of O_2 to the char surface is determined by bulk diffusion through an external boundary layer, in series with pore diffusion through an ash layer that forms over the char surface during the later stages, in series with pore diffusion through the pore system of the carbonaceous char core. These transport mechanisms must balance the consumption of O_2 in the chemical

mechanism for oxidation, which is represented with an nth-order global rate expression. CBK8 differs from CBK7 in that it contains an intrinsic formulation that allows a transition to Zone 1, in which O_2 completely penetrates the internal pore structure and both external film and intraparticle diffusion resistances are negligible. This can be important when overall burning rates are slow and/or particles are small, which occur naturally at lower temperatures or during the latest stages of combustion. The intrinsic formulation allows more accurate extrapolation

Figure 2-4. Radiance from burning levitated particles of bituminous coal chars (top), low rank coal chars (middle), and biomass chars (bottom).

of the primary high temperature data on which CBK is based to lower temperatures.

Although CBK is not specifically designed for predictions far outside the pc-combustion regime, it has been found to yield useful predictions at temperatures as low as 500 °C and is reasonably consistent with TGA data. As an option, the theory contains fuel-general correlations for each of the reactivity parameters, so that predictions can be made with only the proximate and ultimate analyses of the parent coal. This option is useful in many practical applications, as some of the CBK parameters are not readily available to users dealing with a new solid fuel.

CBK8 does not include statistical kinetics. This feature was omitted to ease implementation in other codes. CBK8 also includes a new submodel of the effect of ash on heat transfer during the late stages of combustion. The major changes from CBK7 to CBK8 are designed to provide a better description of extinction phenomena.

Whereas most of CBK's novel features pertain to the latest stages of burnout, the thermal annealing mechanism acts to destroy active oxidation sites before the char begins to burn. Chars are annealed during heat-up and devolatilization, and throughout combustion. The annealing kinetics are so fast that, practically speaking, the maximum temperature determines the extent of reduction of the intrinsic reactivity due to annealing. This aspect is evident in the simulations in Fig. 2-5. These cases consist of a 200 ms annealing period without oxygen, followed by char oxidation in 7% O₂ within a 1200 °C furnace. During the annealing period, the temperature of the reactor was set initially at either 1200, 1500, or 1800 °C, but midway through period, the reactor temperature was reduced to 1200 °C. This two stage annealing process ensured that the initial particle temperature at the onset of char oxidation was the same in all cases. In fact, all the initial conditions for char oxidation were the same, except that CBK8 reduced the burning rate constant according to a first-order rate law for the destruction of active sites.

As evident from the thermal histories and the residual mass profiles during burnout in Fig. 2-5, thermal annealing significantly diminishes char burning rates.

Hence, thermal histories prior to oxidation exert an impact on all subsequent stages of combustion.

Figure 2-5. Temperature histories and residual mass profiles for different annealing temperatures.

The essential tenets of the theory have been partially validated in an extensive evaluation against measured burnout profiles during the later stages of combustion of 8 coals in a drop tube furnace. The evaluations of the predicted impacts of variations in gas temperature, O₂ level, and particle size appear in Fig. 2-6. The ranges of each variable imposed in the tests covers the relevant domain of operating conditions in conventional p. f. firing. Yet the predictions are essentially within experimental uncertainty throughout.

Clearly, CBK8 depicts the impact of operating conditions within useful quantitative tolerances. However, the agreement in Fig. 2-6 could only be achieved by adjusting the initial char reactivity to match the behavior for one of the operating conditions. In other words, CBK's correlation of the initial reactivity of various chars (in terms of the carbon content of the parent coal) only captures the general trend with rank, not the sample-specific behavior.

Given a one-point calibration, CBK can accurately represent the char oxidation behavior of a particular coal over a wide domain of furnace operating conditions. But *a priori* predictions based only on a sample's proximate and ultimate analyses are subject to considerably larger uncertainties than in Fig. 2-6. Since we do not have drop tube data on the coals used in SRI's tunnel furnace, we must match the LOI at a particular operating condition by fitting the initial char reactivity parameter. This calibration issue is much less important for biomass, because the initial reactivity is usually high enough that these chars' burning rates are film diffusion-limited. In our calculations the same value is applied to chars from all forms of biomass.

2.2.4.2 Char-Nitrogen Conversion

Char-N conversion is the predominant contribution to exhaust NOX emissions in low-NOX firing systems, and at least as important as volatile-N conversion in high intensity combustion systems. Unfortunately, the reaction mechanism is only just now beginning to be unraveled, based on recent fundamental kinetics work. It will probably be a few years before these advances improve the status of applications modeling. In the meantime, we implement a

simple scheme based on a direct partitioning of char-N into NO and N₂. Char-N is converted at the rate of char burnout (from CBK8), and a portion is released as NO while the remainder contributes to N₂. The NO fraction is fixed throughout all

Figure 2-6. Evaluations of the predicted impact of variations in gas temperature (top), O₂ level (middle), and size (bottom) on the late-stage burnout of a hvA bituminous coal in a drop-tube furnace.

stages of burnout. Based on similar schemes in previous NO_x simulations, we expect approximately 40 % of char-N to be converted into NO.

2.2.4.3 Char-Oxidation Products

Even though the combustible material in char is mostly carbon, the char in p. f. flames contains non-negligible amounts of hydrogen, very significant amounts of nitrogen and, perhaps, trace amounts of sulfur and oxygen. The conversion of char-H into H₂O and char-S into SO₂ are unambiguous, and we can safely assume that char-O is released as O₂ because the amount being converted is inconsequential. Conversely, char-N conversion is so complex that it is best to adopt the simplest modeling strategy – fixed proportional conversion – as explained in the previous section. This leaves the primary product of the carbon oxidation to consider in more detail.

We know that when char particles in the p. f. size grade burn, the primary product of the carbon oxidation is CO. The CO is then subsequently oxidized to CO₂ in the gas phase as it is transported into the free stream. It is not clear how far from the char surface the CO burns, except that this distance shrinks with larger particles, and the CO oxidation moves into the boundary layer for sizes of the order of 1 mm.

The CO probably burns within about ten diameters of the char particle surface, and is unlikely to make it across the length scales for turbulent mixing into the free stream. This implies that the volume fraction of the furnace flow containing all the char and burning CO is still much less than unity. On this basis we set the primary product of carbon oxidation as CO₂, thereby lumping the heterogeneous chemistry with the near-particle homogeneous chemistry.

Based on these assignments of the char oxidation products, the moles of O₂ required per mole of combustibles in char is defined as

$$\nu_{O_2} = x_C + \frac{x_H}{4} - \frac{x_O}{2} + \frac{x_N}{2} F_{NO} + x_S \quad 2.15$$

where the x_i are the elemental mole fractions in char and F_{NO} is the fraction of char-N converted into NO.

2.3 Summary of Reaction Mechanisms

The main features of the reaction mechanisms included in our analysis are collected in Table 2.4. Collectively, these mechanisms enable the most comprehensive description of fuel quality impacts on p. f. combustion that has ever been assembled. The devolatilization submodel accommodates any coal and petroleum coke and the most widely used forms of biomass. Municipal solid waste, plastics, and rubbers are omitted at this stage, although FLASHCHAIN's basic reaction framework could probably be applied to these fuels as well. Primary devolatilization yields are predicted on a sample-to-sample basis, yet the only input requirements are the fuel's proximate and ultimate analyses. The distribution of primary devolatilization products is resolved into molecular species for gases, plus char and tar and their respective elemental compositions, and the tar MWD. In coal flames, the complex slate of primary products is very rapidly transformed into only a handful of fuel compounds (soot, CO, H₂, CH₄, C₂H₂, and HCN). Our submodel for secondary volatiles pyrolysis represents this transformation, albeit as instantaneous.

The yield and C/H/O/N/S composition of char are determined by FLASHCHAIN[®]. The coal char particle size is estimated from a correlation for swelling factor in terms of the C- and H-contents of the parent coal; biomass chars contract during devolatilization. Bulk particle densities are assigned from the yield and size, whereas the carbon densities are assigned from another correlation.

The homogeneous reaction mechanism for volatiles combustion and volatile-N conversion is believed to be the most comprehensive available for this application. No approximations of any kind are invoked in this submodel, and all the gases that survive secondary volatiles pyrolysis are included. The volatile-N conversion mechanism is also complete and validated for simulations across a broad range of stoichiometric ratio.

In the soot chemistry submodel, we introduced a new elementary reaction mechanism that reproduces NSC-kinetics over the full domain of p. f. flame conditions. The oxidation by O₂ was combined with reaction steps for oxidation

by OH and O-atoms, for recombination of OH and H-atoms, and for NO reduction. This submodel is also believed to be as comprehensive as any in the literature for p. f. flame applications.

Table 2.4. Features of the Reaction Mechanisms.

Devolatilization	
Fuel Type	Any coal or petroleum coke and most forms of biomass (woods, grasses, paper, and agricultural residues).
Yields	Sample-specific predictions from FLASHCHAIN [®] based on only the proximate and ultimate analyses.
Composition	Gases resolved as molecular species. C/H/O/N/S compositions of char and tar.
Secondary Volatiles Pyrolysis	Represents instantaneous soot production from tar with simultaneous release of CO, H ₂ , and HCN and destruction of all hydrocarbons except CH ₄ and C ₂ H ₂ .
Char Properties	
Composition	C/H/O/N/S composition from FLASHCHAIN [®] .
Size Changes	Swelling-factor correlation assigns the char PSD from the fuel PSD.
Bulk Density	Determined from volatiles yield and the swelling factor correlation.
Carbon Density	Correlated with the C-content of the parent coal.
Homogeneous Chemistry	
444 elementary reactions among 66 species, including all products of secondary volatiles pyrolysis and N-species.	
Soot Chemistry	
Oxidation	NEA's four-step elementary reaction mechanism for oxidation by O ₂ matches NSC kinetics. Simultaneous oxidation by O and OH.
Recombinations	Recombinations of H into H ₂ and OH into H ₂ O.
NO Reduction	Single quasi-global process.
Char Burnout	
Oxidation	Burnout based on CBK8, which represents transitions through all combustion regimes, thermal annealing, and ash encapsulation. Initial oxidation rate for a coal char should be calibrated with data.
Char-N Conversion	The fixed portion of char-N converted into NO at the nominal burning rate should be calibrated with baseline NO _x emissions.

CBK8 is our char burnout submodel. Its annealing and ash encapsulation mechanisms are essential to accurate descriptions of the later stages of burnout, particularly the “burnout tail” that exhibits disproportionately long times for conversion of the final 10 % of combustibles. CBK8 also depicts the impacts of variations in size, O₂ level, and gas temperature within useful quantitative tolerances. But the correlation to specify the initial char reactivity in terms of the C-content of the parent coal can only represent the gross trend across the rank spectrum, not the sample-to-sample variability. Consequently, our flame simulations will need to be tuned-in to match LOI for a baseline operating condition.

The submodel for conversion of char-N must also be calibrated against baseline NO_x emissions, because a fixed fraction of char-N is converted into NO throughout all stages of char burnout. The rate of char-N conversion is assigned as the overall rate of char oxidation from CBK.

These features are demonstrated in detail in simulations of SRI’s tunnel furnace in Chapter 3.

3.0 P. F. FLAME SIMULATIONS

3.1 Introduction

The simulations in this chapter illustrate the fuel quality impacts in SRI's single-burner tunnel furnace. This flame is a good test bed for characterizing the fuel quality impacts in detail, because the furnace flow is free of the subtleties of swirling, recirculating flow fields. The operating conditions have been extensively validated against several full-scale T-fired furnaces operated by Southern Company Services (Monroe et al., 1995). Because the swirl intensities were kept well below the threshold for internal recirculation into the burner core, this flame behaves like a single helical fuel jet moving upward through a fireball in a much larger T-fired furnace, at least from the standpoint of emissions.

Ultimately, we plan to explicitly determine the properties of our equivalent reactor networks from CFD simulations. But not all the information needed to completely specify a network for this facility is available at the present time. We do have one baseline CFD simulation (prepared by Reaction Engineering International, Salt Lake City) that provides temperature profiles and nominal residence times in the various regions of the flame. The assigned values are reasonable but not quantitatively exact for all the simulations in this report. Our intent is to first show that the simulations based on the reactor network behave properly for various mixing conditions, and then to propose a mechanistic basis for fuel quality impacts for a wide range of fuel properties, including hv bituminous and Western subbituminous coals, their blends, and bituminous coal co-firing with switchgrass.

The furnace and equivalent network are described in the following two sections, as a preface for the simulations in the rest of this chapter.

3.2 Tunnel Furnace

The cylindrical tunnel furnace is sketched in Fig. 3-1. The structure of this flame comprises the following five elements:

- (1) Core (CR) – Since the swirl is weak, the primary air and fuel stream remains intact for several meters, and this flame core retains virtually all the fuel particles.

Figure 3-1. Flame structure within SRI's tunnel furnace with weak swirl.

- (2) Mixing layer (ML) – Secondary air contacts the air in a mixing layer that remains thin over most of the core length, but then fans out over the entire cross section beyond the tip of the core. Almost all the secondary air mixes with the core flow downstream of the core tip.
- (3) ERZ - A relatively thin external recirculation zone (ERZ) fills the upstream furnace corners, pulling products from the mixing layer into the upstream secondary air stream.
- (4) SOFA Zone – Downstream of the mixing layer, tertiary air is injected as a separated overfire air (SOFA) stream through four off-radius jets. Some eddies alter the gas flow streamlines near the injection ports but particle trajectories are hardly affected by the OFA flows.
- (5) Burnout (BO) Zone – Several seconds of residence time are available for the later stages of char oxidation downstream of the SOFA injectors, before the exhaust passes through a convective section and exhaust cleaning systems.

Perhaps the most remarkable feature of this furnace is that its near-burner flame structure has the same elements as a laminar gaseous diffusion flame. Also, there is very little particle dispersion off the centerline, even through the SOFA zone.

The nominal conditions for each flame region are collected in Table 3.1 based on a CFD simulation with hvA bituminous coal. The core of this flame lasts an unusually long time, due to the weak swirl. Consequently, there is sufficient time for fuel particles to fully devolatilize within the core, then to have the volatile-N species reduced by residual volatiles and soot. The duration in the mixing layer is based on the residence time from the attachment point of the ERZ to the SOFA injectors. Residence times within the much thinner mixing layers surrounding the core from the burner outlet to the attachment point are much shorter than this nominal value. The SOFA zone is not visibly distinct from the BO zone. The residence time in Table 3.1 is based on the mixing time imposed in the simulations, which is not critical because all the volatiles and soot were burned out before this point in the furnace.

Table 3.1. Nominal Operating Conditions in Various Flame Zones.

Flame Region	Residence Time, ms	Temperature, °C	S. R.
Core	250	80 – 1520	0.25
Mixing Layer	470	1520 – 1350	0.95
SOFA Zone	170	1350 – 1225	1.12
Burnout Zone	1,910	1225 – 1050	1.12

The S. R. values in Table 3.1 are nominal values based on complete combustion of the fuel by primary air in the core; by primary plus secondary air in the mixing layer; and by the primary, secondary, and tertiary air streams in the SOFA and BO zones.

The axial temperature profiles on the centerline and averaged over the cross section appear in Fig. 3-2. The maximum temperature appears between the core and mixing layer, because the heat release from combustion of residual

volatiles, soot, and char is greatest at that point. The flow abruptly cools at the SOFA injectors, then cools at essentially a constant rate into the convective section.

Figure 3-2. Axial temperature profiles along the tunnel furnace on the centerline (dashed curve) and averaged over the cross section (solid curve).

3.3 Equivalent Reactor Network

At this point the CFD simulations have been analyzed for the regions in the flame structure, the nominal residence times in each region, and the temperature profiles across each region. In a complete application of the methodology for equivalent reactor networks, the CFD simulation would next be analyzed with particle tracking techniques to determine the residence time distributions within each element, and a conserved scalar field would determine the quantitative mixing rates among the various elements. Such detailed information is not currently available for this flame. So we proceed by using

simple CSTRs-in-series for each flame region, and by setting the mixing rates for the secondary and tertiary streams to yield plausible emissions.

3.3.1 CSTR Network

The CSTR network for the four regions of the flame that contain fuel particles appears in Fig. 3-3. The ERZ was omitted because it is not strong enough in this furnace to entrain fuel particles and, also, because its extent was fairly small. In Fig. 3-3, the core has been subdivided into two regions. The devolatilization zone covers the upstream portion of the core in which volatiles are being released from the fuel suspension and burned with primary air. Since the primary air stream is extremely reducing, no residual O_2 leaves the devolatilization zone. The NO_x reduction zone covers the downstream portion of the core in which only the N-species are converted under the influence of water gas shifting, due to the absence of oxidizers. The CSTR-series for the mixing layer and the SOFA zone represent the mixing of secondary and tertiary air streams, respectively. But there are no additional flows into the CSTR-series for the BO zone.

3.3.1.1 Temperature Assignments

Note that the streams into the devolatilization zone consist of separate flows of volatiles and char. These flows were determined by first assigning a temperature profile across the entire region, making sure that the period was longer than the primary devolatilization time. Then the devolatilization history was subdivided into increments in time, where each increment equaled the nominal residence time of one CSTR in the series of four. The temperature profile was also segmented into four stages, and each stage was assigned a temperature that was determined by averaging the temperature profile over the time increment under consideration.

The process for assigning temperature across the CSTR-series is illustrated in Fig. 3-4. The CFD-based profile exhibits a plausible form, except for the 10 ms lag at the fuel injection point. This feature was deliberately eliminated from the thermal history assigned for the PC Coal Lab[®] simulation of primary devolatilization, which otherwise has a similar heating rate and the same ultimate temperature through 80 ms. Note especially that the four average values are stages of the continuous profile used in PC Coal Lab[®]. The staged temperatures

Figure 3-3. Sequence of CSTR-Series for 2 core-regions, the mixing layer, SOFA zone, and BO zone.

Figure 3-4. Temperature profiles across the devolatilization zone based on a CFD simulation (dashed curve), a devolatilization simulation with PC Coal Lab® (solid curve), and average values for 4 CSTRs-in-series (dashed columns).

are only used to simulate the chemistry in the gas phase involving soot and volatiles. In other words, a continuous thermal history is used in PC Coal Lab® to determine the Lagrangian particle history, whereas the four incrementally averaged values are used in the simulations of the four CSTRs-in-series.

In a similar sense, the incremental yields of all secondary volatiles pyrolysis products during each of the four CSTR residence time increments were assigned from the continuous devolatilization history, based on the continuous simulation with PC Coal Lab®. These yields were converted to incremental rates of volatiles addition to each CSTR in the series with the total fuel feedrate into the furnace. No volatiles are released into the NO_x reduction zone, by definition.

The properties of char entering the core were assigned as the ultimate char properties, from the PC Coal Lab® results for the end of primary devolatilization. It is an approximation to ignore the evolution of char properties in time, but a very good one because the temperatures in the first few reactors are generally too low to sustain any char oxidation anyway.

3.3.1.2 Entrainment Rates

The operating conditions for the CSTR-series in the mixing layer and SOFA zones were assigned with similar procedures. The CFD-based temperature profile was again resolved into increments for the nominal residence times of each CSTR. The addition rates of secondary and tertiary air were based on either of two simple mixing models, whose behavior is illustrated in Fig. 3-5. The curves in this figure depict the volumetric air entrainment rate at each point downstream of a common injection point. For jets in co-flow, the entrainment volume grows with distance from the injection point, according to the following functional form:

$$F_E = \exp(\beta_M(t - \tau_M)) - 1 \quad \text{for } t \geq \tau_M \quad 3.1$$

where F_E is the fraction of the air stream that has been entrained into the process flow to time t ; τ_M is a time lag equal to the nominal residence time to the injection point; and β_M is an empirical constant. According to eq. 3.1, the entrainment rate grows with distance from the injection point until the entire secondary stream has been entrained.

For jets in cross-flow, the entrainment volume diminishes with distance from the injection point, according to:

$$F_E = 1 - \exp(-\beta_M(t - \tau_M)) \quad \text{for } t \geq \tau_M \quad 3.2$$

According to this relation, the entrainment rate diminishes with distance from the injection point until the entire secondary stream has been entrained.

Once one of these mixing models was assigned to all air streams in the furnace, their adjustable parameters were assigned to predict reasonable emissions for the baseline cases under consideration. (Eventually, the

Figure 3-5. Entrainment volumes for two limiting mixing models versus distance from the point of injection.

entrainment rates will be specified from the conserved scalar field in the CFD simulation, then fit to one of the mixing models to assign these parameters.) Then the continuous profile of entrainment rate versus distance from the injection point was resolved into increments for each of the residence times of each CSTR in the series. Whereas the time lag, τ_M , could be assigned directly from the residence times in the CFD simulations, β_M was freely adjusted to illustrate the impact of variable mixing intensities on the furnace emissions.

3.3.2 The Competition for Oxygen

The generic reactor element in the equivalent network appears schematically in Fig. 3-6.

Figure 3-6. Schematic diagram of a single CSTR element in the equivalent network.

Each CSTR in the network is fed by the following three feedstreams:

F_j^C – the inlet char flow into the j th CSTR.

F_j^P – the inlet flow of gaseous fuels and combustion products plus soot into the j th CSTR.

F_j^E – the entrained flow into the j th CSTR.

Outlet flows of char and combustion products, plus residual gaseous fuels and soot, become inlet flows into the next CSTR in the series. According to the material balance imposed on the CSTR, the outlet product stream consists of the inlet product stream plus the entrained flow plus the gaseous products of soot and char oxidation, after they have been converted by homogeneous chemistry in the CSTR. In the devolatilization zone, the entrainment flow consists of volatiles; in all other downstream zones, it consists of air. Generally speaking,

the entrainment flow into any CSTR element can have any composition, including that of recirculated intermediates and combustion products.

The key organizational principle is the competition for O₂ among chemistry in the gas phase versus char oxidation. The following oxygen balance must be satisfied in every CSTR in the series:

$$F_j^E y_{O_2,j}^E + F_j^P y_{O_2,j}^P - F_{j+1}^P y_{O_2,j+1}^P = \frac{\Delta X_j^C F_0^C (1 - x_0^A) \nu_C}{M_C'} - M_{O_2} V_j \omega_{O_2} \quad 3.3$$

where subscript j denotes the index on the CSTR under consideration; superscripts E , P , and C denote entrainment, gaseous product, and char flows, respectively; and y^I denotes the oxygen mass fraction in stream I . Hence, the terms on the left of eq. 3.3 represent the net efflux of O₂ from the j th CSTR. The two terms on the right represent the O₂ consumed by char oxidation and by oxidation of gaseous fuels and soot, respectively. The consumption term for char oxidation is written in terms of the burnout predicted by CBK8 for the residence time increment of the j th CSTR, ΔX_j^C , and the flowrate of ash-free combustibles into the furnace, $F_0^C(1-x_0^A)$. The stoichiometric O₂ requirement, ν_C , and the char molecular weight, M_C' , account for the presence of heteroatoms in the char combustibles. The consumption term for oxidation of gaseous fuels and soot incorporates the molar rate of O₂ consumption per unit volume from CHEMKIN and SURFACE CHEMKIN, ω_{O_2} . This value is determined automatically by the CHEMKIN routines. It is converted to a mass basis by multiplying by the molecular weight of O₂, M_{O_2} , and the CSTR volume, V_j .

Since the composition within a CSTR is uniform and equal to the outlet composition, the only unknown in the oxygen balance in eq. 3.3 is the outlet mass fraction of O₂. In other words, given a value for $y_{O_2,j+1}^P$, the mechanisms in CBK8 and in the soot and homogeneous chemistry submodels can be used to evaluate the incremental char burnout level and the O₂ consumption rate by combustion of gaseous fuels and soot. Note especially that our analysis does not determine the apportioning of O₂ among the various fuels in this reaction system in advance, or through any imposed constraints. The kinetics for oxidation of soot, char, and gaseous fuels govern O₂ apportioning, as in actual p. f. flames. This feature can only be implemented in the context of an equivalent

network, because detailed reaction mechanisms are only feasible within this context.

3.3.3 Numerical Simulation Strategy

Of course, the numerical analysis of the multitude of chemical reaction rates included in our analysis is not trivial. Reasonably stable simulations have been obtained with the following procedure: First, the feasible range of ΔX_j^C is evaluated from zero to the burnout associated with the inlet value of $y_{O_2,j}^P$, omitting all conversion of gaseous fuels and soot. This range is input into a root finder based on Brent's algorithm. At each step in this iteration, the inlet gas composition is first adjusted for the consumption of O_2 and production of CO_2 , H_2O , NO , and N_2 that are associated with the trial burnout level. This fictitious gas composition is then input into a CHEMKIN/SURFACE CHEMKIN simulation for the simultaneous oxidation of gaseous fuels and soot. Actually, each call to CHEMKIN involves a second iteration loop to determine the total area of soot in the exhaust. Trial values are converged in a second application of Brent's algorithm. The outlet O_2 level from the CHEMKIN simulation is used in another char oxidation run with CBK8. When the updated value for the incremental burnout level matches the trial value, the CSTR simulation satisfies the O_2 balance in eq. 3.3, and the calculation sequence moves forward to the next CSTR in the series.

Simulations with 40 CSTRs generally converge for the relevant range of S. R. values in actual p. f. flames. We expect the convergence for diverse fuels and fuel blends to improve as we gain more operating experience. Each simulation with a network of 40 CSTRs takes about 15 minutes on a P4 microcomputer operating at 1.5 GHz.

3.4 Simulation Case Studies

The domain of mixing and staging conditions for the case studies in this report are collected in Table 3.2. The S. R. values are nominal values based on combustion of the entire coal phase with each of the three air streams. The mixing rates are for the jet in co-flow mechanism for all streams. The time lags were estimated directly from the CFD simulation. The baseline case imposes a rate of 3.5 s^{-1} on the secondary air stream, and the other two cases are examined parametrically. Most cases are staged, with all tertiary air injected as SOFA. An unstaged case, in which all tertiary air is mixed with the secondary air

stream, will also be considered. The fractions of the secondary and tertiary air streams entrained for the various mixing cases appear in Fig. 3-7. The abscissa in this plot is an index on each CSTR in the respective series. For example, in the baseline case for secondary air mixing, secondary air is injected into the first five CSTRs in the CSTR-series for the mixing layer. The slow mixing case involves 7 CSTRs, whereas the fast mixing case involves only 3. Tertiary air is mixed into each of the 4 CSTRs in the CSTR-series for the SOFA zone.

Table 3.2. Mixing and Staging Conditions in the Case Studies.

Flame Region	S. R.	Mixing Rates	
		τ_M , ms	β_M , s ⁻¹
Primary Flow	0.25	-	-
Secondary Air	0.95	250	1.5, 3.5, 5.5
Tertiary Air	1.12	720	5.0

The total simulation time for all cases was 1.61 s. This period is shorter than the 2.8 s residence time to the convective passes, because our intent is to resolve emissions production in the near-field. Consequently, the predicted LOI values are much higher than the exhaust levels but, nevertheless, more useful from a comparative standpoint.

The fractional conversion of char-N into NO was 0.40 for all cases except in the sensitivity studies of this parameter. Similarly, the initial char reactivity was assigned from the correlation in CBK8, except in a single sensitivity run. All other parameters in the simulations are based on the proximate and ultimate analyses of the fuels, which are collected in Table 2.1.

We first consider the baseline case with the hvA bituminous coal, then examine parametric variations in the secondary air mixing rate, staging level, and the sensitivity to the char-N conversion fraction and the initial char reactivity. Additional cases characterize the flame structure and performance for the subbituminous coal and blends of bituminous and subbituminous.

Figure 3-7. Entrainment profiles for various mixing rates for secondary (top) and tertiary (bottom) air streams.

3.4.1 High Volatile Bituminous Coal Flames

3.4.1.1 Baseline Flame Structure

The flame structure will be illustrated with axial profiles of gas properties, including the concentrations of O_2 , CO , H_2 , HCN , NH_3 , and NO plus the S. R. value, and the extents of burnout of soot and char. The S. R. value pertains to the gas phase only, and is based on the total amount of all fuel species that have been added to the gas phase up to a specific location in the furnace, including the combustibles in oxidized soot and char. These profiles are plotted versus the CSTR-No. in the series for the furnace. Recall that the first 8 CSTRs represent the flame core, with 4 each for the devolatilization zone and for the NO_x reduction zone; the next 11 represent the mixing layer; the next 4 represent the SOFA zone, and the final 17 represent the first part of the burnout zone. The first 4 CSTRs each have nominal residence times of 20 ms, whereas all the rest have residence times of 42.5 ms.

The baseline flame condition imposes a moderate mixing rate of secondary air on the hv bituminous primary flow, and includes approximately 15 % of the total combustion air as SOFA. The overall S. R. value is 1.12.

The predicted structure of the flame core appears in Fig. 3-8. Roughly 75 % of the volatiles are released into the first CSTR, and almost all the remainder are released into the second. Only minor amounts of CO , H_2 , and HCN are released into the third and fourth CSTRs. But the temperature of the first CSTR is too low for volatiles ignition. All hydrocarbons and nearly all the H_2 burn in the second and third CSTR, while CO accumulates as a partial oxidation product across the entire zone.

Since the overall S. R. value for the flame core is only 0.21, we are inclined to expect N-species conversion under extremely rich conditions in the flame core. Actually, The S. R. value for the gas phase is as large as 1.8 while volatiles are being released. Then it diminishes during volatiles combustion to a steady level of 0.87, which is more than four times larger than the nominal value based on combustion of the entire coal phase. This discrepancy is due to the incomplete conversion of coal into volatiles, the abundance of soot in the volatiles from this hvA bituminous coal (which do not factor into the S. R. value), and the consumption of the available O_2 by the oxidation of soot and char.

Figure 3-8. Profiles of O_2 , gaseous fuels, and S. R. (top), extents of soot and char oxidation (middle), and N-species (bottom) for the flame core in the baseline hvA bituminous flame.

Whereas only a few percent of soot burn in the flame core, nearly 15 % of the char is consumed. Two factors are responsible for the surprisingly high extent of char oxidation. First, only the finest sizes in the char PSD effectively compete for the available O_2 with the gaseous fuel compounds (as seen below in Fig. 3-10), because film diffusion rates are inversely proportional to size. Second, the intrinsic char oxidation reactivity remains relatively very high while the char is being heated because annealing and the associated reduction in reactivity only occur near flame temperatures.

Obviously, the N-conversion chemistry expected for the nominal S. R. value does not materialize within the flame core. The NO concentration initially surges above 300 ppm due to the rapid conversion of HCN, the primary volatile-N species, in the lean core inlet section. But once the available O_2 is consumed, the NO concentration is reduced to only 20 ppm across the 4 CSTRs in the NO_x reduction zone, while HCN gives way to NH_3 as the primary N-species. Clearly, the identity of the primary volatile-N species is inconsequential, because homogeneous chemistry rapidly interconverts any volatile N-species into a mixture of HCN, NH_3 , and NO. Also, note that in addition to the N-conversion chemistry, the NO_x reduction zone sustains sufficient water-gas shifting to nearly double the CO concentration.

Profiles from the mixing layer to the inlet to the SOFA zone appear in Fig. 3-9. This region has the highest temperatures in the flame, plus the addition of all secondary air. As soon as secondary air is injected, the S. R. value in the gas phase exceeds unity and remains firmly in the lean regime for the rest of this flame. Soot and CO are completely burned out in the first 3 CSTRs. Thereafter char oxidation is the only combustion process in the flame. Fortunately, residual HCN and NH_3 from the flame core are eliminated while the gas phase is reducing, so less than a quarter of these volatile-N species are converted into NO. Nevertheless, the NO concentration leaving the mixing layer is 400 ppm.

The profiles across the SOFA and burnout zones remain the same. The gas phase becomes even more oxidizing with the injection of tertiary air. Since soot and CO are no longer present, char oxidation determines the O_2 concentration. The O_2 mass fraction became as large as 4 % at the outlet of the SOFA zone, but then gradually decayed to 3.5 % while char burned across the burnout zone. The only fixed-N species across both zones was NO. The NO

Figure 3-9. Profiles of O₂, CO, and S. R. (top), extents of soot and char oxidation (middle), and N-species (bottom) for the mixing layer in the baseline hvA bituminous flame.

Figure 3-10. Predicted extents of char burnout versus size increment in the char PSD at the outlets of the mixing layer, SOFA zone, and burnout zone.

concentration fell by dilution across the SOFA zone, but slowly increased with the conversion of char-N. The final value in this simulation was 406 ppm.

Additional information on the extents of char burnout as a function of size increment in the PSD is resolved in Fig. 3-10. This figure shows the burnout levels across the 10 size increments in the simulations at the outlets to the flame core, mixing layer, and burnout zone. Only the smallest char particles effectively compete for the available O_2 in the flame core. The entire char PSD is ignited in the mixing layer, yet an acute size dependence persists. At the outlet of the burnout zone, char particles smaller than 100 μm are completely burned out but the largest sizes are only 50 % converted. Clearly, LOI is determined by the combustion behavior of the largest sizes in the char PSD in furnaces such as this one, where all fuel particles remain on the centerline within a core of hot combustion gases and none bypass the main flame zones.

3.4.1.2 Mixing Rate Variations

The NO emissions and extents of char burnout across three flame regions are collected for various mixing conditions in Table 3.3. All cases have the same flame core, and the same basic flame structure as the baseline flame in Figs. 3-8 and 3-9. The extents of soot oxidation were at least 96.9 % for all mixing conditions and all flame regions. The same furnace temperature profile was imposed in all cases. The total residence time was fixed at 1.61 s for all cases, which is significantly shorter than the 2.8 s time to the convective passes in the furnace. The main variation was in the intensity of the secondary air mixing. As shown in Fig. 3-7, secondary air is injected in 3 CSTRs in the fast mixing case, in 5 CSTRs in the baseline, and in 7 CSTRs in the slow mixing case. The final mixing condition combines the tertiary and secondary air streams from the baseline flame into a single secondary air stream, and injects the combined stream at the baseline mixing rate.

Table 3.3. NO Emissions and Char Burnout for Various Mixing Conditions.

	Mixing Layer		SOFA Zone		Burnout Zone	
	NO, ppm	X _C , %	NO, ppm	X _C , %	NO, ppm	X _C , %
Baseline	402	78.0	370	82.7	406	89.9
Slow 2 ⁰	221	60.6	259	74.2	337	89.2
Fast 2 ⁰	473	80.4	426	84.1	456	90.0
3 ⁰ →2 ⁰	406	86.7	414	88.3	429	91.3

The mixing intensity significantly affects predicted NO concentrations and extents of char burnout, as it should. NO emissions from the mixing layer increase from 221 to 473 ppm as the mixing intensity for secondary air is progressively increased over the range in Table 3.3. Extents of burnout increase from 60.6 % to 80.4 % over the same range, although the difference between the baseline and fast mixing case is almost negligible. The predicted range of NO emissions shrinks to 167 ppm (426-259) at the outlet of the SOFA zone, and to 119 ppm (456-337) at the outlet of the burnout zone. Whereas the impact of mixing intensity persists across the entire furnace, the predicted extents of char burnout become essentially the same for all three mixing cases.

The case that combined the tertiary stream with secondary air has the same NO emissions at the mixing layer outlet but a significantly higher extent of char burnout. This is potentially deceptive because the NO emissions without SOFA already reflect dilution by the total air stream into the furnace, whereas the baseline emissions remain to be diluted by a SOFA addition. Consequently, NO emissions for the unstaged case are predicted to be higher than the baseline by 44 ppm at the SOFA zone outlet, and by 23 ppm at the burnout zone outlet. The outlet extent of char burnout is predicted to be 1.4 % higher for the unstaged case.

3.4.1.3 Sensitivity Aspects of Char Conversion

The most important aspects of fuel quality that cannot yet be specified from standard coal properties within useful quantitative tolerances are the fractional char-N conversion to NO, and the initial char oxidation reactivity. These parameters were varied in the cases reported in Table 3.4, while all other baseline operating conditions were retained. NO emissions are increased in direct proportion to increases in F_{NO} , the char-N conversion fraction. Over the range of F_{NO} from 0.30 to 0.50, the predicted NO emissions increase from 322 to 482 ppm across the mixing layer, from 291 to 440 across the SOFA zone, and from 318 to 486 ppm across the burnout zone. Clearly, this parameter is an important scaling factor for NO emissions.

Table 3.4. Sensitivity of NO emissions and Char Burnout to Char Conversion Parameters.

	Mixing Layer		SOFA Zone		Burnout Zone	
	NO, ppm	X _C , %	NO, ppm	X _C , %	NO, ppm	X _C , %
$F_{NO} = 0.30$	322	78.1	291	82.9	318	90.1
$F_{NO} = 0.40$	402	78.0	370	82.7	406	89.9
$F_{NO} = 0.50$	482	78.0	440	82.9	486	90.1
$A_C = 2.5A_C^{COR}$	353	80.1	327	85.5	356	91.3

We were surprised to find that the initial char reactivity also exerts a strong impact on the predicted NO emissions. When the baseline reactivity was increased by a factor of 2.5, NO emissions decreased by 50 ppm across the mixing layer and burnout zone, and by 40 ppm across the SOFA zone. The reason is that the extent of char burnout across the flame core increased from 14.5 to 26.3 %. Recall that virtually all of the NO formed during volatiles combustion is reduced by the outlet of the flame core. When more char-N is released as NO in the core, it will be reduced away plus there is less residual char-N to be released as NO in downstream flame zones. So NO emissions from all succeeding flame zones are lower. Of course, the predicted extents of char burnout increased for the higher initial char reactivity, but the enhancement was only 1.2 % at the outlet of the burnout zone.

3.4.2 Fuel Quality Impacts

3.4.2.1 Subbituminous Coal Flames

A subbituminous coal was simulated at the same macroscopic operating conditions as the baseline bituminous flame, including the same coal PSD. Coal and air flowrates were adjusted to impose the nominal S. R. values in Table 3.1 across all flame zones, and the temperature profile from the CFD simulation of the bituminous coal flame was implemented without adjustment. The only deviation is that the mixing parameter had to be reduced to 3.2 from 3.5 s⁻¹ in the baseline subbituminous flame, to circumvent a convergence problem. The char-N conversion fraction was 0.40. Hence, our intent is to determine how the reaction mechanism shifts to affect NO emissions and extents of char burnout, with special regard for the much higher initial reactivity of subbituminous chars.

The predicted flame structure was the same as the baseline hvA bituminous flame's. The main difference in the near-burner region was the much higher extent of burnout at the outlet of the flame core; i.e., 40.2 % vs. 14.5 %. Like the bituminous flame, very small levels of NO left the flame core despite significant production during volatiles combustion. But the 12.3 % CO concentration leaving the core was nearly six times higher than with the hvA bituminous, due to more extensive water-gas shifting. Soot and CO burned out at the inlet to the mixing layer, albeit with more effective competition for the available O₂ from char oxidation.

The emissions and burnout levels for the downstream flame regions are collected in Table 3.5. The predicted NO emissions are essentially only half those across the baseline bituminous coal flame. The predicted extents of burnout are higher, but only by 1.7 % at the outlet of the burnout zone.

Table 3.5. NO Emissions and Char Burnout for Whole and Blended Subbituminous Flames.

	Mixing Layer		SOFA Zone		Burnout Zone	
	NO, ppm	X _C , %	NO, ppm	X _C , %	NO, ppm	X _C , %
<i>Staged Flames</i>						
hvA Bit.	402	78.0	370	82.7	406	89.9
Subbit.	207	81.5	194	86.8	208	91.6
75% Bit/25% Sub	356	77.7	330	82.6	365	89.9
		75.5/86.9		80.9/89.7		89.4/92.2
70% Bit/30% Sub	339	77.6	314	82.5	348	89.9
		74.9/86.5		80.3/89.5		89.2/92.1
<i>Unstaged Flames</i>						
hvA Bit.	406	86.7	414	88.3	429	91.3
90% Bit/10% Sub	394	86.2	-	-	419	91.1
		85.8/91.0				91.0/92.4
75% Bit/25% Sub	366	86.9	-	-	387	91.3
		85.9/91.0				91.1/92.4

We would expect lower NO emissions from coals of progressively lower ranks of coal, but perhaps not by the reduction seen in these simulations. However, several factors act in concert to dramatically reduce the NO emissions from the subbituminous flame. The coal-N content is only two-thirds of the level in the bituminous coal. This particular subbituminous sample also has an exceptionally high H-content (at 6.4 daf wt. %), which elevates both its total volatiles yield and the soot yield, compared to typical values with this rank. These factors lower NO emissions by subjecting more of the coal-N to the reducing conditions in the downstream flame core, and by adding more surface area for NO reduction and radical recombinations on soot. Compounding these effects, the higher char oxidation reactivity also releases char-N as NO for fast

reduction in the downstream flame core. Collectively, these mechanistic shifts substantially lower NO emissions from this flame.

3.4.2.2 Blended Subbituminous/Bituminous Coal Flames

Flames of blends of the hvA bituminous and subbituminous coals were simulated for the baseline operating conditions, and also for unstaged flames (in which tertiary and secondary air streams were combined and injected at the baseline mixing rate for secondary air). The air and fuel flowrates were adjusted to impose the nominal S. R. values in Table 3.1 across all flame zones, and the temperature profile from the CFD simulation of the bituminous coal flame was implemented without adjustment.

The predicted flame structure was the same as the baseline hvA bituminous flame's, attenuated by tendencies seen in the structure of the subbituminous coal flame. The most important new feature in flames of coal blends is that the more reactive char wins the competition for the available O₂, so the unburned carbon in ash tends to be enriched in the least reactive char. Such behavior is evident in the predicted extents of burnout for both of the char PSDs in a flame fed with a 75%/25% blend of hvA bituminous and subbituminous coal, in Fig. 3-11. Extents of burnout are significantly higher for the subbituminous char at the outlets to the core, mixing layer, and burnout zone. The most important difference is at the outlet to the burnout zone, where even the largest size cut of the subbituminous char shows 30% more burnout. And compared to the baseline hvA bituminous flame, the burnout of the largest size cut is 2.5 % lower at the burnout zone outlet. This difference would affect LOI values if the remaining residence time in this furnace was insufficient to completely burn out these chars, which is likely to be the case.

The emissions and burnout levels for the downstream flame regions for several blended flames are collected in Table 3.5. For the staged flames, the predicted NO emissions in all flame regions are only about 10 ppm higher than the estimates based on arithmetical additivity with the pure coal values. The total extents of burnout are either equal to or only slightly lower than the baseline values for the hvA bituminous flame. However, the two values separated by a slash in Table 3.5 are the predicted extents of burnout for the bituminous and subbituminous chars, respectively. The bituminous char values show lower extents of burnout by about 2 % across the mixing layer and SOFA zone than in

the baseline flame. But the difference is much smaller at the outlet of the burnout zone. These same features are evident in the predictions for the unstaged blended flames in Table 3.5.

Figure 3-11. Predicted extents of char burnout versus size increment in the PSDs of hvA bituminous (solid curves) and subbituminous (dashed curves) chars at the outlets of the mixing layer, SOFA zone, and burnout zone in a 75%/25% bituminous/subbituminous blended flame.

3.4.2.3 Biomass Co-Fired Flames

Biomass releases much more CO than any coal during secondary volatiles pyrolysis, along with more hydrocarbons and much less soot. All the volatile-N is released as NH_3 , and there is very little char-N. Biomass chars are also more reactive than even low-rank coal chars, but they are also fed into flames with much coarser PSDs. To characterized the gross impact of these differences, we simulated a 90% hvA bituminous/10% switchgrass flame at the same macroscopic operating conditions as the baseline bituminous flame. Most

of the characteristics of switchgrass are typical of most biomass, except that it has 2.4 daf wt. %, which is one-third higher than the hvA bituminous coal. Also, the biomass PSD was so much coarser that its mean size of 200 μm was four times larger than the mean hvA bituminous size. This discrepancy diminished after devolatilization because bituminous chars are swollen whereas biomass chars have contracted. Fuel and air flowrates were adjusted to impose the nominal S. R. values in Table 3.1 across all flame zones, and the temperature profile from the CFD simulation of the bituminous coal flame was implemented without adjustment. The char-N conversion fraction was 0.40.

The tradeoffs between the switchgrass's faster char reactivity versus its larger size are characterized in Fig. 3-12 in terms of the predicted extents of burnout for both of the char PSDs in a flame fed with a 80%/20% co-milled blend of hvA bituminous and switchgrass. Extents of burnout are significantly higher for the switchgrass char at the outlet to the core. But the extents crossover in the mixing layer, whereby the bituminous char burns out faster for sizes under 200 μm . At the burnout zone outlet, the switchgrass chars burn significantly slower than the bituminous chars. Due to the inversion in the burning rates of these two chars, there is actually significantly less of the bituminous char in the unburned carbon from the co-fired flame than from the baseline bituminous flame; i. e., the burnout of the largest size cut is 10 % higher at the burnout zone outlet compared to the baseline flame. This difference could affect LOI values because the remaining carbon is mostly composed of much larger annealed switchgrass char. We will need to analyze the simulation results in detail to identify the mechanistic basis.

The emissions and burnout levels for the downstream flame regions for several switchgrass co-fired flames are collected in Table 3.6, showing complex behavior. Adding 10 % switchgrass perturbs the NO emissions by less than 15 ppm in all flame zones, and reduces the extent of burnout by roughly 1 %. But the addition of 20 % switchgrass reduces NO emissions by 20 – 25 % across the furnace, and increases the extent of burnout by almost 3 % across the mixing layer and SOFA zone. With 30 % switchgrass, NO emissions are reduced by only 10 % across all flame zones, and the extent of burnout is reduced by almost 2 %.

Figure 3-12. Predicted extents of char burnout versus size increment in the PSDs of hvA bituminous (solid curves) and switchgrass (dashed curves) chars at the outlets of the mixing layer, SOFA zone, and burnout zone in a 80%/20% bituminous/switchgrass co-milled flame.

Table 3.6. NO Emissions and Char Burnout for Co-Milled Switchgrass/
Bituminous Coal Flames.

	Mixing Layer		SOFA Zone		Burnout Zone	
	NO, ppm	X _C , %	NO, ppm	X _C , %	NO, ppm	X _C , %
h _v A Bit.	402	78.0	370	82.7	406	89.9
90% Bit/10% SG	388	76.8	356	81.7	392	89.3
		77.7/50.1		82.5/54.2		90.1/64.6
80% Bit/20% SG	319	81.9	288	85.1	307	89.4
		83.9/53.4		87.0/57.5		91.0/66.4
70% Bit/30% SG	367	75.3	336	80.0	366	87.5
		78.3/50.3		83.0/54.4		90.2/64.9

Clearly, the simulations predict a minimum in NO emissions versus the switchgrass co-firing percentage. Such behavior was not reported for switchgrass in this furnace, but it was seen during co-firing with saw dust with an h_vA bituminous coal. Since we are not yet making quantitative predictions (until the reactor network is formally specified from the CFD simulations), it remains to be seen whether the peculiar behavior for co-firing in Table 3.6 will be validated against test data.

4.0 SUMMARY

A multitude of fuel species – CO, H₂, CH₄, C₂H₂, HCN, soot, and char – compete for the available O₂ in a p. f. flame. This competition determines local heat release rates, which govern flame stability, combustion efficiency and LOI, and the local oxidizing potential of the gas phase, which governs N-species conversion. The central premise behind our modeling approach is that the crucial outcome this competition cannot be forecast from the burning rates of the individual fuels determined in isolation. Instead, realistic chemical kinetics for each distinctive combustion process must be incorporated into a comprehensive analysis. Our analysis incorporates the most comprehensive chemical reaction submodels available, and joins only two other approaches worldwide that impose no *a priori* assumptions whatsoever regarding the apportioning of O₂.

The devolatilization submodel distinguishes primary devolatilization, which relates fuel properties to the composition of volatiles, from secondary volatiles pyrolysis, which generates the volatiles that actually burn in p. f. flames. FLASHCHAIN[®] determines the complete distribution of primary products from any coal or petroleum coke and most forms of biomass, given only the fuel's proximate and ultimate analyses. The mechanism predicts essential fuel quality impacts within useful quantitative tolerances, including the abundance of tar from hv bituminous coals, the abundance of light hydrocarbons and the oxygenated gases, especially CO, from subbituminous coals, and the predominance of tar and CO from biomass. The mechanism for secondary volatiles pyrolysis transforms the primary volatiles into soot, CO, CO₂, H₂O, H₂, and HCN or NH₃. The central transformation is the conversion of tar plus C₂H₂ into soot, H₂, CO, and HCN. Our mechanism omits the kinetics for this process, because it occurs in flames immediately following fuel injection, prior to ignition and combustion.

FLASHCHAIN[®] also predicts the yield and elemental composition of char. When combined with Hurt's swelling factor correlation and a correlation for the initial carbon density in char, we can specify all the necessary char properties for a char oxidation simulation, again, from only the fuel's proximate and ultimate analyses.

There are no adjustable parameters whatsoever in the submodels for devolatilization. The complete distribution of volatiles, including gaseous fuels

and soot, and all char properties are completely determined from the fuel's proximate and ultimate analyses.

The reaction mechanism for chemistry in the gas phase must describe the ignition and combustion of all secondary volatiles pyrolysis products, as well as the conversion of all N-species. These processes must be described across the full range of S. R. values in p. f. flames, extending from very rich to very lean. Across this range, the primary radical chain carriers in the oxidation chemistry shift from H-atoms to OH to O-atoms, and the dominant N-species shifts from HCN alone, to HCN plus NH_3 for moderately rich conditions, through an abrupt transition to only NO beyond the rich side of the stoichiometric point. The diverse chemistry among the various regions of p. f. flames can only be properly described by mechanisms that represent these crucial transitions. Our reaction mechanism for the homogeneous combustion and N-species conversion is believed to be the best available for applications in p. f. flames. It contains 444 elementary reactions among 66 species, including all relevant radicals and N-species. It is implemented in the simulations without any approximations whatsoever. All rate parameters were assigned independently by the primary developers of this mechanism, so there are also no adjustable parameters in the submodel for gas phase chemistry.

Soot plays several important roles. As it burns, it directly competes for the available O_2 and also consumes O-atoms and OH that would otherwise sustain homogeneous chemistry. Soot also promotes recombinations of H-atoms and OH that would otherwise sustain homogeneous chemistry. And soot reduces NO directly into N_2 . This soot chemistry is crucial in mixing layers where S. R. values for the gas phase traverse the stoichiometric point, particularly in its impact on N-species conversion. Soot chemistry clearly alters the transition of the N-species from HCN/ NH_3 mixtures to only NO, and indirectly affects NO production rates.

Our soot chemistry submodel depicts all these effects. NEA's elementary reaction mechanism for oxidation by O_2 reproduces NSC-kinetics across the full domain of operating conditions in p. f. flames. This submechanism was successfully combined with elementary reactions for all the other effects within the SURFACE CHEMKIN framework. However, we have little confidence that the rate parameters in the steps involving radicals, atoms, and NO have assumed their ultimate values, because we simply took the values reported by the first group to incorporate such detailed soot surface chemistry into our p. f.

simulations. We also assumed that the surface sites for oxidation also promote recombinations and NO reduction, for lack of any empirical guidance. It may become necessary to refine these aspects as our flame simulations are developed further.

Char burning rates also factor into the competition for the available O₂, and low-rank chars are the most effective competitors. In turn, overall burning rates are determined by a surprising number of reaction mechanisms, especially during the later stages of burnout. Thermal annealing, ash encapsulation (of low-rank chars), and a transition to chemical kinetic control are collectively responsible for the burnout tail. CBK was the first char burnout submodel to include all these effects, and remains the most thoroughly validated. CBK8 certainly depicts the impact of variation in gas temperature, O₂ level, and char particle size within useful quantitative tolerances. However, it is not yet possible to specify the initial char reactivity within useful tolerances from the standard coal properties. We must calibrate this value with LOI predictions or some other suitable index on combustion efficiency.

The submodel for char-N conversion is subject to the same ambiguities and a similar calibration requirement (with NO emissions), compounded by its simplistic mechanistic premise; viz., that a fixed fraction of char-N is converted into NO at the overall burning rate throughout all stages of char oxidation. This simple view is implemented in all CFD simulations, primarily because there are no suitable alternatives. Detailed reaction mechanisms have been used in fluidized bed combustor simulations, for more moderate temperatures than in p. f. flames. But more promising developments are the detailed reaction mechanisms emerging from fundamental kinetics work, particularly the latest work by Prof. Tomita at Tohoku University and by Prof. Haynes at the University of Sydney. We will monitor these developments for opportunities to incorporate them into our simulations.

To summarize the status of our reaction mechanisms for applications modeling, the initial char reactivity and the fraction of char-N converted to NO can only be specified from calibration procedures. Otherwise, all other model parameters can be assigned from the fuel's proximate and ultimate analyses within useful quantitative tolerances, or directly adopted from the literature. We believe that the submodels for devolatilization, homogeneous chemistry, and

char burnout are complete, whereas those for soot/radical chemistry and for char-N conversion will probably be subject to revisions in the near term.

Simulations of a 1 MW tunnel furnace fired with various p. f. demonstrated several tangible benefits of all the mechanistic complexity. Based on a CFD simulation of a hvA bituminous coal flame, the flame structure in this furnace was resolved into four regions: In the flame core, the S. R. for the gas phase progressed from lean to rich while the volatiles were released. Hydrocarbons and H₂ were partially oxidized into synthesis gas, which shifted toward progressively higher CO concentrations (due to water gas shifting) across the downstream half of the core. The core also sustained combustion of the smallest sizes in the char PSD until the O₂ was completely consumed, but negligible soot oxidation. A few hundred ppm of NO were generated just beyond the injection point, but all but 20 ppm of the N-species were converted into HCN/NH₃ mixtures by the core outlet.

The mixing layer supported a transition from rich to lean mixtures while secondary air was added, and sustained the highest temperatures in the furnace. Both soot and CO burned completely in the mixing layer, along with extents of char burnout that are determined by the rank-dependent char reactivity. The fixed N-species underwent the transition from HCN/NH₃ mixtures to only NO, but not quantitatively. Less than one-fourth of the reduced fixed-N species were converted into NO.

The SOFA and burnout zones sustained only char oxidation. Oxygen levels rose with the addition of tertiary air, then decayed slowly during the later stages of burnout. NO levels initially fell due to the dilution by tertiary air, then recovered with the additional conversion of residual char-N during burnout.

Parametric variations of the mixing intensity of the secondary air stream produced higher NO emissions for higher mixing rates, as expected. An evaluation of staged versus unstaged firing configurations was also qualitatively satisfied, but remains to be quantitatively validated. Predicted NO emissions increased in direct proportion to increases in the fraction of char-N converted into NO. Somewhat surprisingly, NO emissions were significantly lower for higher values of the initial char reactivity because there was more NO generated in the core and subsequently reduced before the mixing layer, and also less residual char-N to generate NO during succeeding stages of burnout.

Subbituminous flames had three times higher extents of char burnout in the core than bituminous flames. This factor, in conjunction with a lower coal-N level and a much higher coal-H level, explained the reduction in NO emission by a factor of two. Subbituminous flames also generated much higher CO concentrations in the flame core, and the ultimate extent of char burnout was higher by almost 2 %.

Simulations with coal blends highlighted a new aspect of the competition for the available O₂. The most reactive char wins the competition at the expense of the least reactive char, so that unburned carbon becomes enriched in the least reactive char component. Blending with subbituminous coal actually lowered the burnout of the hv bituminous char at the outlet of the burnout zone, compared to the bituminous coal flame. Predicted NO emissions for the blends were only 10 ppm higher than estimates based on simple additivity with the emissions from the whole coal flames. Extents of char burnout were either equal to or slightly lower than those for the bituminous coal flame.

Simulations of biomass co-firing introduced yet another tradeoff in the char burnout profiles, because switchgrass has a much higher char reactivity but is usually fed at much larger sizes. The smaller switchgrass size cuts burned faster in the core. But once they were annealed, the largest size fractions of these chars burned slower than the smaller bituminous chars. Consequently, unburned carbon became enriched in the largest size fractions of the switchgrass chars. The predicted NO emissions for switchgrass co-firing also exhibited very complex behavior. With 10 % switchgrass, NO emission were hardly perturbed, but with 20 %, NO emissions fell by almost 25 %. Then, with 30 % switchgrass, NO emissions fell by only 10 %. Such a nonlinear influence has been seen with saw dust co-firing, but remains to be validated for switchgrass co-firing.

5.0 REFERENCES

- D. Benedetto, S. Pasini, M. Falcitelli, C. La Marca, and L. Tognotti. "NO_x emission prediction from 3-D complete modeling to reactor network analysis." *Combust. Sci. and Technol.* 153: 279-294 (2000).
- O. S. L. Bruinsma, Geertsma, R. S., Bank, P., Moulijn, J. A., *Fuel*, 67:334 (1988).
- J. C. Chen, Castagnoli, C., Niksa, S., *Energy Fuels*, 6:64 (1992).
- S. Cho, Marlow, D., Niksa, S., *Combust. Flame*, 101:399 (1995).
- P. Glarborg, Alzueta, M. U., Dam-Johansen, K., and Miller, J. A., "Kinetic modeling of hydrocarbon/nitric oxide interactions in a flow reactor." *Combust. Flame*, 115:1-27 (1998).
- R. H. Hurt, E. G. Brehob, and D. J. Maloney, "Statistical Kinetics for Coal Combustion and Carbon Burnout." Eighth International Conference on Coal Science, Oviedo, Spain, Elsevier Science B. V., 1995, pp. 611-614.
- R. H. Hurt, M. M. Lunden, E. G. Brehob, and D. J. Maloney, "Statistical Kinetics for Pulverized Coal Combustion." Twenty-Sixth Symposium (International) on Combustion, Naples, Italy, Combustion Institute, 1996, pp. 3169-3177.
- R. H. Hurt, J.-K. Sun, and M. Lunden, "A Kinetic Model of Carbon Burnout in Pulverized Coal Combustion." *Combust. Flame* 113(1/2): 181 (1997).D. Marlow, Niksa, S., Kruger, C. H., Twenty-Fourth Int. Symp. on Combust., Combustion Institute, Pittsburgh, 1992, p.1251.
- L. S. Monroe, et al., "Comparison of Pilot-Scale Furnace Experiments and Predictions to Full-Scale Boiler Performance of Compliance Coals," EPRI/EPA 1995 Joint Symp. On Stationary Combustion NO_x Control, Book 3, EPRI, Palo Alto, CA, May 1995.
- P. F. Nelson, Tyler, R., Twenty-First Int. Symp. on Combust., Combustion Institute, Pittsburgh, 1986, p.427.
- K. G. Neoh, Howard, J. B., and Sarofim, A. E., "Soot Oxidation in Flames," in *Particulate Carbon Formation During Combustion* (Eds. D. C. Siegla and G. W. Smith), Plenum Press, NY, 1981, pp. 261-282.
- S. Niksa, "Predicting the Rapid Devolatilization of Diverse Forms of Biomass with bio-FLASHCHAIN," Twenty-Eighth Int. Symp. On Combust., The Combustion Institute, Pittsburgh, PA, 2000, pp. 2727-2733.
- S. Niksa, "Predicting the Complete Distributions of Volatile Products From Diverse Fuel Types With FLASHCHAIN[®]," Fifth Int. Conf. on Technol. and Combust. for a Clean Environ., Lisbon, Portugal, Calouste Gulbenkian Foundation, 1999.
- S. Niksa, Cho, S., Twenty-Seventh Int. Symp. on Combust., Combustion Institute, Pittsburgh, 1998, pp. 2905-2913.
- S. Niksa and Cho, S., *Energy Fuels*, 10(2):463-473 (1996).

- S. Niksa, "Predicting the Devolatilization Behavior of Any Coal From Its Ultimate Analysis," *Combustion and Flame*, 100: 384-394 (1995a).
- S. Niksa and A. R. Kerstein, "Flashchain Theory for Rapid Coal Devolatilization Kinetics. Part 1. Formulation," *Energy and Fuels*, 5(5): 647-664 (1991a).
- S. Niksa, "Flashchain Theory for Rapid Coal Devolatilization Kinetics. Part 2. Impact of Operating Conditions," *Energy and Fuels*, 5(5): 647-664 (1991b).
- S. Niksa, "Predicting the Evolution of Fuel Nitrogen From Various Coals," Twenty-Fifth Symposium (International) On Combustion, The Combustion Institute, Pittsburgh, 1994a, pp. 537-544.
- S. Niksa, "Flashchain Theory for Rapid Coal Devolatilization Kinetics. Part 4. Predicting Ultimate Yields from Ultimate Analyses Alone," *Energy and Fuels*, 8: 659 (1994b).
- S. Niksa, "Flashchain Theory for Rapid Coal Devolatilization Kinetics. Part 5. Interpreting Rates of Devolatilization for Various Coal Types and Operating Conditions," *Energy and Fuels*, 8: 671 (1994c).
- S. Niksa, "Flashchain Theory for Rapid Coal Devolatilization Kinetics. Part 6. Predicting the Evolution of Fuel Nitrogen from Various Coals," *Energy and Fuels*, 9: 467-478 (1995b).
- S. Niksa, "Flashchain Theory for Rapid Coal Devolatilization Kinetics. Part 7. Predicting the Release of Oxygen Species from Various Coals," *Energy and Fuels*, 10: 173-187 (1996).
- S. Niksa, "Rapid Coal Devolatilization as an Equilibrium Flash Distillation," *AIChE Journal*, 34(5): 790-802 (1988a).
- C. Park and Appleton, J. P., "Shock-tube measurements of soot oxidation rates," *Combust. Flame*, 20:369-379 (1973).
- L. S. Pedersen, P. Glarborg, et al., "A chemical engineering model for predicting NO emissions and burnout from pulverized coal flames." *Combust. Sci. and Technol.* 132: 251-314 (1998a).
- L. S. Pedersen, P. Glarborg, et al., "A reduced reaction scheme for volatile nitrogen conversion in coal combustion." *Combust. Sci. and Technol.* 131: 193-223 (1998b).
- D. M. Roessler, Faxvog, F. R., Stevenson, R. and Smith, G. W., "Optical Properties and Morphology of Particulate Carbon: Variation with Air/Fuel Ratio," in *Particulate Carbon Formation During Combustion* (Eds. D. C. Sieglä and G. W. Smith), Plenum Press, NY, 1981, pp. 57-90.
- J.-K. Sun and R. H. Hurt. "A Numerical Study of the Origin of Unburned Carbon." Ninth International Conference on Coal Science, Essen, Germany, DGMK Tagungsberichte 9703, 1997, pp. 927-930.

**APPENDIX A. REACTIONS IN THE REBURNING MECHANISM REPORTED
BY GLARBORG AND COWORKERS**

Table of Reactions in the Reburning Mechanism Reported by Glarborg and Coworkers.

No.	Reaction	A-Factor	T-Expon.	E _a , cal/m
H₂/O₂ Subset				
1.	O+OH=O ₂ +H	2.00E+14	-0.40	0
2.	O+H ₂ =OH+H	5.00E+04	2.67	6,290
3.	OH+H ₂ =H ₂ O+H	2.10E+08	1.52	3,450
4.	2OH=O+H ₂ O	4.30E+03	2.70	-2,486
5.	H+H+M=H ₂ +M	1.00E+18	-1.00	0
6.	H+H+H ₂ O=H ₂ +H ₂ O	6.00E+19	-1.25	0
7.	H+O+M=OH+M	6.20E+16	-0.60	0
8.	H+OH+M=H ₂ O+M	1.60E+22	-2.00	0
9.	O+O+M=O ₂ +M	1.90E+13	0.00	-1,788
10.	H+O ₂ +M=HO ₂ +M	2.10E+18	-1.00	0
11.	H+O ₂ +N ₂ =HO ₂ +N ₂	6.70E+19	-1.42	0
12.	H+HO ₂ =H ₂ +O ₂	4.30E+13	0.00	1,411
13.	H+HO ₂ =2OH	1.70E+14	0.00	874
14.	H+HO ₂ =O+H ₂ O	3.00E+13	0.00	1,721
15.	O+HO ₂ =O ₂ +OH	3.30E+13	0.00	0
16.	OH+HO ₂ =H ₂ O+O ₂	1.90E+16	-1.00	0
17.	HO ₂ +HO ₂ =H ₂ O ₂ +O ₂	4.20E+14	0.00	11,982
18.	HO ₂ +HO ₂ =H ₂ O ₂ +O ₂	1.30E+11	0.00	-1,629
19.	H ₂ O ₂ +M=OH+OH+M	1.30E+17	0.00	45,500
20.	H ₂ O ₂ +H=HO ₂ +H ₂	1.70E+12	0.00	3,755
21.	H ₂ O ₂ +H=OH+H ₂ O	1.00E+13	0.00	3,576
22.	H ₂ O ₂ +O=OH+HO ₂	6.60E+11	0.00	3,974
23.	H ₂ O ₂ +OH=H ₂ O+HO ₂	7.80E+12	0.00	1,330
24.	H ₂ O ₂ +OH=H ₂ O+HO ₂	5.80E+14	0.00	9,560
CO SUBSET				
25.	CO+O+M=CO ₂ +M	6.20E+14	0.00	3,000
26.	CO+OH=CO ₂ +H	1.50E+07	1.30	-758
27.	CO+O ₂ =CO ₂ +O	2.50E+12	0.00	47,700
28.	HO ₂ +CO=CO ₂ +OH	5.80E+13	0.00	22,934
CH₂O/HCO Subset				
29.	CH ₂ O+M=HCO+H+M	3.30E+16	0.00	81,000
30.	CH ₂ O+H=HCO+H ₂	1.30E+08	1.62	2,166
31.	CH ₂ O+O=HCO+OH	1.80E+13	0.00	3,080
32.	CH ₂ O+OH=HCO+H ₂ O	3.40E+09	1.18	-447
33.	CH ₂ O+HO ₂ =HCO+H ₂ O	3.00E+12	0.00	13,000
34.	CH ₂ O+O ₂ =HCO+HO ₂	6.00E+13	0.00	40,660
35.	HCO+M=H+CO+M	1.90E+17	-1.00	17,000
36.	HCO+H=CO+H ₂	1.20E+13	0.25	0
37.	HCO+O=CO+OH	3.00E+13	0.00	0
38.	HCO+O=CO ₂ +H	3.00E+13	0.00	0
39.	HCO+OH=H ₂ O+CO	1.00E+14	0.00	0
40.	HCO+O ₂ =HO ₂ +CO	7.60E+12	0.00	400
CH₄/CH₃/CH₂/CH/C Subset				
41.	CH ₃ +H(+M)=CH ₄ (+M)	1.30E+16	-0.63	383
42.	CH ₄ +H=CH ₃ +H ₂	1.30E+04	3.00	8,040
43.	CH ₄ +O=CH ₃ +OH	1.00E+09	1.50	8,600

44.	CH ₄ +OH=CH ₃ +H ₂ O	1.60E+06	2.10	2,460
45.	CH ₄ +HO ₂ =CH ₃ +H ₂ O ₂	1.80E+11	0.00	18,700
46.	CH ₄ +O ₂ =CH ₃ +HO ₂	7.90E+13	0.00	56,000
47.	CH ₃ +H=CH ₂ +H ₂	9.00E+13	0.00	15,100
48.	CH ₂ (S)+H ₂ =CH ₃ +H	7.20E+13	0.00	0
49.	CH ₃ +O=CH ₂ O+H	8.40E+13	0.00	0
50.	CH ₃ +OH=CH ₂ +H ₂ O	7.50E+06	2.00	5,000
51.	CH ₂ (S)+H ₂ O=CH ₃ +OH	3.00E+15	-0.60	0
52.	CH ₂ OH+H=CH ₃ +OH	1.00E+14	0.00	0
53.	CH ₃ O+H=CH ₃ +OH	1.00E+14	0.00	0
54.	CH ₃ +OH(+M)=CH ₃ OH(+M)	6.30E+13	0.00	0
55.	CH ₃ +HO ₂ =CH ₃ O+OH	8.00E+12	0.00	18,700
56.	CH ₃ +O ₂ =CH ₃ O+O	2.90E+13	0.00	30,480
57.	CH ₃ +O ₂ =CH ₂ O+OH	1.90E+12	0.00	20,315
58.	CH ₃ +CH ₃ (+M)=C ₂ H ₆ (+M)	2.10E+16	-0.97	620
59.	CH ₃ +CH ₂ O=CH ₄ +HCO	7.80E-08	6.10	1,967
60.	CH ₃ +HCO=CH ₄ +CO	1.20E+14	0.00	0
61.	CH ₂ +H=CH+H ₂	1.00E+18	-1.56	0
62.	CH ₂ +O=CO+H+H	5.00E+13	0.00	0
63.	CH ₂ +O=CO+H ₂	3.00E+13	0.00	0
64.	CH ₂ +OH=CH+H ₂ O	1.10E+07	2.00	3,000
65.	CH ₂ +OH=CH ₂ O+H	2.50E+13	0.00	0
66.	CH ₂ +O ₂ =CO+H ₂ O	2.20E+22	-3.30	2,867
67.	CH ₂ +O ₂ =CO ₂ +H+H	3.30E+21	-3.30	2,867
68.	CH ₂ +O ₂ =CH ₂ O+O	3.30E+21	-3.30	2,867
69.	CH ₂ +O ₂ =CO ₂ +H ₂	2.60E+21	-3.30	2,867
70.	CH ₂ +O ₂ =CO+OH+H	1.60E+21	-3.30	2,867
71.	CH ₂ +CO ₂ =CH ₂ O+CO	1.10E+11	0.00	1,000
72.	CH ₂ +CH ₄ =CH ₃ +CH ₃	4.30E+12	0.00	10,030
73.	CH ₂ +CH ₃ =C ₂ H ₄ +H	4.20E+13	0.00	0
74.	CH ₂ +CH ₂ =C ₂ H ₂ +H+H	4.00E+13	0.00	0
75.	CH ₂ +HCCO=C ₂ H ₃ +CO	3.00E+13	0.00	0
76.	CH ₂ (S)+M=CH ₂ +M	1.00E+13	0.00	0
77.	CH ₂ (S)+N ₂ =CH ₂ +N ₂	1.30E+13	0.00	430
78.	CH ₂ (S)+AR=CH ₂ +AR	1.50E+13	0.00	884
79.	CH ₂ (S)+H=CH ₂ +H	2.00E+14	0.00	0
80.	CH ₂ (S)+H ₂ O=CH ₂ +H ₂ O	3.00E+13	0.00	0
81.	CH ₂ (S)+H=CH+H ₂	3.00E+13	0.00	0
82.	CH ₂ (S)+O=CO+H+H	3.00E+13	0.00	0
83.	CH ₂ (S)+OH=CH ₂ O+H	3.00E+13	0.00	0
84.	CH ₂ (S)+O ₂ =CO+OH+H	7.00E+13	0.00	0
85.	CH ₂ (S)+CO ₂ =CH ₂ O+CO	3.00E+12	0.00	0
86.	CH ₂ (S)+CH ₄ =CH ₃ +CH ₃	4.30E+13	0.00	0
87.	CH ₂ (S)+CH ₃ =C ₂ H ₄ +H	2.00E+13	0.00	0
88.	CH ₂ (S)+CH ₂ CO=C ₂ H ₄ +CO	1.60E+14	0.00	0
89.	CH ₂ (S)+C ₂ H ₆ =CH ₃ +C ₂ H ₅	1.20E+14	0.00	0
90.	CH+H=C+H ₂	1.50E+14	0.00	0
91.	CH+O=CO+H	5.70E+13	0.00	0
92.	CH+OH=HCO+H	3.00E+13	0.00	0
93.	CH+OH=C+H ₂ O	4.00E+07	2.00	3,000

94.	CH+O2=HCO+O	3.30E+13	0.00	0
95.	CH+H2O=CH2O+H	5.70E+12	0.00	-751
96.	CH+CO2=HCO+CO	3.40E+12	0.00	690
97.	CH+CH4=C2H4+H	6.00E+13	0.00	0
98.	CH+CH3=C2H3+H	3.00E+13	0.00	0
99.	CH+CH2=C2H2+H	4.00E+13	0.00	0
100.	CH+CH2O=CH2CO+H	9.50E+13	0.00	-515
101.	CH+HCCO=C2H2+CO	5.00E+13	0.00	0
102.	C+OH=CO+H	5.00E+13	0.00	0
103.	C+O2=CO+O	2.00E+13	0.00	0
104.	C+CH3=C2H2+H	5.00E+13	0.00	0
105.	C+CH2=C2H+H	5.00E+13	0.00	0
CH3OH/CH2OH/CH2O Subset				
106.	CH3OH+H=CH2OH+H2	1.70E+07	2.10	4,868
107.	CH3OH+H=CH3O+H2	4.20E+06	2.10	4,868
108.	CH3OH+O=CH2OH+OH	3.90E+05	2.50	3,080
109.	CH3OH+OH=CH2OH+H2O	5.30E+04	2.53	960
110.	CH3OH+OH=CH3O+H2O	1.32E+04	2.53	960
111.	CH3OH+HO2=CH2OH+H2O2	9.60E+10	0.00	12,578
112.	CH2O+H(+M)=CH3O(+M)	5.40E+11	0.45	2,600
113.	CH3O+H=CH2O+H2	2.00E+13	0.00	0
114.	CH3O+O=CH2O+OH	1.00E+13	0.00	0
115.	CH3O+OH=CH2O+H2O	1.00E+13	0.00	0
116.	CH3O+O2=CH2O+HO2	6.30E+10	0.00	2,600
117.	H+CH2O(+M)=CH2OH(+M)	5.40E+11	0.45	3,600
118.	CH2OH+H=CH2O+H2	2.00E+13	0.00	0
119.	CH2OH+O=CH2O+OH	1.00E+13	0.00	0
120.	CH2OH+OH=CH2O+H2O	1.00E+13	0.00	0
121.	CH2OH+O2=CH2O+HO2	1.60E+15	-1.00	0
122.	CH2OH+O2=CH2O+HO2	7.20E+13	0.00	3,577
C2H6/C2H5/C2H4/C2H3/C2H2/C2H/C2 Subset				
123.	C2H6+H=C2H5+H2	5.40E+02	3.50	5,210
124.	C2H6+O=C2H5+OH	3.00E+07	2.00	5,115
125.	C2H6+OH=C2H5+H2O	7.20E+06	2.00	864
126.	C2H6+HO2=C2H5+H2O	1.30E+13	0.00	20,460
127.	C2H6+O2=C2H5+HO2	5.00E+13	0.00	55,000
128.	C2H6+CH3=C2H5+CH4	5.50E-01	4.00	8,300
129.	C2H4+H(+M)=C2H5(+M)	1.10E+12	0.45	1,822
130.	C2H5+H(+M)=C2H6+M	5.20E+17	0.00	20,460
131.	C2H5+H=CH3+CH3	4.90E+12	0.35	0
132.	C2H5+O=CH3+CH2O	4.20E+13	0.00	0
133.	C2H5+O=CH3HCO+H	5.30E+13	0.00	0
134.	C2H5+O=C2H4+H	3.00E+13	0.00	0
135.	C2H5+OH=C2H4+H2O	2.40E+13	0.00	0
136.	C2H5+O2=C2H4+HO2	1.00E+10	0.00	-2,190
137.	C2H5+CH2O=C2H6+HCO	5.50E+03	2.81	5,860
138.	C2H5+HCO=C2H6+CO	1.20E+14	0.00	0
139.	C2H5+CH3=C2H4+CH4	1.10E+12	0.00	0
140.	C2H5+C2H5=C2H6+C2H4	1.50E+12	0.00	0

141.	$\text{C}_2\text{H}_3 + \text{H}(+\text{M}) = \text{C}_2\text{H}_4(+\text{M})$	$6.10\text{E}+12$	0.27	280
142.	$\text{C}_2\text{H}_4 + \text{M} = \text{C}_2\text{H}_2 + \text{H}_2 + \text{M}$	$3.50\text{E}+16$	0.00	71,500
143.	$\text{C}_2\text{H}_4 + \text{H} = \text{C}_2\text{H}_3 + \text{H}_2$	$5.40\text{E}+14$	0.00	14,900
144.	$\text{C}_2\text{H}_4 + \text{O} = \text{CH}_2\text{HCO} + \text{H}$	$4.70\text{E}+06$	1.88	180
145.	$\text{C}_2\text{H}_4 + \text{O} = \text{CH}_3 + \text{HCO}$	$8.10\text{E}+06$	1.88	180
146.	$\text{C}_2\text{H}_4 + \text{O} = \text{CH}_2\text{CO} + \text{H}_2$	$6.80\text{E}+05$	1.88	180
147.	$\text{C}_2\text{H}_4 + \text{OH} = \text{C}_2\text{H}_3 + \text{H}_2\text{O}$	$2.00\text{E}+13$	0.00	5,940
148.	$\text{C}_2\text{H}_4 + \text{HO}_2 = \text{CH}_3\text{HCO} + \text{OH}$	$2.20\text{E}+12$	0.00	17,200
149.	$\text{C}_2\text{H}_4 + \text{O}_2 = \text{CH}_2\text{HCO} + \text{OH}$	$2.00\text{E}+08$	1.50	39,000
150.	$\text{C}_2\text{H}_4 + \text{CH}_3 = \text{C}_2\text{H}_3 + \text{CH}_4$	$5.00\text{E}+11$	0.00	15,000
151.	$\text{H} + \text{C}_2\text{H}_2(+\text{M}) = \text{C}_2\text{H}_3(+\text{M})$	$3.10\text{E}+11$	0.58	2,590
152.	$\text{C}_2\text{H}_3 + \text{H} = \text{C}_2\text{H}_2 + \text{H}_2$	$4.00\text{E}+13$	0.00	0
153.	$\text{C}_2\text{H}_3 + \text{O} = \text{CH}_2\text{CO} + \text{H}$	$3.00\text{E}+13$	0.00	0
154.	$\text{C}_2\text{H}_3 + \text{OH} = \text{C}_2\text{H}_2 + \text{H}_2\text{O}$	$2.00\text{E}+13$	0.00	0
155.	$\text{C}_2\text{H}_3 + \text{O}_2 = \text{CH}_2\text{O} + \text{HCO}$	$1.10\text{E}+23$	-3.29	3,890
156.	$\text{C}_2\text{H}_3 + \text{O}_2 = \text{CH}_2\text{HCO} + \text{O}$	$2.50\text{E}+15$	-0.78	3,135
157.	$\text{C}_2\text{H}_3 + \text{O}_2 = \text{C}_2\text{H}_2 + \text{HO}_2$	$5.20\text{E}+15$	-1.26	3,310
158.	$\text{C}_2\text{H}_3 + \text{CH}_2\text{O} = \text{C}_2\text{H}_4 + \text{HCO}$	$5.40\text{E}+03$	2.81	5,860
159.	$\text{C}_2\text{H}_3 + \text{HCO} = \text{C}_2\text{H}_4 + \text{CO}$	$9.00\text{E}+13$	0.00	0
160.	$\text{C}_2\text{H}_3 + \text{CH}_3 = \text{C}_2\text{H}_2 + \text{CH}_4$	$2.10\text{E}+13$	0.00	0
161.	$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 = \text{C}_2\text{H}_4 + \text{C}_2\text{H}_2$	$1.50\text{E}+13$	0.00	0
162.	$\text{C}_2\text{H}_2 + \text{M} = \text{C}_2\text{H} + \text{H} + \text{M}$	$9.10\text{E}+30$	-3.70	127,138
163.	$\text{H}_2 + \text{C}_2\text{H} = \text{C}_2\text{H}_2 + \text{H}$	$4.10\text{E}+05$	2.39	864
164.	$\text{C}_2\text{H}_2 + \text{O} = \text{CH}_2 + \text{CO}$	$6.10\text{E}+06$	2.00	1,900
165.	$\text{C}_2\text{H}_2 + \text{O} = \text{HCCO} + \text{H}$	$1.40\text{E}+07$	2.00	1,900
166.	$\text{C}_2\text{H}_2 + \text{O} = \text{C}_2\text{H} + \text{OH}$	$3.20\text{E}+15$	-0.60	15,000
167.	$\text{OH} + \text{C}_2\text{H}_2 = \text{C}_2\text{H} + \text{H}_2\text{O}$	$3.40\text{E}+07$	2.00	14,000
168.	$\text{OH} + \text{C}_2\text{H}_2 = \text{HCCOH} + \text{H}$	$5.00\text{E}+05$	2.30	13,500
169.	$\text{OH} + \text{C}_2\text{H}_2 = \text{CH}_2\text{CO} + \text{H}$	$2.20\text{E}-04$	4.50	-1,000
170.	$\text{OH} + \text{C}_2\text{H}_2 = \text{CH}_3 + \text{CO}$	$4.80\text{E}-04$	4.00	-2,000
171.	$\text{OH} + \text{C}_2\text{H}_2(+\text{M}) = \text{C}_2\text{H}_2\text{OH}(+\text{M})$	$1.50\text{E}+08$	1.70	1,000
172.	$\text{HO}_2 + \text{C}_2\text{H}_2 = \text{CH}_2\text{HCO} + \text{O}$	$1.00\text{E}+12$	0.00	10,000
173.	$\text{HO}_2 + \text{C}_2\text{H}_2 = \text{CH}_2\text{O} + \text{HCO}$	$1.00\text{E}+12$	0.00	10,000
174.	$\text{C}_2\text{H}_2 + \text{O}_2 = \text{HCO} + \text{HCO}$	$2.00\text{E}+08$	1.50	30,100
175.	$\text{C}_2 + \text{H}_2 = \text{C}_2\text{H} + \text{H}$	$4.00\text{E}+05$	2.40	1,000
176.	$\text{C}_2\text{H} + \text{O} = \text{CH} + \text{CO}$	$5.00\text{E}+13$	0.00	0
177.	$\text{C}_2\text{H} + \text{OH} = \text{HCCO} + \text{H}$	$2.00\text{E}+13$	0.00	0
178.	$\text{C}_2\text{H} + \text{OH} = \text{C}_2 + \text{H}_2\text{O}$	$4.00\text{E}+07$	2.00	8,000
179.	$\text{C}_2\text{H} + \text{O}_2 = \text{CO} + \text{CO} + \text{H}$	$2.50\text{E}+13$	0.00	0
180.	$\text{C}_2\text{H} + \text{CH}_4 = \text{CH}_3 + \text{C}_2\text{H}_2$	$7.20\text{E}+12$	0.00	976
181.	$\text{C}_2 + \text{OH} = \text{C}_2\text{O} + \text{H}$	$5.00\text{E}+13$	0.00	0
182.	$\text{C}_2 + \text{O}_2 = \text{CO} + \text{CO}$	$5.00\text{E}+13$	0.00	0
$\text{CH}_3\text{HCO}/\text{CH}_2\text{HCO}/\text{CH}_3\text{CO}/\text{CH}_2\text{CO}/$ $\text{HCCOH}/\text{HCCO}/\text{C}_2\text{O}$ Subset				
183.	$\text{CH}_3\text{HCO} = \text{CH}_3 + \text{HCO}$	$7.10\text{E}+15$	5.60	2,464
184.	$\text{CH}_3\text{HCO} + \text{H} = \text{CH}_3\text{CO} + \text{H}_2$	$4.10\text{E}+09$	0.00	42,000
185.	$\text{CH}_3\text{HCO} + \text{O} = \text{CH}_3\text{CO} + \text{OH}$	$5.80\text{E}+12$	0.00	42,000
186.	$\text{CH}_3\text{HCO} + \text{OH} = \text{CH}_3\text{CO} + \text{H}_2\text{O}$	$2.30\text{E}+10$	0.73	-1,110
187.	$\text{CH}_3\text{HCO} + \text{HO}_2 = \text{CH}_3\text{CO} + \text{H}_2\text{O}_2$	$3.00\text{E}+12$	0.00	12,000
188.	$\text{CH}_3\text{HCO} + \text{O}_2 = \text{CH}_3\text{CO} + \text{HO}_2$	$3.00\text{E}+13$	0.00	39,000

189.	CH ₃ HCO+CH ₃ =CH ₃ CO+CH ₄	2.00E-06	5.60	2,464
190.	CH ₂ HCO=CH ₃ +CO	1.00E+13	0.00	42,000
191.	ICH ₂ HCO+M=CH ₃ +CO+M	2.00E+16	0.00	42,000
192.	CH ₂ HCO+H=CH ₃ +HCO	1.00E+14	0.00	0
193.	CH ₂ HCO+H=CH ₃ CO+H	3.00E+13	0.00	0
194.	CH ₂ HCO+O=CH ₂ O+HCO	5.00E+13	0.00	0
195.	CH ₂ HCO+OH=CH ₂ CO+H ₂ O	2.00E+13	0.00	0
196.	CH ₂ HCO+OH=CH ₂ OH+HCO	1.00E+13	0.00	0
197.	CH ₂ HCO+O ₂ =CH ₂ O+CO+OH	2.20E+11	0.00	1,500
198.	CH ₂ HCO+CH ₃ =C ₂ H ₅ CHO	5.00E+13	0.00	0
199.	CH ₂ HCO+CH ₂ =C ₂ H ₄ +HCO	5.00E+13	0.00	0
200.	CH ₂ HCO+CH=C ₂ H ₃ +HCO	1.00E+14	0.00	0
201.	C ₂ H ₅ +HCO=C ₂ H ₅ CHO	1.80E+13	0.00	0
202.	C ₂ H ₅ CHO+H=C ₂ H ₅ CO+H ₂	8.00E+13	0.00	0
203.	C ₂ H ₅ CHO+O=C ₂ H ₅ CO+OH	7.80E+12	0.00	1,730
204.	C ₂ H ₅ CHO+OH=C ₂ H ₅ CO+H ₂ O	1.20E+13	0.00	0
205.	C ₂ H ₅ +CO=C ₂ H ₅ CO	1.50E+11	0.00	4,800
206.	C ₂ H ₂ OH+H=CH ₂ HCO+H	5.00E+13	0.00	0
207.	C ₂ H ₂ OH+O=OCHCHO+H	5.00E+13	0.00	0
208.	C ₂ H ₂ OH+O ₂ =OCHCHO+OH	1.00E+12	0.00	5,000
209.	CH ₃ CO(+M)=CH ₃ +CO(+M)	2.80E+13	0.00	17,100
210.	CH ₃ CO+H=CH ₃ +HCO	2.10E+13	0.00	0
211.	CH ₃ CO+H=CH ₂ CO+H ₂	1.20E+13	0.00	0
212.	CH ₃ CO+O=CH ₃ +CO ₂	1.50E+14	0.00	0
213.	CH ₃ CO+O=CH ₂ CO+OH	4.00E+13	0.00	0
214.	CH ₃ CO+OH=CH ₂ CO+H ₂ O	1.20E+13	0.00	0
215.	CH ₂ +CO(+M)=CH ₂ CO(+M)	8.10E+11	0.50	4,510
216.	CH ₂ CO+H=CH ₃ +CO	5.90E+06	2.00	1,300
217.	CH ₂ CO+H=HCCO+H ₂	3.00E+07	2.00	10,000
218.	CH ₂ CO+O=CO ₂ +CH ₂	1.80E+12	0.00	1,350
219.	CH ₂ CO+O=HCCO+OH	2.00E+07	2.00	10,000
220.	CH ₂ CO+OH=HCCO+H ₂ O	1.00E+07	2.00	3,000
221.	CH ₂ CO+OH=CH ₂ OH+CO	7.20E+12	0.00	0
222.	CH ₂ CO+OH=CH ₃ +CO ₂	3.00E+12	0.00	0
223.	HCCOH+H=HCCO+H ₂	3.00E+07	2.00	1,000
224.	HCCOH+OH=HCCO+H ₂ O	1.00E+07	2.00	1,000
225.	HCCOH+O=HCCO+OH	2.00E+07	3.00	1,900
226.	OCHCHO+M=HCO+HCO+M	1.00E+17	0.00	58,000
227.	OCHCHO+H=CH ₂ O+HCO	3.00E+13	0.00	0
228.	CH+CO(+M)=HCCO(+M)	5.00E+13	0.00	0
229.	HCCO+O ₂ =CO ₂ +CO+H	1.40E+07	1.70	1,000
230.	HCCO+O ₂ =CO+CO+OH	2.90E+07	1.70	1,000
231.	HCCO+HCCO=C ₂ H ₂ +CO+CO	1.00E+13	0.00	0
232.	C ₂ O+H=CH+CO	1.00E+13	0.00	0
233.	C ₂ O+O=CO+CO	5.00E+13	0.00	0
234.	C ₂ O+OH=CO+CO+H	2.00E+13	0.00	0
235.	C ₂ O+O ₂ =CO+CO+O	2.00E+13	0.00	0
H/N/O Subset				
236.	H+NO+M=HNO+M	2.70E+15	0.00	-600
237.	H+NO+N ₂ =HNO+N ₂	7.00E+19	-1.50	0

238.	NO+O+M=NO2+M	7.50E+19	-1.41	0
239.	OH+NO+M=HONO+M	5.10E+23	-2.51	-68
240.	HO2+NO=NO2+OH	2.10E+12	0.00	-479
241.	NO2+H=NO+OH	8.40E+13	0.00	0
242.	NO2+O=NO+O2	3.90E+12	0.00	-238
243.	NO2+O(+M)=NO3(+M)	1.30E+13	0.00	0
244.	NO2+NO2=NO+NO+O2	1.60E+12	0.00	26,123
245.	NO2+NO2=NO3+NO	9.60E+09	0.73	20,900
246.	NO3+H=NO2+OH	6.00E+13	0.00	0
247.	NO3+O=NO2+O2	1.00E+13	0.00	0
248.	NO3+OH=NO2+HO2	1.40E+13	0.00	0
249.	NO3+HO2=NO2+O2+OH	1.50E+12	0.00	0
250.	NO3+NO2=NO+NO2+O2	5.00E+10	0.00	2,940
251.	HNO+H=H2+NO	4.50E+11	0.72	655
252.	HNO+O=NO+OH	1.00E+13	0.00	0
253.	HNO+OH=NO+H2O	3.60E+13	0.00	0
254.	HNO+O2=HO2+NO	1.00E+13	0.00	25,000
255.	HNO+NO2=HONO+NO	6.00E+11	0.00	2,000
256.	HNO+HNO=N2O+H2O	9.00E+08	0.00	3,100
257.	HNO+NH2=NH3+NO	3.63E+06	1.63	-1,252
258.	H2NO+M=HNO+H+M	2.50E+15	0.00	50,000
259.	H2NO+H=HNO+H2	3.00E+07	2.00	2,000
260.	H2NO+H=NH2+OH	5.00E+13	0.00	0
261.	H2NO+O=HNO+OH	3.00E+07	2.00	2,000
262.	H2NO+O=NH2+O2	2.00E+14	0.00	0
263.	H2NO+OH=HNO+H2O	2.00E+07	2.00	1,000
264.	H2NO+NO=HNO+HNO	2.00E+04	2.00	13,000
265.	H2NO+NO2=HNO+HONO	6.00E+11	0.00	2,000
266.	HONO+H=H2+NO2	1.20E+13	0.00	7,352
267.	HONO+O=OH+NO2	1.20E+13	0.00	5,961
268.	HONO+OH=H2O+NO2	4.00E+12	0.00	0
269.	NH3+M=NH2+H+M	2.20E+16	0.00	93,470
270.	NH3+H=NH2+H2	6.40E+05	2.39	10,171
271.	NH3+O=NH2+OH	9.40E+06	1.94	6,460
272.	NH3+OH=NH2+H2O	2.00E+06	2.04	566
273.	NH3+HO2=NH2+H2O2	3.00E+11	0.00	22,000
274.	NH2+H=NH+H2	4.00E+13	0.00	3,650
275.	NH2+O=HNO+H	6.60E+14	-0.50	0
276.	NH2+O=NH+OH	6.80E+12	0.00	0
277.	NH2+OH=NH+H2O	4.00E+06	2.00	1,000
278.	NH2+HO2=H2NO+OH	5.00E+13	0.00	0
279.	NH2+HO2=NH3+O2	1.00E+13	0.00	0
280.	NH2+NO=NNH+OH	8.90E+12	-0.35	0
281.	NH2+NO=N2+H2O	1.30E+16	-1.25	0
		8.90E+12	-0.35	0
282.	NH2+NO2=N2O+H2O	3.20E+18	-2.20	0
283.	NH2+NO2=H2NO+NO	3.50E+12	0.00	0
284.	NH2+H2NO=NH3+HNO	3.00E+12	0.00	1,000
285.	HONO+NH2=NO2+NH3	71.1	3.02	-4,941
286.	NH2+NH2=N2H2+H2	8.50E+11	0.00	0

287.	NH ₂ +NH=N ₂ H ₂ +H	5.00E+13	0.00	0
288.	NH ₂ +N=N ₂ +H+H	7.20E+13	0.00	0
289.	NH+H=N+H ₂	3.00E+13	0.00	0
290.	NH+O=NO+H	9.20E+13	0.00	0
291.	NH+OH=HNO+H	2.00E+13	0.00	0
292.	NH+OH=N+H ₂ O	5.00E+11	0.50	2,000
293.	NH+O ₂ =HNO+O	4.60E+05	2.00	6,500
294.	NH+O ₂ =NO+OH	1.30E+06	1.50	100
295.	NH+NO=N ₂ O+H	2.90E+14	-0.40	0
		2.20E+13	-0.23	0
296.	NH+NO=N ₂ +OH	2.20E+13	-0.23	0
297.	NH+NO ₂ =N ₂ O+OH	1.00E+13	0.00	0
298.	NH+NH=N ₂ +H+H	2.50E+13	0.00	0
299.	NH+N=N ₂ +H	3.00E+13	0.00	0
300.	N+OH=NO+H	3.80E+13	0.00	0
301.	N+O ₂ =NO+O	6.40E+09	1.00	6,280
302.	N+NO=N ₂ +O	3.30E+12	0.30	0
303.	N ₂ H ₂ +M=NNH+H+M	5.00E+16	0.00	50,000
304.	N ₂ H ₂ +H=NNH+H ₂	5.00E+13	0.00	1,000
305.	N ₂ H ₂ +O=NH ₂ +NO	1.00E+13	0.00	0
306.	N ₂ H ₂ +O=NNH+OH	2.00E+13	0.00	1,000
307.	N ₂ H ₂ +OH=NNH+H ₂ O	1.00E+13	0.00	1,000
308.	N ₂ H ₂ +NO=N ₂ O+NH ₂	3.00E+12	0.00	0
309.	N ₂ H ₂ +NH ₂ =NH ₃ +NNH	1.00E+13	0.00	1,000
310.	N ₂ H ₂ +NH=NNH+NH ₂	1.00E+13	0.00	1,000
311.	NNH=N ₂ +H	1.00E+07	0.00	0
312.	NNH+H=N ₂ +H ₂	1.00E+14	0.00	0
313.	NNH+O=N ₂ +OH	8.00E+13	0.00	0
314.	NNH+O=N ₂ O+H	1.00E+14	0.00	0
315.	NNH+O=NH+NO	5.00E+13	0.00	0
316.	NNH+OH=N ₂ +H ₂ O	5.00E+13	0.00	0
317.	NNH+O ₂ =N ₂ +HO ₂	2.00E+14	0.00	0
318.	NNH+O ₂ =N ₂ +O ₂ +H	5.00E+13	0.00	0
319.	NNH+NO=N ₂ +HNO	5.00E+13	0.00	0
320.	NNH+NH ₂ =N ₂ +NH ₃	5.00E+13	0.00	0
321.	NNH+NH=N ₂ +NH ₂	5.00E+13	0.00	0
322.	N ₂ O+M=N ₂ +O+M	4.00E+14	0.00	56,100
323.	N ₂ O+H=N ₂ +OH	3.30E+10	0.00	4,729
		4.40E+14	0.00	19,254
324.	N ₂ O+O=NO+NO	6.60E+13	0.00	26,630
325.	N ₂ O+O=N ₂ +O ₂	1.00E+14	0.00	28,000
326.	N ₂ O+OH=N ₂ +HO ₂	1.30E-02	4.72	36,561
327.	N ₂ O+OH=HNO+NO	1.20E-04	4.33	25,081
329.	N ₂ O+NO=NO ₂ +N ₂	5.30E+05	2.23	46,281
Cyanide Subset				
330.	CN+H ₂ =HCN+H	3.00E+05	2.45	2,237
331.	HCN+O=NCO+H	1.40E+04	2.64	4,980
332.	HCN+O=NH+CO	3.50E+03	2.64	4,980
333.	HCN+O=CN+OH	2.70E+09	1.58	29,200
334.	HCN+OH=CN+H ₂ O	3.90E+06	1.83	10,300

335.	HCN+OH=HOCN+H	5.90E+04	2.40	12,500
336.	HCN+OH=HNCO+H	2.00E-03	4.00	1,000
337.	HCN+OH=NH ₂ +CO	7.80E-04	4.00	4,000
338.	HCN+CN=C ₂ N ₂ +H	1.50E+07	1.71	1,530
339.	CN+O=CO+N	7.70E+13	0.00	0
340.	CN+OH=NCO+H	4.00E+13	0.00	0
341.	CN+O ₂ =NCO+O	7.50E+12	0.00	-389
342.	CN+CO ₂ =NCO+CO	3.70E+06	2.16	26,884
343.	CN+NO ₂ =NCO+NO	5.30E+15	-0.75	344
344.	CN+NO ₂ =CO+N ₂ O	4.90E+14	-0.75	344
345.	CN+NO ₂ =N ₂ +CO ₂	3.70E+14	-0.75	344
346.	CN+HNO=HCN+NO	1.80E+13	0.00	0
347.	CN+HONO=HCN+NO ₂	1.20E+13	0.00	0
348.	CN+N ₂ O=NCN+NO	3.90E+03	2.60	3,696
349.	CN+HNCO=HCN+NCO	1.50E+13	0.00	0
350.	CN+NCO=NCN+CO	1.80E+13	0.00	0
351.	HNCO+M=NH+CO	1.10E+16	0.00	86,000
352.	HNCO+H=NH ₂ +CO	2.20E+07	1.70	3,800
353.	HNCO+O=HNO+CO	1.50E+08	1.57	44,012
354.	HNCO+O=NH+CO ₂	9.80E+07	1.41	8,524
355.	HNCO+O=NCO+OH	2.20E+06	2.11	11,425
356.	HNCO+OH=NCO+H ₂ O	6.40E+05	2.00	2,563
357.	HNCO+HO ₂ =NCO+H ₂ O ₂	3.00E+11	0.00	22,000
358.	HNCO+O ₂ =HNO+CO ₂	1.00E+12	0.00	35,000
359.	HNCO+NH ₂ =NH ₃ +NCO	5.00E+12	0.00	6,200
360.	HNCO+NH=NH ₂ +NCO	3.00E+13	0.00	23,700
361.	HOCN+H=NCO+H ₂	2.00E+07	2.00	2,000
362.	HOCN+O=NCO+OH	1.50E+04	2.64	4,000
363.	HOCN+OH=NCO+H ₂ O	6.40E+05	2.00	2,563
364.	HCNO+H=HCN+OH	1.00E+14	0.00	12,000
365.	HCNO+O=HCO+NO	2.00E+14	0.00	0
366.	HCNO+OH=CH ₂ O+NO	4.00E+13	0.00	0
367.	NCO+M=N+CO+M	3.10E+16	-0.50	48,000
368.	NCO+H=NH+CO	5.00E+13	0.00	0
369.	NCO+O=NO+CO	4.70E+13	0.00	0
370.	NCO+OH=NO+HCO	5.00E+12	0.00	15,000
371.	NCO+O ₂ =NO+CO ₂	2.00E+12	0.00	20,000
372.	NCO+H ₂ =HNCO+H	7.60E+02	3.00	4,000
373.	NCO+HCO=HNCO+CO	3.60E+13	0.00	0
374.	NCO+NO=N ₂ O+CO	6.20E+17	-1.73	763
375.	NCO+NO=N ₂ +CO ₂	7.80E+17	-1.73	763
376.	NCO+NO ₂ =CO+NO+NO	2.50E+11	0.00	-707
377.	NCO+NO ₂ =CO ₂ +N ₂ O	3.00E+12	0.00	-707
378.	NCO+HNO=HNCO+NO	1.80E+13	0.00	0
379.	NCO+HONO=HNCO+NO ₂	3.60E+12	0.00	0
380.	NCO+N=N ₂ +CO	2.00E+13	0.00	0
381.	NCO+NCO=N ₂ +CO+CO	1.80E+13	0.00	0
382.	C ₂ N ₂ +O=NCO+CN	4.60E+12	0.00	8,880
383.	C ₂ N ₂ +OH=HOCN+CN	1.90E+11	0.00	2,900
384.	NCN+O=CN+NO	1.00E+14	0.00	0

385.	NCN+OH=HCN+NO	5.00E+13	0.00	0
386.	NCN+H=HCN+N	1.00E+14	0.00	0
387.	NCN+O2=NO+NCO	1.00E+13	0.00	0
388.	H+CH3CN=HCN+CH3	4.00E+07	2.00	2,000
389.	H+CH3CN=CH2CN+H2	3.00E+07	2.00	1,000
390.	O+CH3CN=NCO+CH3	1.50E+04	2.64	4,980
391.	OH+CH3CN=CH2CN+H2O	2.00E+07	2.00	2,000
392.	CH2CN+O=CH2O+CN	1.00E+14	0.00	0
393.	CN+CH2OH=CH2CN+OH	5.00E+13	0.00	0
394.	H2CN+M=HCN+H+M	3.00E+14	0.00	22,000
Subset for C_xH_yO_z+N-Species				
395.	CO+NO2=CO2+NO	9.00E+13	0.00	33,779
396.	CO+N2O=N2+CO2	3.20E+11	0.00	20,237
397.	CO2+N=NO+CO	1.90E+11	0.00	3,400
398.	CH2O+NCO=HNCO+HCO	6.00E+12	0.00	0
399.	CH2O+NO2=NCO+HONO	8.00E+02	2.77	13,730
400.	HCO+NO=HNO+CO	7.20E+12	0.00	0
402.	HCO+NO2=CO+HONO	1.20E+23	-3.29	2,355
403.	HCO+NO2=H+CO2+NO	8.40E+15	-0.75	1,930
404.	HCO+HNO=CH2O+NO	6.00E+11	0.00	2,000
405.	CH4+CN=CH3+HCN	6.20E+04	2.64	-437
406.	NCO+CH4=CH3+HNCO	9.80E+12	0.00	8,120
407.	CH3+NO=HCN+H2O	1.50E-01	3.52	3,950
408.	CH3+NO=H2CN+OH	1.50E-01	3.52	3,950
409.	CH3+NO2=CH3O+NO	1.40E+13	0.00	0
410.	CH3+N=H2CN+H	7.10E+13	0.00	0
411.	CH3+CN=CH2CN+H	1.00E+14	0.00	0
412.	CH3+HOCN=CH3CN+OH	5.00E+12	0.00	2,000
413.	CH2+NO=HCN+OH	2.20E+12	0.00	-378
414.	CH2+NO=HCNO+H	1.30E+12	0.00	-378
415.	CH2+NO2=CH2O+NO	5.90E+13	0.00	0
416.	CH2+N=HCN+H	5.00E+13	0.00	0
417.	CH2+N2=HCN+NH	1.00E+13	0.00	74,000
418.	H2CN+N=N2+CH2	2.00E+13	0.00	0
419.	CH2(S)+NO=HCN+OH	2.00E+13	0.00	0
420.	CH2(S)+NO=CH2+NO	1.00E+14	0.00	0
421.	CH2(S)+HCN=CH3+CN	5.00E+13	0.00	0
422.	CH+NO2=HCO+NO	1.00E+14	0.00	0
423.	CH+NO=NCN+O	4.80E+13	0.00	0
424.	CH+NO=HCO+N	3.40E+13	0.00	0
425.	CH+NO=NCO+H	1.90E+13	0.00	0
426.	CH+N=CN+H	1.30E+13	0.00	0
427.	CH+N2=HCN+N	3.70E+07	1.42	20,723
428.	CH+N2O=HCN+NO	1.90E+13	0.00	-511
429.	C+NO=CN+O	2.00E+13	0.00	0
430.	C+NO=CO+N	2.80E+13	0.00	0
431.	C+N2=CN+N	6.30E+13	0.00	46,019
432.	C+N2O=CN+NO	5.10E+12	0.00	0
433.	C2H6+CN=C2H5+HCN	1.20E+05	2.77	-1,788
434.	C2H6+NCO=C2H5+HNCO	1.50E-09	6.89	-2,910

435.	$\text{C}_2\text{H}_4 + \text{CN} = \text{C}_2\text{H}_3 + \text{HCN}$	$5.90\text{E}+14$	-0.24	0
436.	$\text{C}_2\text{H}_3 + \text{NO} = \text{C}_2\text{H}_2 + \text{HNO}$	$1.00\text{E}+12$	0.00	1,000
437.	$\text{C}_2\text{H}_3 + \text{N} = \text{HCN} + \text{CH}_2$	$2.00\text{E}+13$	0.00	0
438.	$\text{C}_2\text{H}_2 + \text{NCO} = \text{HCCO} + \text{HCN}$	$1.40\text{E}+12$	0.00	1,815
439.	$\text{C}_2\text{H} + \text{NO} = \text{CN} + \text{HCO}$	$2.10\text{E}+13$	0.00	0
440.	$\text{CH}_2\text{CO} + \text{CN} = \text{HCCO} + \text{HCN}$	$2.00\text{E}+13$	0.00	0
441.	$\text{HCCO} + \text{NO} = \text{HCNO} + \text{CO}$	$7.20\text{E}+12$	0.00	0
442.	$\text{HCCO} + \text{NO} = \text{HCN} + \text{CO}_2$	$1.60\text{E}+13$	0.00	0
443.	$\text{HCCO} + \text{NO}_2 = \text{HCNO} + \text{CO}_2$	$1.60\text{E}+13$	0.00	0
444.	$\text{HCCO} + \text{N} = \text{HCN} + \text{CO}$	$5.00\text{E}+13$	0.00	0

APPENDIX B

Advanced CFD Post-Processing for Coal Flame Structure and Emissions

S. Niksa and G.-S. Liu

Niksa Energy Associates
1745 Terrace Drive
Belmont, CA 94002, USA
Fax: (650) 654 3179
neasteve@pacbell.net

and

L. G. Felix and P. V. Bush

Southern Research Institute
2000 Ninth Avenue South
Birmingham, AL 35255-5305

Submitted for Oral Presentation to the Colloquium on
10. Combustion of Solid Fuels
at the
Twenty-Ninth International Symposium on Combustion
Hokkaido University, Sapporo, Japan
July 2002

Abstract

The simulation strategy described in this paper provides an alternative to conventional CFD post-processing to estimate exhaust NO_x emissions. The method first analyzes a CFD furnace simulation to specify temperature histories and mixing rates. Then the bulk flow patterns are represented with an equivalent network of idealized reactor elements. Detailed reaction mechanisms are then applied over the reactor network, including the most fully validated reaction mechanisms for coal devolatilization and char oxidation and complete elementary reaction mechanisms for chemistry in the gas phase and in soot. The analysis predicted the NO_x emissions from a 1.7 MW_t pilot-scale coal flame within experimental uncertainty over a broad range of O_2 concentrations, with and without staging. The predicted unburned carbon emissions were qualitatively correct for all test conditions, but char reactivity parameters would need to be specified in a one-point calibration for quantitative predictions. The analysis also characterized distinctive chemistry within the flame core, a mixing layer for secondary air entrainment, an overfire air zone, and a char burnout zone. The main practical benefit of the mechanistic complexity is that simulations based on detailed mechanisms require far fewer parameter adjustments than conventional CFD simulations whenever different fuels are considered.

Introduction

The rudimentary chemistry in CFD simulations of coal-fired furnaces has proven to be adequate for predicting exhaust NO_x emissions across the normal operating range of utility boilers, which is limited. But it is too simple to connect to any fuel properties, so a multitude of model parameters must be adjusted for every new fuel to forecast emissions in fuel switching or co-firing scenarios. One obvious remedy would be to incorporate more chemistry into the CFD reaction submodels, but this has not happened during the past decade. However, the means to incorporate realistic reaction mechanisms into coal combustor simulations are now evident in the literature [1,2]: Ignore the turbulence/chemistry interactions and use equivalent networks of idealized reactor elements to depict only the bulk flow patterns. This single premise enables the most advanced coal reaction submodels and elementary reaction mechanisms to be used in furnace simulations, without approximations. In this paper, predictions based on such mechanisms are evaluated with the NO_x and unburned carbon (UBC) emissions from a 1.7 MW_t pilot-scale coal flame for a wide range of exhaust O_2 level, with and without staging.

Test Facility and Evaluation Data

The test facility consisted of fuel handling and feeding systems, a vertical refractory lined furnace with a single up-fired burner, a horizontal convective pass, heat exchangers and conventional exhaust cleaning devices. Emissions from this system have been qualified against those from full-scale, tangential-fired furnaces for the operating conditions imposed in this work [3]. The 8.5 m by 1.07 m (i.d.) cylindrical furnace handles gas velocities from 3 to 6 m/s, and residence times from 1.3 to 2.5 s. A single burner generates a core of pulverized fuel and primary air surrounded by weakly swirled secondary air. Overfire air (OFA) is injected through 4 off-radius ports located 4.6 m down the furnace. The staged test series was collected with 19 % primary air, 66 % secondary air, and 15 % OFA. In the unstaged series, the OFA was combined with secondary air. Feedrates were varied to produce exhaust (wet) O_2 levels between 2.5 and 5 %.

The hv bituminous coal in these tests had 82.9 daf wt. %C; 5.7 %H, 7.5 %O; 1.8 %N; and 2.1 %S, and was fed with 1.5 wt. % moisture, 12.2 % ash, and 35.8 % volatile matter. Its grind size

distribution was represented with a Rosin-Rammler distribution having parameters of 1.311 and 752.06 cm, and a mean size of 48.4 μm .

Computer Simulations

The simulations were developed in three stages, as described separately in more detail [4]. First, a conventional CFD simulation was prepared to assign the thermal histories, temperature profiles, and mixing characteristics for a staged test with 3.3 % O_2 in the exhaust. Second, the CFD simulations were analyzed to subdivide the flow into five regions that sustained the distinctive chemistry. Each region was characterized with 1-D average profiles of temperature and residence time and a residence time distribution (RTD), which were subsequently used to specify a reactor network for the entire flow. Third, the process chemistry was simulated with detailed reaction mechanisms across all elements in the reactor network.

Regions in the flame were delineated with the mass fraction of combustibles, *regardless of phase*, which was evaluated from the sum of all the organic carbon, hydrogen, oxygen, nitrogen, and sulfur in the fuel, *regardless of their appearance in reactants, intermediates, or products*. This variable is a conserved scalar, so its local value indicates the extent of mixing between the various regions in the flow. For the test flame in this study, the normalized combustibles mass fraction delineates five regions, as seen in Fig. 1. The boundary to the core is the locus of positions where the combustibles mass fraction has a value of 0.4, which is the minimum value that avoids convection of secondary air into the core at the inlet. The threshold for the boundary to the mixing layer is 0.3, which is the well-mixed value for the secondary air and primary streams. The OFA injection zone was delineated with an O_2 mass fraction of 0.075. The flame core sustains a competition for the available primary O_2 among volatiles, soot, and the smallest portion of the char particle size distribution (PSD). It is surrounded by a mixing layer that combines volatiles, soot, and char with secondary air across a temperature profile that contains a locus of maximum values for the entire furnace. The secondary air stream moves between the mixing layer and an external recirculation zone (ERZ); however, the ERZ in this furnace is very small and too weak to entrain anything other than combustion products, so it was omitted from the analysis. Downstream of the mixing layer, the post-flame gases are intensely mixed with OFA before moving in

near-plug flow through the char burnout zone. The char particles remain close to the furnace centerline as they move through all zones, including the OFA zone.

Fluid (massless) particle tracking was used to assign thermal histories and residence time distributions (RTDs) for each region. Thermal histories of individual particles were averaged to assign nominal thermal histories throughout each region. A number of continuous stirred tank reactors (CSTRs) in series was assigned to each region by fitting the analytical RTD expression for a series of CSTRs to the CFD-based RTDs. Whenever more than 75 CSTRs were assigned, the flow pattern was regarded as plug flow. RTDs for the core, mixing layer, and burnout zone appear in Fig. 2, along with their analytical representations. The RTD for the core was deconvoluted into one component for 13 CSTRs-in-series and another for plug flow with respective mean residence times of 138 and 192 ms. The plug flow component represents the fluid motion under the influence of particle drag, and the CSTR-component represents flow with significant radial velocities. The RTD for the mixing layer was matched with a series of 19 CSTRs, and that for the OFA zone (not shown) was represented by 6 CSTRs-in-series. The burnout zone is essentially in plug flow.

The reactor elements assigned from the RTDs were connected in order of the flowpath through the various regions to generate the equivalent network of reactors in Fig. 3. Next, the averaged gas and wall temperatures as functions of residence time across each region were approximated as discrete isothermal values for each CSTR in the series. Since many CSTRs were used for the flow patterns, the uncertainties in the discrete representation were negligible. The average particle temperature history during the first 100 ms was used to specify a thermal history for predicting the devolatilization behavior in the furnace. The predicted distributions of volatiles as a function of time were rendered into discrete entrainments of volatiles into each of the appropriate CSTRs or plug flow sectors in the series. As seen in Fig. 3, the reactor network for the core flow was fed with char and injected with volatiles at rates assigned to be consistent with the predicted dynamic devolatilization behavior.

FLASHCHAIN[®], the devolatilization submodel, determined the complete distribution of primary volatiles given only the fuel's proximate and ultimate analyses [5]. A mechanism for secondary volatiles pyrolysis transformed the primary volatiles into soot, CO, CO₂, H₂O, H₂, and HCN, which were the fuels injected into the CSTR network. FLASHCHAIN[®] also predicted the yield and elemental composition of

char, and was combined with a swelling factor correlation and a correlation for the initial carbon density in char to provide all the necessary input for a char oxidation simulation. There are no adjustable parameters in the submodel for devolatilization.

We use the reaction mechanism for the homogeneous combustion and N-species conversion reported by Glarborg et al. [6], which contains 444 elementary reactions among 66 species, including all relevant radicals and N-species. It is implemented in the simulations without any approximations. All rate parameters were assigned independently by the primary developers, so there are also no adjustable parameters in the submodel for gas phase chemistry.

Soot plays several important roles. As it burns, it directly competes for the available O_2 and also consumes O-atoms and OH and recombines H-atoms and OH that would otherwise sustain homogeneous chemistry. And soot reduces NO directly into N_2 . Our soot chemistry submodel accounts for oxidation by O_2 , O-atoms, and OH. A four-step sequence for oxidation by O_2 generates the same overall oxidation rate law as Nagle-Strickland-Constable kinetics, and the rate constants were adjusted to match these kinetics over the range of conditions in a coal flame. Parameters in the oxidation rates by O-atoms and OH, in the recombination reactions, and in the NO reduction on soot were taken from literature [2].

Burning char also competes for the available O_2 , especially the smaller portion of the PSD. The burning rates were determined by various mechanisms, including thermal annealing, ash encapsulation (of low-rank chars), and a transition to chemical kinetic control during the latest stages. These aspects were represented with the Carbon Burnout Kinetics Model (CBK) [7]. The rate parameters were assigned from CBK's internal correlation in terms of the ultimate analysis of the parent coal. However, these parameter assignments need to be refined with a one-point calibration to achieve quantitative accuracy in most applications. The submodel for char-N conversion converts a fixed fraction of char-N into NO at the overall burning rate throughout all stages of char oxidation. This fraction was fixed at 0.39, based on a one-point calibration to the reported NO_x emission for 3.7 % exhaust O_2 with 15 % staging.

All the chemical submodels were implemented in the conservation equations for each CSTR in the network. The j th CSTR is fed by an inlet char flow, F_j^C , an inlet flow of gaseous fuels and combustion

products plus soot, F_j^P , and an entrainment flow, F_j^E , which consists of only volatiles in the test facility in this application. In the analysis, the key organizational principle is the competition for O_2 among chemistry in the gas phase versus the oxidation of soot and char, which is apparent in the following oxygen balance for a CSTR in the network:

$$F_j^E y_{O_2,j}^E + F_j^P y_{O_2,j}^P - F_{j+1}^P y_{O_2,j+1}^P = \frac{\Delta X_j^C F_0^C (1 - x_0^A) \nu_C}{M_C'} - M_{O_2} V_j \omega_{O_2}$$

where subscript j denotes the index on the CSTR under consideration; superscripts E , P , and C denote entrainment, gaseous product, and char flows, respectively; and y^l denotes the oxygen mass fraction in stream l . The terms on the left of the balance represent the net efflux of O_2 from the j th CSTR. The two terms on the right represent the O_2 consumed by char oxidation and by oxidation of gaseous fuels and soot, respectively. The consumption term for char oxidation is written in terms of the burnout predicted by CBK for the residence time increment of the j th CSTR, ΔX_j^C , and the flowrate of ash-free combustibles into the furnace, $F_0^C(1 - x_0^A)$. The stoichiometric O_2 requirement, ν_C , and the char molecular weight, M_C' , account for the presence of heteroatoms in the char combustibles. The consumption term for oxidation of gaseous fuels and soot incorporates the molar rate of O_2 consumption per unit volume, ω_{O_2} . These rates were determined with CHEMKIN and SURFACE CHEMKIN software, then incorporated into the iteration routine that satisfied the oxygen balance. Rates were converted to a mass basis by multiplying by the molecular weight of O_2 , M_{O_2} , and the CSTR volume, V_j .

Note that the analysis does not determine the apportioning of O_2 among the various fuels in this reaction system in advance, or through any imposed constraints. The kinetics for oxidation of soot, char, and gaseous fuels govern O_2 apportioning, as in actual p. f. flames. This feature can only be implemented in an equivalent reactor network because detailed reaction mechanisms are only feasible within this context.

Results

The predicted NO_x and unburned carbon (UBC) emissions are evaluated with data for a range of exhaust O_2 levels with and without staging in Fig. 4. The predicted NO_x emissions are within experimental uncertainty for the complete range of exhaust O_2 for the unstaged flame, and for all cases with the staged flame except for 2.62 % O_2 . In this evaluation, the fraction of char-N converted to NO was adjusted to match the predicted and reported value for 3.4 % O_2 for the staged flames. No other parameter adjustments were involved. The predicted UBC values are qualitatively correct for both flames across the entire range of exhaust O_2 , but high by 2 % throughout this domain. The qualitative consistency indicates that the initial char reactivity in CBK could be increased to match the predicted and reported UBC values at one operating condition, which would restore the accuracy across the entire domain.

The flame structure will be illustrated with axial profiles of the concentrations of O_2 , CO, H_2 , HCN, NH_3 , and NO plus the S. R. value, and the extents of burnout of soot and char. The S. R. value pertains to the gas phase only, and is based on the total amount of all fuel species that have been added to the gas phase up to a specific location in the furnace, including the combustibles in oxidized soot and char. These profiles are plotted versus the CSTR-No. in the series for the core and mixing layer of the staged flame with 4 % exhaust O_2 in Fig. 5.

Volatiles are released into the first 7 CSTRs, 60 % of which entered the second CSTR. Only minor amounts of CO, H_2 , and HCN are released into succeeding CSTRs. The volatiles ignite in the second CSTR and all hydrocarbons and nearly all the H_2 burn while CO accumulates as a partial oxidation product across the entire zone.

Since the overall S. R. value for the flame core is only 0.22, we are inclined to expect N-species conversion under extremely rich conditions in the flame core. Actually, the S. R. value for the gas phase diminishes from infinity (because no fuels appear in the gas phase at the inlet), and is as large as 1.7 while volatiles are burning. Then it diminishes during volatiles combustion to a steady level of 0.87, which is four times larger than the nominal value. This discrepancy is due to the incomplete conversion of coal

into volatiles, the abundance of soot in the volatiles from this hvA bituminous coal (which do not factor into the S. R. value), and the consumption of the available O_2 by the oxidation of soot and char.

Whereas only a few percent of soot burn in the flame core, nearly 15 % of the char is consumed. Two factors are responsible for the surprisingly high extent of char oxidation. First, only the finest sizes in the char PSD effectively compete for the available O_2 with the gaseous fuel compounds (as seen below in Fig. 6), because film diffusion rates are inversely proportional to size. Second, the intrinsic char oxidation reactivity remains relatively very high while the char is being heated because annealing and the associated reduction in reactivity only occur near flame temperatures.

Obviously, the N-conversion chemistry expected for the nominal S. R. value does not materialize within the flame core. The NO concentration initially surges above 300 ppm due to the rapid conversion of HCN, the primary volatile-N species, in the lean core inlet section. But once the available O_2 is consumed, the NO concentration is reduced to only 34 ppm across the 8 CSTRs in the NO_x reduction zone, while NH_3 contributes more to the inventory of fixed-N species. Clearly, the identity of the primary volatile-N species is inconsequential, because homogeneous chemistry rapidly interconverts any volatile N-species into a mixture of HCN, NH_3 , and NO. Also, note that in addition to the N-conversion chemistry, water-gas shifting more-than-doubles the CO concentration across the NO_x reduction zone.

Profiles from the mixing layer to the inlet to the OFA zone also appear in Fig. 5. This region has the highest temperatures in the flame, plus the addition of all secondary air. As soon as secondary air is injected, the S. R. value in the gas phase exceeds unity and remains lean for the rest of this flame. Soot and CO are completely burned out in the first 6 CSTRs. Thereafter char oxidation is the only combustion process in the flame. Most of the residual HCN and NH_3 from the flame core are eliminated while the gas phase is reducing, so only a quarter of these volatile-N species are converted into NO. Nevertheless, the NO concentration leaving the mixing layer is 428 ppm.

The profiles across the OFA and burnout zones remain the same. The gas phase becomes even more oxidizing with the injection of tertiary air. Since soot and CO are no longer present, char oxidation determines the O_2 concentration. The O_2 mass percentage became as large as 4.6 % in the OFA zone, but then gradually decayed to 4.0 % while char burned across the burnout zone. The only fixed-N

species across both zones was NO. The NO concentration fell by dilution across the OFA zone, but slowly increased with the conversion of char-N. The final value in this simulation was 418 ppm (wet).

Extents of char burnout as a function of size increment in the PSD appear in Fig. 6. This figure shows the burnout levels across the 10 size increments in the simulations at the outlets to the flame core, mixing layer, OFA and burnout zones. Only the smallest char particles effectively compete for the available O₂ in the flame core. The entire char PSD is ignited in the mixing layer, yet an acute size dependence persists. At the outlet of the burnout zone, char particles smaller than 125 μm are completely burned out but the largest sizes are only 80 % converted. UBC is determined by the combustion behavior of the largest sizes in the char PSD in furnaces such as this one, where all fuel particles remain on the centerline within a core of hot combustion gases and none bypass the main flame zones.

The simulated flames for all other test conditions have essentially the same structure. The main difference with staging is that the fixed-N species leaving the core are converted under more oxidizing conditions in the mixing layer, and additional char-N is converted before the end of the mixing layer.

Discussion

The simulation strategy described in this paper provides an alternative to conventional CFD post-processing whereby rudimentary N-conversion schemes are applied to the primary CFD temperature and concentration fields to estimate exhaust NO_x emissions. One key difference is that CFD simulations are used in our method only to specify temperature histories and mixing rates, not the species concentration fields that directly reflect the rudimentary chemical reaction schemes. Another key difference is that the furnace is subdivided into regions that delineate the structure of p. f. flames according to the rate-determining chemical and transport processes, as it is in gaseous flames. In the flame core, the S. R. for the gas phase progressed from lean to rich while the volatiles were released. Hydrocarbons and H₂ were partially oxidized into synthesis gas which shifted toward progressively higher CO concentrations (due to water gas shifting) across the downstream half of the core. The core also sustained combustion of the smallest sizes in the char PSD until the O₂ was completely consumed, but negligible soot oxidation. A

few hundred ppm of NO were generated just beyond the injection point, but all but 34 ppm of the N-species were converted into HCN/NH₃ mixtures by the core outlet.

The mixing layer supported a transition from rich to lean mixtures while secondary air was added, and sustained the highest temperatures in the furnace. Both soot and CO burned completely in the mixing layer, along with extents of char burnout that are determined by the rank-dependent char reactivity. The fixed N-species underwent the transition from HCN/NH₃ mixtures to only NO, but not quantitatively. Only one-fourth of the reduced fixed-N species were converted into NO. The OFA and burnout zones sustained only char oxidation. Oxygen levels rose with the addition of tertiary air, then decayed slowly during the later stages of burnout. NO levels initially fell due to the dilution by tertiary air, then recovered with the additional conversion of residual char-N during burnout.

The predicted NO_x emissions agreed with the reported values over nearly the entire test domain, based on a one-point calibration to assign the fraction of char-N converted to NO. Adjustments to the initial char oxidation reactivity in CBK would restore the quantitative accuracy to the predicted UBC values, because they were qualitatively correct. Our simulation method – like any other method – must be calibrated with some macroscopic combustion characteristic that directly pertains to char reactivity and the char-N conversion fraction, such as the burnout level at any single point in the combustion history, including the flyash, and one NO_x emission. Notwithstanding such heuristic adjustments in the char oxidation submodel, simulations based on detailed reaction mechanisms require far fewer parameter adjustments than conventional CFD simulations whenever different fuels are considered. This is the main practical benefit of the mechanistic complexity.

The third key difference was prominent in the relatively simple flowfield in the test facility considered in this study: A multitude of fuel species – CO, H₂, CH₄, C₂H₂, HCN, soot, and char – compete for the available O₂ in a p. f. flame. This competition determines local heat release rates, which govern flame stability, combustion efficiency and unburned carbon emissions, and the local oxidizing potential of the gas phase, which governs N-species conversion. The central premise behind our modeling approach is that the outcome of this competition cannot be forecast from the burning rates of

the individual fuels determined in isolation. Instead, realistic chemical kinetics for each distinctive combustion process must be incorporated into a comprehensive kinetic analysis.

Acknowledgements

Dr. K. Davis and Mr. H.-S. Shim of Reaction Engineering International provided the CFD simulation. Partial financial support was provided through a subcontract from the Southern Research Institute, under the Biomass Cofiring Opportunities sponsored by the U. S. Department of Energy (DE-FC26-00NT40895). Additional support was provided under Alliant Energy's Combustion Initiative.

References

1. Benedetto, D., Pasini, S., Falcitelli, M., La Marca, C., and Tognotti, L., Combust. Sci. Technol. 153: 279-294 (2000).
2. Pedersen, L. S., Glarborg, P., et al. Combust. Sci. Technol. 132: 251-314 (1998).
3. Monroe, L. S. et al. EPRI/EPA 1995 Joint Symp. On Stationary Combustion NO_x Control, Book 3, EPRI, Palo Alto, CA, 1995.
4. Liu, G.-S. and Niksa, S., Fuel, submitted (2001).
5. Niksa, S., Combust. Flame 100: 384-394 (1995).
6. Glarborg, P., Alzueta, M. U., Dam-Johansen, K., and Miller, J. A., Combust. Flame 115:1-27 (1998).
7. Hurt, R. H., Sun, J.-K., and Lunden, M., Combust. Flame 113(1/2):181 (1997).

Figure Captions

1. Extents of the core, mixing layer, ERZ, OFA zone and burnout zone in the furnace from the CFD simulation.
2. RTDs from the CFD simulation (columns) and assigned analytically (curves) for the core, mixing layer, and burnout zone.
3. Equivalent network of reactors for the furnace.
4. Evaluation of predicted (top) NO_x and (bottom) UBC emissions for staged (dashed curves) and unstaged (solid curves) flames.
5. Profiles of (top) O_2 , gaseous fuels, and S. R., (middle) extents of soot and char oxidation, and (bottom) N-species for the flame core (left panels) and mixing layer (right panels) for a staged flame with 4 % exhaust O_2 .
6. Predicted extents of char burnout versus size increment in the char PSD at the outlets of the core, mixing layer, OFA zone, and burnout zone.

Niksa et al., Figure 1

Niksa et al., Figure 2

Niksa et al., Figure 3

Niksa et al., Figure 4

Niksa et al., Figure 5

Niksa et al., Figure 6

APPENDIX C

Reaction Engineering International, Inc.

Re-Simulation of Biomass Co-milled Injection Case

80% Pratt Seam Coal and 20% Biomass

Re-Simulation of Biomass Co-milled Injection Case: *80% Pratt Seam Coal and 20% Sawdust*

January 2, 2002

Reaction Engineering International
Salt Lake City, Utah

Update

- 80% Pratt Seam coal and 20% Sawdust co-milled case
- Actual particle size distributions of sawdust and prattseam coal were used for the current simulation.
- All operating conditions are the same as before.
- The results from the current simulation were compared with those of the previous simulation
 - Lower furnace sections have small differences in temperature, CO, and CO₂ level, but overall there is no significant difference.
 - Coal particles may have already been fine enough to make effects.

New Particle Size Distribution

Finer coal particles
and coarser
Sawdust particles

Operating Conditions

- Based on the operating condition with 3.33% furnace exit O_2 concentration ([20% Sawdust-80% PrattSeam- 3.33% FEO-15.1% OFA.xls](#))
- 80% Pratt seam coal and 20% Sawdust co-firing

Primary air flow rate [SCFM]	133.0
Secondary air flow rate [SCFM]	474.7
Tertiary air flow rate [SCFM]	108.0
Primary air temperature [DEGF]	150.1
Secondary air temperature [DEGF]	600.1
Firing Rate [MMBTU/HR]	3.65
Pulverized coal feed rate to furnace [LB/HR]	317.2
Furnace Exit Oxygen, wet [%]	3.33
Burner Stoichiometric Ratio	1.0
Stoichiometric Ratio	1.2

Gas Temperature

Previous Simulation

Current Simulation

Axial Temperature Profile

Temperature along the center line

Average temperature at each plane

Gas Temperature: Horizontal Profile

Gas Temperature: Horizontal Profile

CO Concentration

Previous Simulation

Current Simulation

Axial CO Profile

CO along the center line

Average CO at each plane

CO₂ Concentration

Previous Simulation

Current Simulation

Axial CO₂ Profile

CO₂ along the center line

Average CO₂ at each plane

APPENDIX D

Southern Research Institute Project Status Report

Presented at Project Review Meeting, 11/13/01

Development of a Validated Model for Use in Minimizing NO_x Emissions and Maximizing Carbon Utilization When Cofiring Biomass with Coal

SoRI Project A162 Review

11/12/01

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Project Team

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Specific Program Objectives

- Develop a consistent, extensive biomass cofiring database
 - relationships between NO_x and biomass cofiring parameters
 - effects on flame stability, carbon burnout, slagging and fouling, and particulate and gaseous emissions
- Develop and validate a biomass cofiring model
 - forecast NO_x and LOI for given fuel combination with specified cofiring configuration
 - optimize cofiring configuration to minimize NO_x and unburned carbon for specified fuels

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Project Flow Chart

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Overall Project Timeline

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Recent Project Timeline

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REI - CFD Modeling of Combustor

- Completed simulation of furnace firing Pratt Seam Coal with single register burner
 - *GLACIER* simulation of single register burner, furnace, and convective section (July, 2001)
 - Good agreement with measured furnace temperatures
- Completed simulation of furnace cofiring Biomass with coal
 - Sawdust comilled with Pratt seam coal (July, 2001)
 - Processed sawdust core-injected with Pratt seam coal (July, 2001)
 - Compare with parametric test results (September, 2001)

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CFD Modeling of Combustor-To Do

- Complete Simulation of furnace with single register burner and Powder River Basin coal (December, 2001)
- Complete simulation of furnace with dual register burner
 - Pratt seam, Galatia, and Powder River Basin coals
 - Sawdust and other biomasses
- Simulate furnace with other biomass injection schemes:
 - Prepare simulation of 100% Galatia coal and 20% sawdust comilled and core-injected with Galatia coal (November, 2001)
 - Near quarl (intersecting flame and parallel to flame) and above quarl, into flame
- Continue comparison with parametric Test Results

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REI CFD Results – 100% Pratt Seam Coal

Temperature

Local Stoichiometric Ratio

CO Mole Fraction

To convective section

O₂ Mole Fraction

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REI CFD Results - Temperature

100% Pratt seam coal

Co-milled 20% Sawdust 80% Pratt seam coal*

Core injection of biomass : 20% Sawdust 80% Pratt seam coal*

To convective section

* Note that operating conditions are slightly different from each other.

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REI CFD Results – Local Stoichiometric Ratio

100% Pratt seam coal

Co-milled 20% Sawdust 80% Pratt seam coal*

Core injection of biomass : 20% Sawdust 80% Pratt seam coal*

To convective section

* Note that operating conditions are slightly different from each other.

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REI - NO_x Prediction by *GLACIER* - 1

Predictions are in close agreement with the measurements.

FEO : furnace exit oxygen concentration, wet,

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REI - NOx Prediction by *GLACIER* - 2

BIOMASS CO-MILLED (SCHEME 1) 15% OFA

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REI - NOx Prediction by *GLACIER* - 3

BIOMASS CORE INJECTION with 15% OFA

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NEA - NO_x / LOI Model

- Simulate detailed chemistry of biomass cofiring over an equivalent network of idealized reactors
 - Provide advanced submodels for coal/biomass devolatilization and burnout
 - Work with REI to specify the network of equivalent reactors from the CFD simulations
 - Develop a computer program that incorporates detailed chemical reaction mechanisms into the equivalent network
- Validate the simulations for every test case in the SoRI/SCS furnace
 - First, validate for coal-only baseline cases
 - Compare with parametric test results

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NEA - NO_x / LOI Model Needs

- Detailed Chemical Mechanisms and Turbulent Mixing Submodels are Needed for This Application
 - Use CFD simulations to characterize **the temperature fields and mixing intensities** in the SRI test facility
 - Develop an **equivalent network** of idealized reactor elements for each cofiring configuration
 - Apply **detailed chemical submodels** to describe fuel-N conversion and burnout throughout the reactor network

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NEA - NO_x / LOI Model Components

- Independent Components of the Model Development:
 - Incorporate fuel decomposition submodels, including NEA's **bio-FLASHCHAIN®** for biomass & coal devolatilization and Prof. R. H. Hurt's **CBK** model for char burnout
 - Simulate combustion and fuel-N conversion in the gas phase, based on Prof. **Glarborg's reburning mechanism**
 - Identify an **equivalent network** of Continuously Stirred Tank Reactors (CSTR) from the CFD simulations

NEA – Progress to Date - 1

- Submodels for biomass devolatilization and combustion have been successfully incorporated into a comprehensive fuel decomposition submodel (PC Coal Lab®)
- NEA specified rate constants for biomass/coal devolatilization and combustion for REI's CFD simulations
- A computer program has been developed to simulate the chemistry of fuel decomposition and N-conversion in the near-burner region of a single-burner flame

NEA – Progress to Date - 2

- NEA has compiled all the information required to specify the equivalent reactor network for the SoRI/SCS furnace from REI CFD simulations (40 CSTR's are required)
- NEA is proceeding to calibrate/validate chemistry simulations with the coal-only baseline case
- Preliminary results indicate that char oxidation rates predicted by CFD are inconsistent with the temperatures and mixing of secondary air in the burner region

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NEA – To Be Done

- Complete the calibration/validation of chemistry simulations with the coal-only baseline case, after resolving the char oxidation rate question (immediate)
- Begin simulations for the available coal-only test cases (November and December of 2001)
- Begin simulations for all available coal-only test cases (November and December of 2001)
- Begin simulations for all available co-firing test cases (Pratt Seam, Galatia, and PRB coal, with sawdust and switchgrass, for comilling, core injection, and side injection)

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NEA – Flame Structure Defined

- ◆ **Core (CR)** – Since the swirl is weak, the primary air and fuel stream remains intact for several meters, and this flame core retains virtually all the fuel particles.
- ◆ **Mixing layer (ML)** – Secondary air contacts the air in a mixing layer that remains thin over most of the core length, but then fans out over the entire cross section beyond the tip of the core. Almost all the secondary air mixes with the core flow downstream of the core tip.
- ◆ **External Recirculation Zone (ERZ)** - A relatively thin external recirculation zone fills the upstream furnace corners, pulling products from the mixing layer into the upstream secondary air stream.
- ◆ **SOFA Zone** – Downstream of the mixing layer, tertiary air is injected as a separated overfire air (SOFA) stream through four off-radius jets. Some eddies alter the gas flow streamlines near the injection ports but particle trajectories are hardly affected by the OFA flows.
- ◆ **Burnout (BO) Zone** – Several seconds of residence time are available for the later stages of char oxidation downstream of the SOFA injectors, before the exhaust passes through a convective section and exhaust cleaning systems.

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NEA – Flame Structure Detailed

External Recirculation Zone

Flame Region	Residence Time (ms)	Temperature, °C	S. R.
Core	250	80 – 1520	0.25
Mixing Layer	470	1520 – 1350	0.95
SOFA Zone	170	1350 – 1225	1.12
Burnout Zone	1910	1225 – 1050	1.12

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NEA – CSTR Terminology

NEA – Reactor Network – 40 CSTR's

NEA – Predicted NO and Char Burnout (X_c)

NO Emissions and Char Burnout for Co-Milled Switchgrass/Bituminous Coal Flames

PRELIMINARY	Mixing Layer		SOFA Zone		Burnout Zone	
	NO, ppm	X_c , %*	NO, ppm	X_c , %*	NO, ppm	X_c , %*
hva Bit.	402	78.0	370	82.7	406	89.9
90% Bit/10% SG	388	76.8 77.7/50.1	356	81.7 82.5/54.2	392	89.3 90.1/64.6
80% Bit/20% SG	319	81.9 83.9/53.4	288	85.1 87.0/57.5	307	89.4 91.0/66.4
70% Bit/30% SG	367	75.3 78.3/50.3	336	80.0 83.0/54.4	366	87.5 90.2/64.9

* Single values are averages over the zone for coal and switchgrass
values expressed as xx.x/xx.x are burnout percentages for coal (first)
and switchgrass (second)

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SoRI/SCS – Combustion Research Facility

- All testing conducted at the SoRI/SCS 6 MBtu/hr Combustion Research Facility (at 3.5 MBtu/hr)
- Continuous measurement and logging of over 180 pertinent process parameters (Yokogawa CS-1000 DCS)
- In-situ testing for mass emissions, particle size, furnace temperature, ash resistivity, gases (O_2 at furnace exit and at CEM location, CO , CO_2 , SO_2 , NO_x - Adding H_2O , HCl).
- On-site wet chemical flue gas and ash analyses, CHN (for LOI), fuel heat value measurement
- Instrumented CE-Raymond Model 352 Deep Bowl mill

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Combustion Research Facility

6 MBtu/hr (1.75 MW_t)

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Combustion Research Facility

Furnace & LNB

Control Room

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Combustion Research Facility

CE-Raymond Bowl Mill

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Furnace Convective Section

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Controlled Variables in Cofiring Tests

- Biomass types (spanning the range of fuel nitrogen and volatile/fixed carbon ratios that may be encountered)
- Biomass particle size
- Coal types (representing the most widely used coals in the utility market)
- Fuel mixing conditions
- Burner configurations
- Time-temperature profile and fuel-air mixing conditions in the combustion region have to match full-scale boilers

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Major Variables within the Test Matrix

COAL

- 1 Jacobs Ranch - PRB
- 2 Shoal Creek – Alabama – Low S
- 3 Pratt Seam – Alabama – Moderate S
- 4 Galatia – Illinois Basin

Biomass

- 1 Switchgrass (0.5% N)
- 2 Corn Stover (1.25% N)
- 3 Hardwood Sawdust (Dry)
- 4 Hardwood Sawdust (Wet)
- 5 Rice Hulls
- 6 Willow
- 7 Hybrid Poplar
- 8 Poultry Litter

Burner Configuration

- A Single Register (Tangential) Burner
- B Generic Low NOx Dual Register Burner

Biomass Injection Scheme (Either Burner)

- 0 Burner alone, no Biomass
- 1 Co-milled, Injected with Coal
- 2 Through Center of Burner
- 3 Off-Axis, Direct Injection into flame
- 4 Off-Axis, Direct Injection parallel to flame
- 5 Off-Axis, Above Flame

Biomass Quantity

- 0% - 100% Coal
- 10% - 90% Coal
- 20% - 80% Coal

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Biomass Selected for Pilot-Scale Tests

Switchgrass: preferred herbaceous crop, 0.5% fuel N

Corn Stover: abundant crop waste, 1.25% fuel N

Dry sawdust: abundant forest products waste, 0.15% fuel N

Wet sawdust: evaluate combustion thermal effects

Coastal Bermuda: grass with relatively high fuel N

Poplar & willow: preferred woody crops, low fuel N

Poultry litter: available farm waste, 5% fuel N

Rice hulls: regional agricultural residue, high silica

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Locations for Biomass Injection

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Matrix of Proposed Tests

Test Number	Coal First	Choice Second	Burner-Injection Scheme		Biomass Fuel - % Biomass				
			First	Second	Day 1	Day 2	Day 3	Day 4	Day 5
1	1		A - 0	A - 2	1 - 0	1 - 10	1 - 20	2 - 10	2 - 20
2	1		A - 2		3 - 10	4 - 10	5 - 10	5 - 20	6 - 10
3	1		A - 2	A - 1	7 - 10	8 - 10	1 - 10	2 - 10	5 - 10
4	1		A - 1		3 - 10	4 - 10	6 - 10	7 - 10	8 - 10
5	1		A - 3		1 - 10	1 - 20	2 - 10	2 - 20	5 - 10
6	1		A - 4		1 - 10	1 - 20	2 - 10	2 - 20	5 - 10
7	2		A - 0	A - 2	1 - 0	1 - 10	1 - 20	2 - 10	2 - 20
8	2		A - 2		3 - 10	4 - 10	5 - 10	5 - 20	6 - 10
9	2		A - 2	A - 1	7 - 10	8 - 10	1 - 10	2 - 10	5 - 10
10	2		A - 1		3 - 10	4 - 10	6 - 10	7 - 10	8 - 10
11	2		A - 3		1 - 10	1 - 20	2 - 10	2 - 20	5 - 10
12	2		A - 4		1 - 10	1 - 20	2 - 10	2 - 20	5 - 10
13	3		B - 0	B - 2	1 - 0	1 - 10	2 - 10	5 - 10	8 - 10
14	4		B - 0	B - 2	1 - 0	1 - 10	2 - 10	5 - 10	8 - 10
15	3	4	B - 1		1 - 10	2 - 10	5 - 10	1 - 10	2 - 10
16	3	4	B - 3		1 - 10	2 - 10	5 - 10	1 - 10	2 - 10
17	3	4	B - 4		1 - 10	2 - 10	5 - 10	1 - 10	2 - 10
18	1	2	B - 2		1 - 10	2 - 10	5 - 10	1 - 10	2 - 10

Grayed areas are used to delineate the second of two conditions within a week of testing.

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Coals Selected for Pilot-Scale Tests

Analysis	Coal Source				
	Galatia	Jacobs Ranch	Pratt Seam	Shoal Creek	Lone Mountain
Proximate (As Received)					
Moisture, %	8.96	10.19	2.25	6.80	1.89
Ash, %	6.31	6.49	12.84	14.08	6.50
Volatile, %	31.00	39.73	29.02	22.43	34.15
Fixed Carbon, %	3.73	43.59	55.89	56.69	57.45
Sulfur, %	0.97	0.51	1.49	0.72	0.87
Heating Value, Btu/lb	12402	10356	12919	12305	13958
Ultimate Analysis (Dry)					
Carbon, %	75.55	68.97	74.53	74.94	79.68
Hydrogen, %	5.25	4.25	4.33	3.76	4.94
Nitrogen, %	1.69	0.99	1.45	1.50	1.55
Sulfur, %	1.06	0.57	1.52	0.77	0.89
Ash, %	6.93	7.23	13.14	15.11	6.63
Oxygen, % (Diff)	9.52	17.99	5.03	3.92	6.31
Total, %	100.0	100.0	100.0	100.0	100.0
Chlorine, %	0.31	0.04	0.01	0.02	0.03

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Biomasses Selected for Pilot-Scale Tests - 1

Analysis	Biomass Source				
	Sawdust (Red Oak)	Sawdust (Maple)	Switchgrass (Field Chopped)	Switchgrass (Baled)	Corn Stover
Proximate (As Received)					
Moisture, %	3.11	4.97	15.18	5.28	7.15
Ash, %	0.52	0.36	29.53	3.52	8.96
Volatile, %	82.45	80.08	47.69	73.04	66.26
Fixed Carbon, %	13.92	14.60	7.60	18.16	17.63
Sulfur, %	0.01	0.01	0.21	0.07	0.09
Heating Value, Btu/lb	8017	7868	5891	7615	7166
Ultimate Analysis (Dry)					
Carbon, %	48.97	48.94	36.59	46.91	46.28
Hydrogen, %	6.09	5.95	3.50	5.86	5.40
Nitrogen, %	0.15	0.03	1.59	0.69	1.24
Sulfur, %	0.01	0.01	0.25	0.07	0.10
Ash, %	0.54	0.37	34.82	3.72	9.65
Oxygen, % (Diff)	44.24	44.70	23.25	42.75	37.33
Total, %	100.0	100.0	100.0	100.0	100.0
Chlorine, %	0.01	NA	0.10	NA	0.13

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Biomasses Selected for Pilot-Scale Tests - 2

	Coal	Coal + Biomass		Biomass		
Ash Mineral Analysis	100% Coal	80% Pratt 20% Wood	80% Pratt 20% Swgrass	Sawdust (Maple)	Switchgrass (Baled)	Corn Stover
Ignited as Oxide						
Li ₂ O, wt %	0.12	0.13	0.12	0.03	0.07	0.03
Na ₂ O, wt %	0.38	0.32	0.36	1.2	1.4	1.4
K ₂ O, wt %	1.6	1.9	2.1	11.5	16.0	14.8
MgO, wt %	0.97	1.0	1.0	9.4	6.7	6.2
CaO, wt %	1.6	1.7	1.9	38.9	17.4	7.8
Fe ₂ O ₃ , wt %	8.7	9.3	8.5	4.9	3.6	2.8
Al ₂ O ₃ , wt %	26.8	27.2	27.3	3.8	5.1	5.0
SiO ₂ , wt %	54.1	53.6	52.9	20.8	40.1	58.6
TiO ₂ , wt %	2.2	2.2	2.1	0.34	0.41	0.38
P ₂ O ₅ , wt %	0.87	1.2	1.4	4.00	4.50	3.0
SO ₃ , wt %	1.2	0.63	0.66	2.7	5.7	2.1
V ₂ O ₅ , wt %	<0.08	<0.08	<0.09	<0.18	<0.15	<0.04
Sum	99.54	99.18	98.34	97.57	100.98	102.11
% LOI, (750°F)	81.9	1.4	1.6	99.6	93.5	98.2

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Completed Tests - 1

- Test 1: Pratt Seam Coal – Comilled Biomass, single register burner, 15%, 20% Switchgrass, 10%, 20% Sawdust. 0%, 15%, 30% overfire air. 1/28-2/3/01
- Test 2: Pratt Seam Coal – Biomass through center of burner (scheme 2), single register burner, 10% Sawdust. 0%, 15% overfire air. Problems with biomass injection scheme and flame stability. 2/25-3/2/01
- Test 3: Pratt Seam Coal – Biomass through center of burner (scheme 2), single register burner, 10%, 20% Switchgrass, 10%, 20% Sawdust. 0%, 15% overfire air. Continued problems with flame stability. 4/8-14/01

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Completed Tests - 2

- Test 4: Pratt Seam Coal – no biomass, single register burner, extensive characterization of coal-only firing at 0% and 15% overfire air. Corrected flame stability problem. 5/14-17/01
- Test 5: Pratt Seam Coal – Biomass injection toward quarl (scheme 3), single register burner, 10%, 20% Switchgrass, 10%, 20% Sawdust. 0%, 15% overfire air. 6/10-15/01
- Test 6: Galatia Coal – Comilled Biomass, single register burner, 10%, 20% Sawdust. 0%, 15%, overfire air. 7/8-7/13/01 (switchgrass not delivered in time for test)

Completed Tests - 3

- Test 7: Galatia Coal – Comilled Biomass, single register burner, 10%, 20% Switchgrass. 0%, 15%, overfire air. Pratt Seam Coal comilled with 20% sawdust. 8/5-10/01
- Test 8: Jacobs Ranch Coal – Comilled Biomass, single register burner, 10%, 20% Switchgrass, 10%, 20% Sawdust. 0%, 15% overfire air. 9/16-21/01
- Test 9: Jacobs Ranch Coal – Biomass through center of burner (scheme 2), single register burner, 10%, 20% Switchgrass, 10%, 15% Sawdust. 0%, 15% overfire air. 10/21-26/01

Upcoming Tests

- Dual register burner with Pratt seam, Galatia, Jacobs Ranch, and possibly Shoal Creek coal with various biomasses and schemes of biomass addition. Choices dictated by modeling effort
- Single register burner with Shoal Creek coal, previous coals with various injection schemes or additional biomasses as dictated by the modeling effort.

Typical Combustor Cofiring Test Data

Combustor Cofiring Test Data – Zoom In

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Raw and Averaged Test Data

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Comilled vs Center vs Side Injection

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Pratt Seam Comilled with Biomass – No OFA

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Pratt Seam Comilled with Biomass – No OFA

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Pratt Seam Comilled with Biomass – 15% OFA

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Pratt Seam Comilled with Biomass – NO_x Red.

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Pratt Seam Comilled with Biomass – UBC

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Pratt Seam Coal - Axial Biomass Inj. – No OFA

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Pratt Seam Coal - Axial Biomass Inj. – 15% OFA

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Pratt Seam Coal - Axial Injection – NO_x Red.

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Pratt Seam Coal - Axial Injection – UBC

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Pratt Seam – Side Injection – No OFA

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Pratt Seam – Side Injection – 15% OFA

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Pratt Seam – Side Injection – NO_x Red.

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Pratt Seam – Side Injection – UBC

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Pratt Seam – Galatia Comparison

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Lower Furnace Temperature – Coal Only

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Galatia Comilled with Biomass – No OFA

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Galatia Comilled with Switchgrass – No OFA

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Galatia Comilled with Biomass – 15% OFA

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Galatia Comilled with Switchgrass – 15% OFA

Radial Temperature Profiles Compared for Switch Grass Co-Fired with Galatia Coal at 15% OFA and 3.5% FEO

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Galatia Comilled with 20% Switchgrass – All

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Galatia Comilled with Biomass – NO_x Red.

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Galatia Comilled with Biomass – UBC

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Ongoing Analyses Not Shown

- * In situ mass concentrations (EPA Method 17), fly ash particle size distributions (cascade impactor), and ash resistivity
- * Chemical analyses of coal, biomass, fly ash, furnace bottom, and furnace convective section ash
- * Sieve analyses of pulverized coal, comilled coal and biomass, and milled biomass (from MESA Reductions)
- * Gas analyses (other than NO_x) from CEM system

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