

*This report includes color pictures*

## **JOINT FINAL REPORT**

# **ADVANCED BIOMASS REBURNING FOR HIGH EFFICIENCY NO<sub>x</sub> CONTROL**

USDA Phase II SBIR, Contract # 97-33610-4470

and

## **BIOMASS REBURNING - MODELING/ENGINEERING STUDIES**

DOE NETL, Contract # DE-FC26-97FT-97270

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## ABSTRACT

This report presents results of studies under a Phase II SBIR program funded by the U. S. Department of Agriculture, and a closely coordinated project sponsored by the DOE National Energy Technology Laboratory (NETL, formerly FETC). The overall Phase II objective of the SBIR project is to experimentally optimize the biomass reburning technologies and conduct engineering design studies needed for process demonstration at full scale. The DOE project addresses supporting issues for the process design including modeling activities, economic studies of biomass handling, and experimental evaluation of slagging and fouling.

The performance of biomass has been examined in a 300 kW ( $1 \times 10^6$  Btu/hr) Boiler Simulator Facility under different experimental conditions. Fuels under investigation include furniture waste, willow wood and walnut shells. Tests showed that furniture pellets and walnut shells provided similar  $\text{NO}_x$  control as that of natural gas in basic reburning at low heat inputs. Maximum  $\text{NO}_x$  reduction achieved with walnut shell and furniture pellets was 65% and 58% respectively. Willow wood provided a maximum  $\text{NO}_x$  reduction of 50% and was no better than natural gas at any condition tested.

The efficiency of biomass increases when N-agent is injected into reburning and/or burnout zones, or along with OFA (Advanced Reburning). Co-injection of  $\text{Na}_2\text{CO}_3$  with N-agent further increases efficiency of  $\text{NO}_x$  reduction. Maximum  $\text{NO}_x$  reduction achieved with furniture pellets and willow wood in Advanced Reburning was 83% and 78% respectively.

All combustion experiments of the Phase II project have been completed. All objectives of the experimental tasks were successfully met.

The kinetic model of biomass reburning has been developed. Model agrees with experimental data for a wide range of initial conditions and thus correctly represents main features of the reburning process. Modeling suggests that the most important factors that provide high efficiency of biomass in reburning are low fuel-N content and high content of alkali metals in ash. These results indicate that the efficiency of biomass as a reburning fuel may be predicted based on its ultimate, proximate, and ash analyses.

The results of experimental and kinetic modeling studies were utilized in applying a validated methodology for reburning system design to biomass reburning in a typical coal-fired boiler. Based on the trends in biomass reburning performance and the characteristics of the boiler under study, a preliminary process design for biomass reburning was developed. Physical flow models were applied to specific injection parameters and operating scenarios, to assess the mixing performance of reburning fuel and overfire air jets which is of paramount importance in achieving target  $\text{NO}_x$  control performance. The two preliminary cases studied showed potential as candidate reburning designs, and demonstrated that similar mixing performance could be achieved in operation with different quantities of reburning fuel.

Based upon this preliminary evaluation, EER has determined that reburning and advanced reburning technologies can be successfully applied using biomass. Pilot-scale studies on biomass reburning conducted by EER have indicated that biomass is an excellent reburning fuel. This generic design study provides a template approach for future demonstrations in specific installations.

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## 1.0 Introduction

The major environmental problem faced by the power generation industry is controlling flue gas emissions of nitrogen oxides ( $\text{NO}_x$ ) from coal and oil fired boilers.  $\text{NO}_x$  is produced during the combustion process from molecular nitrogen and fuel nitrogen. The main form of  $\text{NO}_x$  is nitric oxide, NO. Some nitrogen dioxide,  $\text{NO}_2$ , is also formed, but its concentration is less than 5% of the total  $\text{NO}_x$  which is typically 200-1000 ppm. The nitrogen oxides are the subject of concern because they are toxic compounds and the precursors to acid rain deposition and photochemical smog. In some combustion regimes, nitrous oxide,  $\text{N}_2\text{O}$  - a "greenhouse" gas, can be also formed. The 1990 Clean Air Act Amendments (CAAA) mandate a 2,000,000 ton per year decrease in nitrogen oxide emissions. Title I of the CAAA requires high efficiency  $\text{NO}_x$  control in ozone non-attainment areas. The most significantly affected area is the Ozone Transport Region (including Pennsylvania and the states North and East). EPA regulations require many plants in this area to reduce  $\text{NO}_x$  to as low as  $0.15 \text{ lb}/10^6 \text{ Btu}$  by the year 2003. For most units, this corresponds to 65-80%  $\text{NO}_x$  reduction, and  $\text{NO}_x$  regulatory requirements have a tendency to be more stringent in the future.

Reburning is a combustion modification technology that removes  $\text{NO}_x$  from combustion products by using fuel as a reducing agent and is based on the principle that hydrocarbon fragments can react with NO. Reburning can be applied to any type of utility boiler firing configuration. The reburning fuel can be the same as the primary fuel or it can be a different fuel such as coal, biomass, gas, or fuel oil. Conventional reburning technology is applied to a utility boiler by the staged addition of fuel and air to the boiler furnace following the main burners or primary combustion zone. The process can be divided conceptually into three zones as illustrated in Figure 1.1.

*Primary Zone:* During reburning, the primary combustion zone will account for approximately 80 percent of the total heat input. In this zone, the primary fuel will be burned under fuel lean conditions. In most cases, the air/fuel ratio to the main burners can be reduced which will lower the initial  $\text{NO}_x$  entering the reburning zone, and reduce the amount of reburning fuel necessary to achieve optimum conditions for  $\text{NO}_x$  reduction in the reburning zone.

*Reburning Zone:* Above the main burners, additional fuel is added to create a slightly fuel rich environment or "reburning zone" which reduces nitrogen oxides formed in the primary combustion zone to molecular nitrogen. Depending upon the primary excess air level, the reburning fuel typically accounts for up to 20 percent of the total heat input. The process begins when hydrocarbon radicals formed from the reburning fuel in the fuel rich reburning zone, primarily CH species, react with NO from the primary zone to form other nitrogen species such as HCN and  $\text{NH}_3$ . Once formed, these species rapidly react with other primary NO molecules to form molecular nitrogen ( $\text{N}_2$ ). EER has extensively studied the reduction of NO to molecular nitrogen in the reburning process.

*Burnout Zone:* Following the reburning zone, overfire air is added to the boiler to produce overall lean conditions and to oxidize carbon monoxide and any remaining fuel fragments exiting the reburning zone. The remaining fixed nitrogen species will either be oxidized to  $\text{NO}_x$  or reduced to molecular nitrogen.

In advanced reburning technology, a  $\text{NO}_x$  reducing reagent (such as urea or ammonia) is added to the reburning process to further reduce  $\text{NO}_x$  emissions. The reagent can be added before, with or after the overfire air depending upon the flue gas temperature at the point of overfire air

injection. Although advanced reburning is essentially the combination of gas reburning with selective non-catalytic reduction (SNCR) technology, its implementation combines the technologies in a fashion that reduces the cost of SNCR implementation and can improve performance of the reagent injection step.

While biomass cofiring has been successfully demonstrated in several coal-fired utility boilers, a value-added option is to utilize biomass above the main burner as a reburning fuel. Biomass which may include wastewood, straw, agricultural waste, etc. can be inexpensive and has a potential for lower cost  $\text{NO}_x$  reduction with comparable performance to that of gas and coal reburning. Utilization of biomass in advanced reburning has a potential to achieve about 90%  $\text{NO}_x$  control in coal fired boilers and promises certain advantages over other fuels. This new concept presents a means for utilizing both energy content of biomass and its chemical constituents (nitrogen- and alkali-containing compounds) which can promote the chemical reactions of NO removal from combustion flue gas.

GE Energy and Environmental Research Corp. (EER) has conducted a Phase II SBIR project sponsored by the U. S. Department of Agriculture. The objective of the Phase II project is to move the biomass reburning technology to the full-scale demonstration level. This project is supported by a closely coordinated project sponsored by DOE NETL (formerly FETC). The division of tasks between the two projects was designed to keep process optimization and design tasks within the SBIR project. The DOE project involves modeling activities, economic studies of biomass handling, and experimental evaluation of slagging and fouling.

The overall objective of the total R&D program (both USDA and DOE projects) is to develop information and experience to move the technology to a full-scale demonstration. This is the combined final report for both projects.

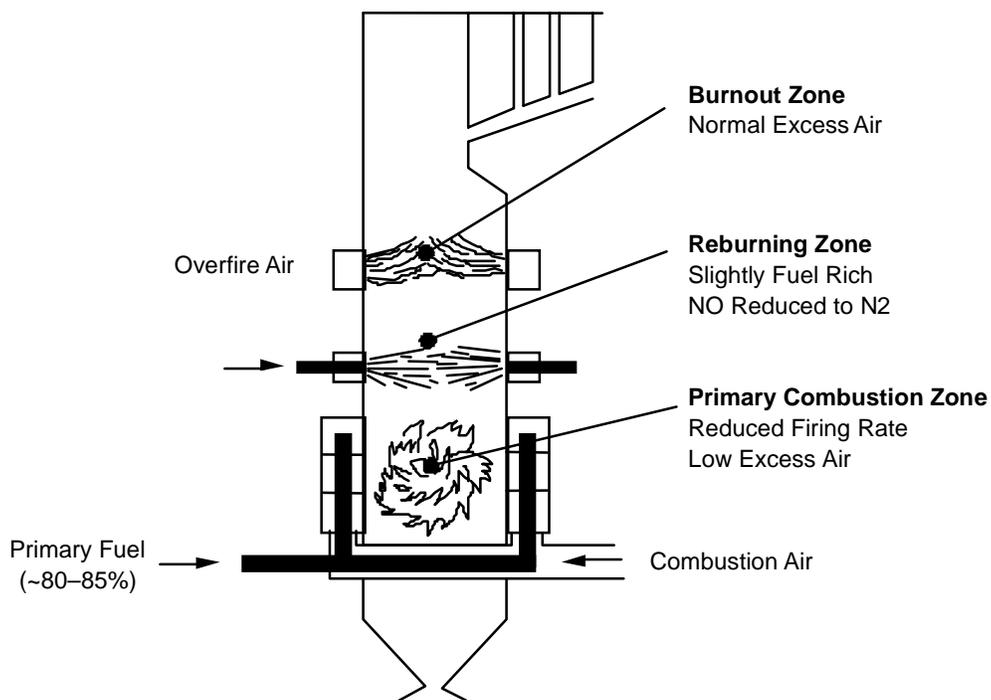


Figure 1.1. Application of reburning to a utility boiler.

## 2.0 Technical Objectives and Tasks

The overall USDA Phase II SBIR objective is to experimentally optimize the biomass reburning technologies and conduct engineering design studies needed for process demonstration at full scale. Specific objectives of the program include:

- optimization of biomass reburning in pilot-scale tests;
- development of engineering modeling tools for commercial applications of biomass reburning;
- evaluation of potential boiler impacts, such as slugging and fouling; and
- evaluation of biomass fuel processing/handling economics as part of an overall economics and performance analysis for biomass reburning.

The following six tasks were conducted in the scope of the USDA Phase II project (conducted by EER):

1. Preparation of the pilot-scale combustion facility (*Sec. 3*)
2. Optimization of basic biomass reburning (*Sec. 4*)
3. Optimization of the Advanced Biomass Reburning process (*Sec. 5*)
4. Economic analysis of biomass reburning technologies (*Sec. 8*)
5. Design methodology and application (*Sec. 9*)
6. Project management and reporting.

Specific objectives of the DOE NETL project include:

- Develop engineering modeling tools for application of biomass reburning
- Evaluate slagging and fouling caused by biomass reburning
- Determine economics of biomass handling

The DOE project included 7 tasks:

1. Kinetic Modeling of Biomass Reburning (*Sec. 6 - EER*)
2. Computational Fluid Dynamics (CFD) Modeling (*Appendix D - NETL R&D*)
3. Physical Modeling (*Sec. 7 - EER*)
4. Biomass Preparation Economics (*Appendix E - NETL R&D*)
5. Evaluation of Slagging and Fouling (*Appendix F - NETL R&D*)
6. Reburning vs. Cofiring Evaluation (*Appendix C - Antares, Inc.*)
7. Project Management and Reporting (*EER*)

The Organizational Structure of the two projects is as shown in Figure 2-1. Project participants for the combined effort include: GE Energy and Environmental Research Corporation (EER), NETL R&D group, Niagra Mohawk Power Corporation (NMPC), and Antares, Inc. EER was the prime contractor and responsible for coordinating the combined effort. NETL conducted several of the technical tasks in the DOE project, including CFD Modeling, Biomass Preparation

Economics, and Evaluation of Slagging and Fouling. Antares conducted the Reburning vs. Cofiring Evaluation in the DOE Project. Niagra Mohawk was to provide a site for subsequent demonstration of the technology.

During the course of the program, Niagra Mohawk did participate in discussions on the approach to demonstration and commercialization of the technology. However, before the conclusion of the current contracts, Niagra Mohawk withdrew from the proposed demonstration agreement following a change in ownership. At the time of this report, a host site agreement has not yet been reached with any other candidate site. To complete the program objectives, modeling and design studies were conducted on a representative boiler design, rather than a specific candidate site. The boiler selected is a tangentially fired furnace using coal as the primary fuel. EER has previously conducted reburning studies on this boiler, and so already has the benefit of experience in evaluating this unit.

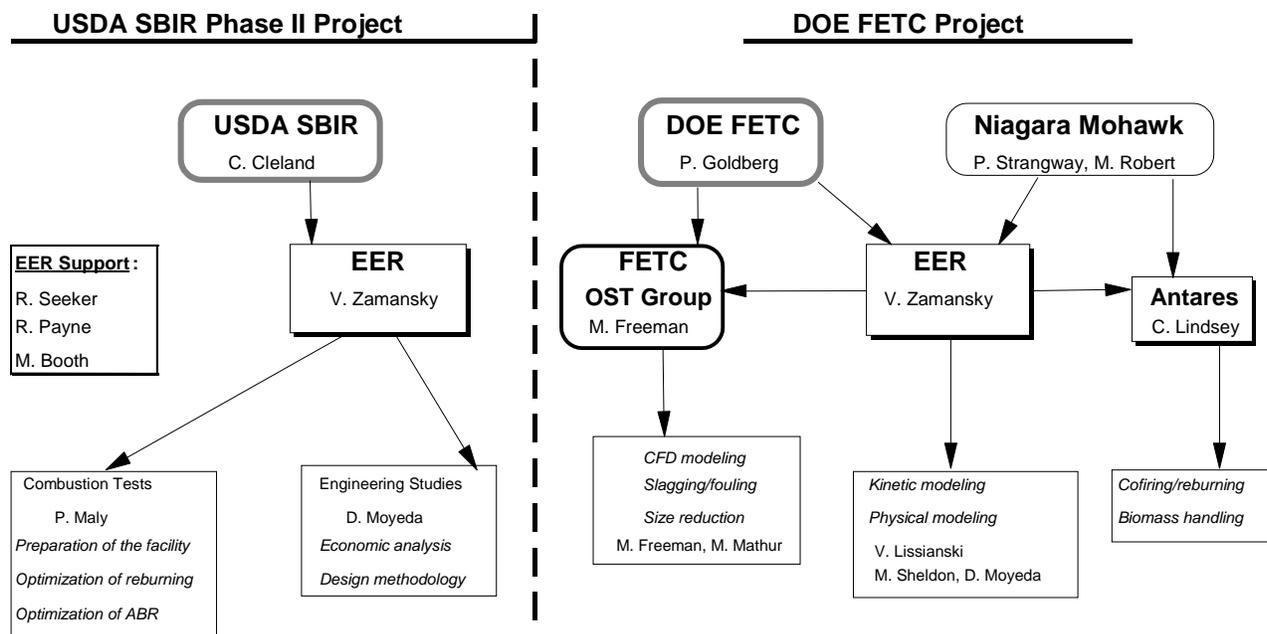


Figure 2.1. Organizational structure of the R&D program.

The following Sections provide a coordinated discussion of the joint program tasks.

### 3.0 Preparation of the Pilot-Scale Combustion Facility

[USDA Task 1]

#### 3.1 Boiler Simulator Facility

The pilot scale tests were conducted in EER's 300 kW ( $1 \times 10^6$  Btu/hr) Boiler Simulator Facility (BSF). The BSF (Fig. 3.1) is designed to provide an accurate sub-scale simulation of the flue gas temperatures and composition found in a full scale boiler. It consists of a burner, vertically down-fired radiant furnace, and horizontal convective pass. A variable swirl diffusion burner

with an axial fuel injector is used to simulate the approximate temperature and gas composition of a commercial burner in a full scale boiler. Primary air is injected axially, while the secondary air stream is injected radially through the swirl vanes to provide controlled fuel/air mixing. Numerous ports located along the axis of the facility allow supplementary equipment such as reburning injectors, additive injectors, overfire air injectors, and sampling probes to be placed in the furnace.

The cylindrical furnace section is constructed of eight modular refractory-lined sections with an inside diameter of 0.56 m (22 in). The convective pass is also refractory lined, and contains air cooled tube bundles to simulate the superheater and reheater sections of a full scale utility boiler. Heat extraction in the radiant furnace and convective pass is controlled such that the residence time-temperature profile matched that of a typical full scale boiler. A suction pyrometer is used to measure furnace temperatures. The temperature gradient in the range 1200-1700 K (1650-2600 °F) is about  $-300 \text{ K/s}$  ( $-540 \text{ °F/s}$ ).

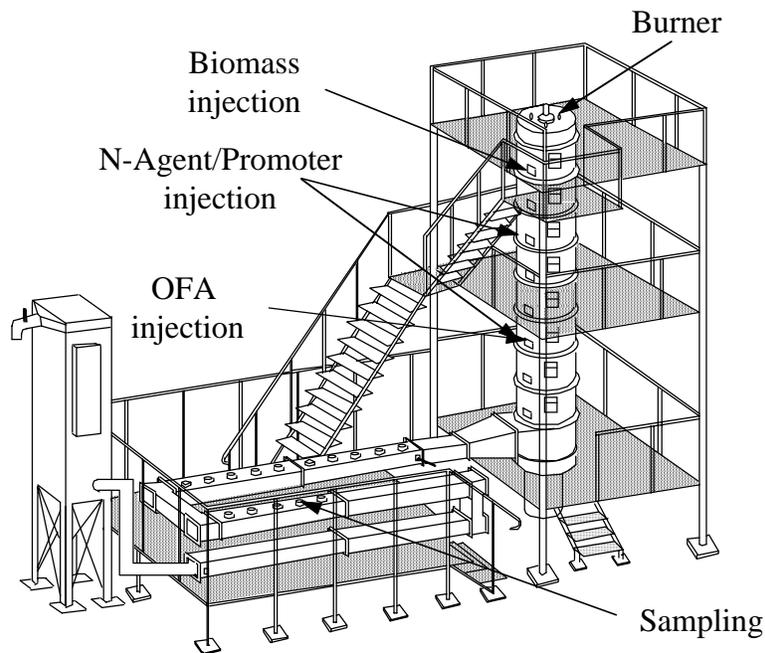


Figure 3.1. Boiler Simulator Facility (BSF).

A series of pilot scale tests was conducted in the BSF to characterize biomass reburning performance as a function of key process variables. The reburning fuels of primary interest were a pelletized furniture waste and willow wood. For comparison, several tests were also conducted with natural gas and walnut shells. Natural gas and Illinois and Ohio coals were used as primary fuels.

All solid fuels were pulverized for the tests. The coals were pulverized in a bowl mill such that 70% passed through a 200 mesh sieve. The furniture waste and walnut shells were pulverized in a hammer mill. Size distribution was varied by installing different screens in the hammer mill and by running samples through the mill multiple times. For the furniture waste four grinds were

tested: 9%, 21%, 27%, and 48% through 200 mesh. The 48% < 200 mesh grind was used for most of the tests. The walnut shells were more brittle than the furniture waste pellets and provided a finer size distribution. For the walnut shells a single grind of 55% < 200 mesh was tested.

It was found that the willow wood was fibrous and considerably more difficult to process than other biomass samples. It was received as branches up to 0.6 m long. It was pre-processed by running through an industrial wood chipper and then pulverized in a hammer mill. The willow wood was difficult to convey through the hammer mill and provided larger size particles than those obtained with other biomass samples. For example, passing the willow wood through the hammer mill with a 1.5 mm screen gave a size fraction of 23% less than 200 mesh, whereas under the same conditions the furniture waste size was 40% less than 200 mesh. The baseline size fraction for the willow wood reburning tests was 23% less than 200 mesh.

### **3.2 Reburning and Additive Injection Systems**

The reburning injector was elbow-shaped, and was installed along the centerline of the furnace, aligned in the direction of gas flow. A gaseous transport medium was added along with biomass to provide sufficient momentum for good mixing with the furnace gas. Both air and bottled nitrogen were tested as transport media. Overfire air (OFA) was injected through an elbow-shaped injector to burn out combustibles generated in the reburning zone. The OFA injection temperature was varied as required by the test plan. Nitrogen agents and sodium promoters were injected as aqueous solutions. Twin fluid atomizers made by Delavan Corp. were used, employing both air and nitrogen as transport media. The additives were injected into reburning or burnout zone and/or with the OFA. In the latter case, the OFA itself was used as the atomizing medium.

### **3.3 Sampling and Analysis Methods**

Sampling included a continuous emissions monitoring system (CEMS) for on-line analysis, manual method sampling for ammonia and HCN, and ash sampling for carbon burnout determination. CEMS components included a water cooled sample probe, sample conditioning system (to remove water and particulate), and gas analyzers. High purity dry nitrogen were used to zero each analyzer before and after each test. Certified span gases were used to calibrate and check linearity of the analyzer. Test data were recorded on both a chart recorder and personal computer based data acquisition system. Species analyzed, detection technique, and detection limits can be summarized as follows:

- O<sub>2</sub>: paramagnetism, 0.1%
- NO<sub>x</sub>: chemiluminescence, 1 ppm
- CO: nondispersive infrared spectroscopy, 1 ppm
- CO<sub>2</sub>: nondispersive infrared spectroscopy, 1 ppm
- NH<sub>3</sub>: SCAQMD Method 207 (sampling, Nessler reagent, colorimetry), 0.1 ppm
- HCN: sampling, ion-specific electrode, 0.03 ppm
- Carbon in ash: extractive ash sampling with induction furnace analysis.

## 4.0 Optimization of Basic Biomass Reburning

[USDA Task 2]

The goal of this task was to determine efficiency of biomass reburning as a function of process parameters. The following sections describe test fuel characteristics and results of the biomass reburning test series with natural gas and coal as primary fuels.

### 4.1 Test Fuel Characteristics

Reburning fuels tested included furniture waste pellets, willow wood, walnut shells, and natural gas. Main fuels tested included bituminous Illinois coal, bituminous Ohio coal, and natural gas. Table 4.1 presents analytical data for each of the solid fuels. The furniture waste had notably high volatiles, low total ash and low fuel nitrogen, as well as somewhat high chlorine. The furniture waste ash was high in both sodium and potassium. The willow wood had high volatiles and low ash. The ash from the willow wood had low sodium and notably high  $P_2O_5$ .

### 4.2 Results of Reburning Tests with Coal and Natural Gas Primary

Figure 4.1 shows reburning performance for willow wood, furniture waste, walnut shells and natural gas as a function of reburning heat input for Illinois coal as primary fuel.

NO reduction provided by the furniture waste was better than natural gas at 10% reburning. For furniture waste reburning, maximum NO reduction was 58%, achieved at 15% reburning heat input. The walnut shells provided a maximum of 65% NO reduction at 20% reburning. Willow wood reburning gave a maximum of 51% NO reduction at 20% reburning. Walnut shell reburning performance was slightly better than that of natural gas at lower reburning heat inputs, and worse than natural gas at higher reburning heat inputs. Performance of willow wood was worse than natural gas at all reburning heat inputs. Difference in the performance of biomass fuels are due to their different compositions: walnut shells have high volatiles, low nitrogen, and very high potassium content. The willow wood has high volatiles and low ash. The ash from the willow wood has low sodium and notably high  $P_2O_5$ .

EER's previous reburning test work has shown that the main fuel type can have an impact on reburning performance. It is believed that main fuel parameters of importance include concentrations of sodium, potassium, chlorine, and sulfur. Figure 4.2 compares results for furniture waste and willow wood reburning obtained with Illinois coal, Ohio coal, and natural gas as main fuels. NO reductions were very similar for the two main coals for both biomass fuels, with natural gas slightly better than both coals.

### 4.3 Effect of Biomass Size Distribution on Performance

The degree to which biomass is pulverized involves trade-offs between improved reburning performance and increased fuel processing cost. To provide data to assist with making such value judgments, reburning tests were performed at different particle size distribution.

Four furniture waste grinds were tested: 9%, 21%, 27%, and 48% through 200 mesh. As shown in Figure 4.3, performance improved with decreasing biomass particle size. At 10% reburning, NO reduction increased from 42% at 9% < 200 mesh to 67% at 48% < 200 mesh. The finer grinds also exhibited some advantages with respect to carbon burnout. However as shown in Figure 4.3, with

willow wood reburning particle size had minimal effect on reburning performance. At 15% and 20% reburning NO reduction decreased slightly with decreasing particle size, whereas at 10% reburning NO reduction stayed the same. It is possible that due to the extremely high volatiles content of the willow wood (82.29%, dry basis), the fuel is so highly reactive that finer grinding provides limited benefits. Since finer grinding corresponds to significantly greater processing cost, it is advantageous for willow wood to provide high performance with large particles.

TABLE 4.1. TEST FUEL ANALYTICAL PROPERTIES

Parameter	Units	Illinois Coal	Ohio Coal	Furniture Waste	Walnut Shells	Willow Wood
<u>Proximate analysis</u>						
Ash	% dry	9.60	10.66	1.31	1.93	1.60
Volatiles	% dry	41.15	40.83	79.06	72.02	82.29
Fixed Carbon	% dry	49.25	48.51	19.63	26.05	16.11
Moisture	% as fired	6.00	8.68	6.37	12.43	1.97
<u>Ultimate analysis</u>						
Carbon	% dry	66.48	70.14	53.91	51.00	50.48
Hydrogen	% dry	4.12	4.66	6.07	5.72	5.98
Nitrogen	% dry	1.30	1.32	0.56	0.32	0.53
Sulfur	% dry	3.11	2.49	0.03	0.00	0.04
Oxygen (difference)	% dry	9.60	10.73	38.12	41.03	41.37
Ash	% dry	15.39	10.66	1.31	1.93	1.60
Chlorine	% dry	0.005	0.010	0.190	0.130	0.040
Higher Heating Value	Btu/lb dry	11,210	12,296	8,824	8,624	8,539
<u>Ash analysis</u>						
SiO <sub>2</sub>	% dry	60.54	55.96	13.86	34.98	2.65
Al <sub>2</sub> O <sub>3</sub>	% dry	18.08	23.99	3.29	6.09	0.41
TiO <sub>2</sub>	% dry	0.87	1.31	6.72	0.21	0.50
Fe <sub>2</sub> O <sub>3</sub>	% dry	9.45	9.92	8.25	10.71	2.42
CaO	% dry	2.56	2.43	24.10	23.25	41.80
MgO	% dry	0.69	0.73	3.00	3.16	4.80
K <sub>2</sub> O	% dry	2.55	3.22	7.50	11.15	14.00
Na <sub>2</sub> O	% dry	0.69	0.66	11.16	6.64	0.24
SO <sub>3</sub>	% dry	2.98	0.67	6.73	1.59	1.80
P <sub>2</sub> O <sub>5</sub>	% dry	0.26	0.24	2.20	1.92	9.50
SrO	% dry	0.03	0.08	0.13	0.02	0.34
BaO	% dry	0.10	0.24	3.83	0.08	0.06
Mn <sub>3</sub> O <sub>4</sub>	% dry	0.03	0.00	1.75	0.10	0.18
Undetermined	% dry	1.17	0.55	7.48	0.10	21.30

#### 4.4 Effect of Initial NO Concentration on Performance

Initial NO concentration ( $\text{NO}_i$ ) was varied from 400 to 900 ppm with furniture waste and from 400 to 800 ppm with willow wood as reburning fuels and Illinois coal as the main fuel. For the most part furniture waste performance (Fig. 4.4) was fairly flat at  $\text{NO}_i$  decreased from 900 to 600 ppm, and then began to fall off as  $\text{NO}_i$  further decreased to 400 ppm. The furniture waste performed better than natural gas at 10% reburning, although natural gas was better at 15% reburning. For willow wood NO reduction increased by 10 to 12 percentage points as  $\text{NO}_i$  increased from 400 to 800 ppm. Willow wood reburning performance was significantly worse than natural gas reburning performance.

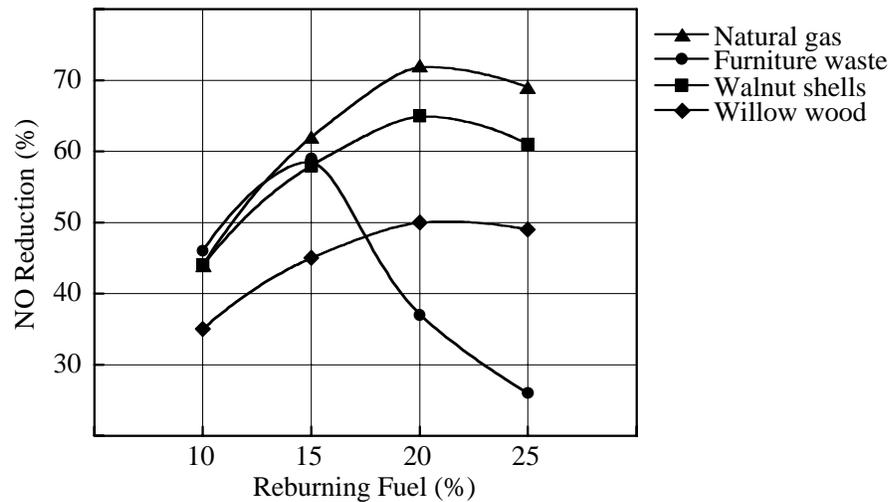


Figure 4.1. Reburning performance of different fuels. Main fuel: Illinois coal. Reburning fuel is injected at 1700 K,  $[\text{NO}]_i = 416$  ppm. OFA is injected at 1450 K. Furniture waste size: 48% < 200 mesh, walnut shells size: 55% < 200 mesh, willow wood size 23% < 200 mesh.

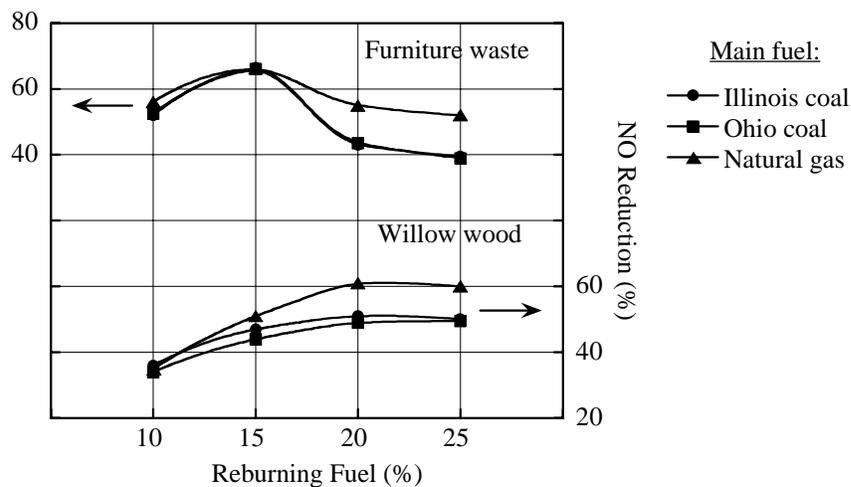


Figure 4.2. Comparison of furniture waste and willow wood reburning with different primary fuels.

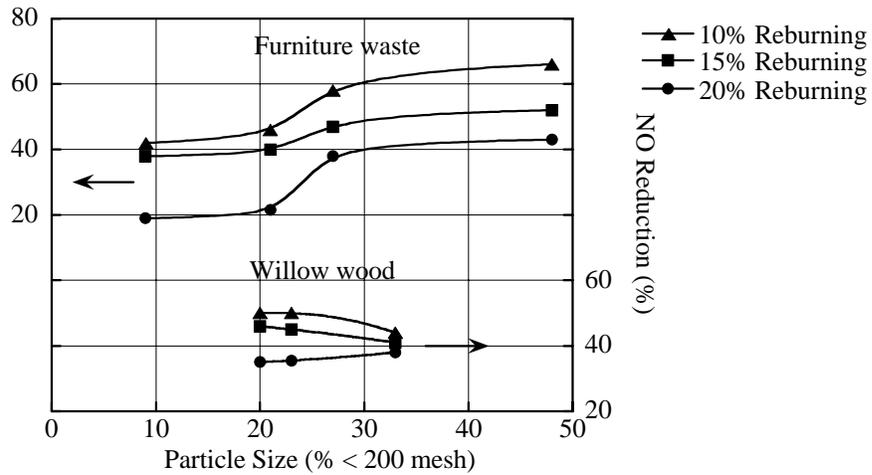


Figure 4.3. Furniture waste and willow wood reburning performance as a function of particle size.

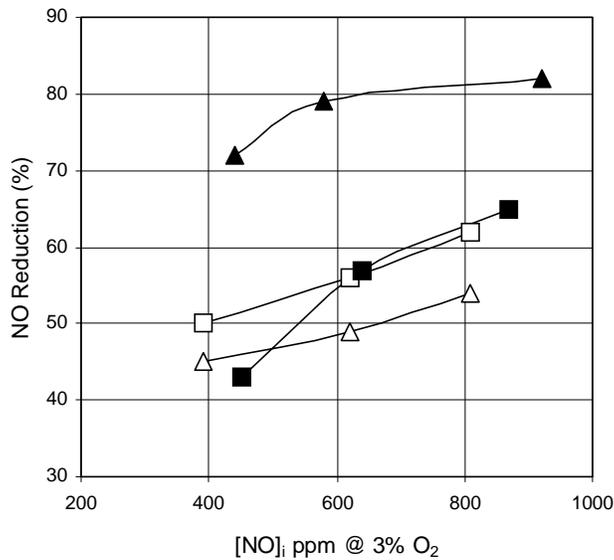


Figure 4.4. Reburning performance as a function of initial NO<sub>x</sub> concentration. Filled symbols represent furniture pellets, open willow wood. Triangulars represent 15% reburning, squares 20%.

#### 4.5 Effect of Overfire Air Injection Temperature on Performance

Reburning performance generally improves with decreasing overfire air (OFA) injection temperature, i.e. with increasing reburning zone residence time. In the current program OFA temperature was varied from 1530 to 1370 K, corresponding to a range of residence times of 0.37 to 1.20 sec. Figure 4.5 shows furniture waste and willow wood reburning performance as a function of OFA temperature. NO reduction decreased with increasing OFA temperature.

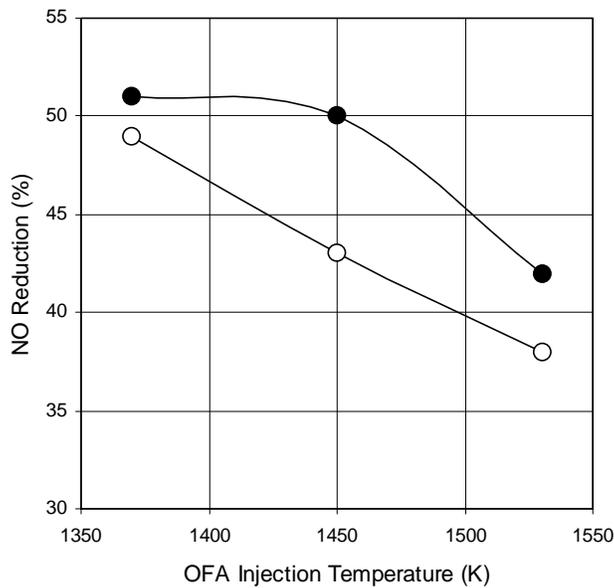


Figure 4.5 Biomass reburning performance as a function of OFA injection temperature. Filled symbols represent willow wood, open symbols furniture pellets.

#### 4.6 Carbon in Ash Analytical Results

Fly ash carbon content is important both from the standpoint of recovering fuel energy content and finding a market for the fly ash; fly ash can generally be sold to the construction industry if it contains less than 5% carbon. Fly ash samples were obtained and sent to a contract laboratory for carbon analysis. Test conditions included baseline coal firing, natural gas reburning, furniture waste reburning at three particle size distributions, and walnut shells reburning. For all tests Illinois coal was the main fuel. Results are summarized in Table 4.2.

Carbon in ash was slightly higher for biomass reburning than for baseline coal firing. However, carbon in ash decreased with finer reburning fuel size distributions. Carbon in ash for biomass reburning was slightly better than that for natural gas reburning, and in all cases carbon concentrations were well below 5%.

TABLE 4.2 CARBON IN ASH RESULTS

Reburning fuel	%<200 mesh	Reburning Heat Input (%)	C in Ash (%)
None (baseline)	-	None	0.07
Natural gas	-	20	0.61
Furniture waste	48%	20	0.19
Furniture waste	27%	20	0.25
Furniture waste	21%	20	0.31
Walnut shells	55%	20	0.20

## 5.0 Optimization of the Advanced Biomass Reburning Process

[USDA Task 3]

Three Advanced Reburning (AR) technologies tested were: AR-Lean, AR-Rich, and reburning + SNCR. In all tests biomass was used as the reburning fuel. With AR-Lean the nitrogen agent was co-injected along with the OFA. With AR-Rich the nitrogen agent was injected into the fuel-rich reburning zone. With reburning + SNCR the nitrogen agent was injected downstream of the OFA. Test variables included additive injection temperature, N-agent to NO stoichiometric ratio (NSR), and sodium promoter concentration. A high-sulfur bituminous Illinois coal was primarily used as the main fuel, with a few tests conducted with natural gas for comparison.

Two N-agents were tested, including ammonia and urea. Each N-agent was formulated as an aqueous solution and injected by means of a twin fluid nozzle. For the AR-Lean tests the overfire air itself served as the atomization medium. Sodium was added in the form of  $\text{Na}_2\text{CO}_3$ , and was dissolved into the N-agent solution. For all tests the reburning fuel was injected at 1700 K. Reburning heat input was 10%, corresponding to a reburning zone stoichiometry of 0.99. This ratio was shown to be optimum in previous test work. Primary zone stoichiometry was 1.10 and final burnout zone stoichiometry was 1.15.

The test work focused on the biomass fuels believed to be most promising for commercial application, i.e. waste furniture pellets and willow wood.

### 5.1 AR-Lean Test Results

AR-Lean tests were conducted with both furniture pellets and willow wood. Test variables included the injection temperature of the N-agent + OFA, Nitrogen Stoichiometric Ratio (N/NO in moles, NSR), and concentration of sodium promoter. Figure 5.1 shows AR-Lean results for furniture pellets as a function of injection temperature with Illinois coal as the main fuel. Urea was the N-agent, and was added at NSR = 0.75. Reburning alone provided approximately 47% NO reduction. With urea, performance improved with decreasing injection temperature. The highest NO reduction achieved was 68% at an injection temperature of 1280 K.

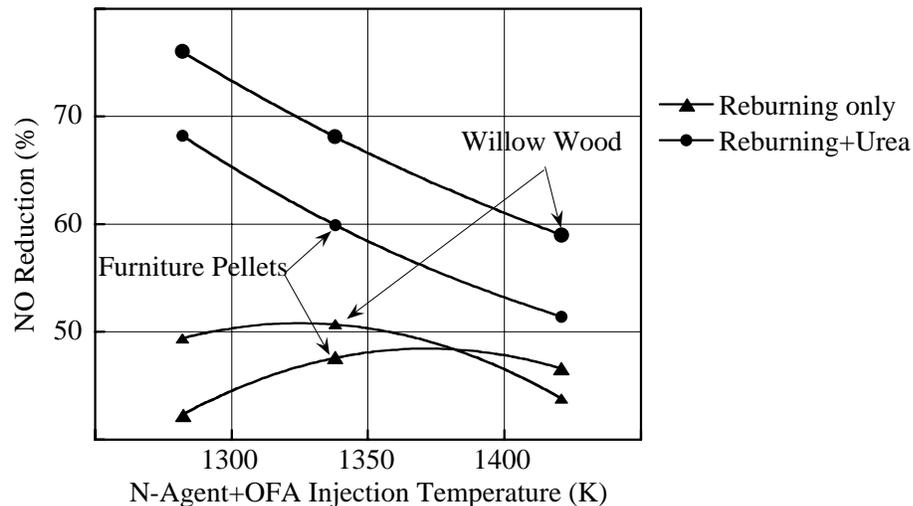


Figure 5.1. Willow wood and furniture pellets AR-Lean results with Illinois coal primary.

Figure 5.1 also shows AR-Lean results for willow wood as a function of injection temperature with Illinois coal as the main fuel. Urea was the N-agent, and was added at NSR = 1.0. Reburning alone provided 45% to 50% NO reduction. With urea, performance improved with decreasing injection temperature. The highest NO reduction achieved was 76% at an injection temperature of 1280 K.

Sodium promoter tests were performed during the furniture pellets AR-Lean tests with both natural gas and Illinois coal as main fuels. Sodium was added at concentrations corresponding to 10, 30, and 50 ppm in the flue gas. As shown in Figure 5.2, as the sodium concentration was increased, NO reduction increased significantly (up to 17 percentage points) during natural gas firing, but only minimally (4 percentage points) during coal firing. It is possible that coal constituents such as ash and sulfur may have reacted with and partially deactivated the sodium promoter.

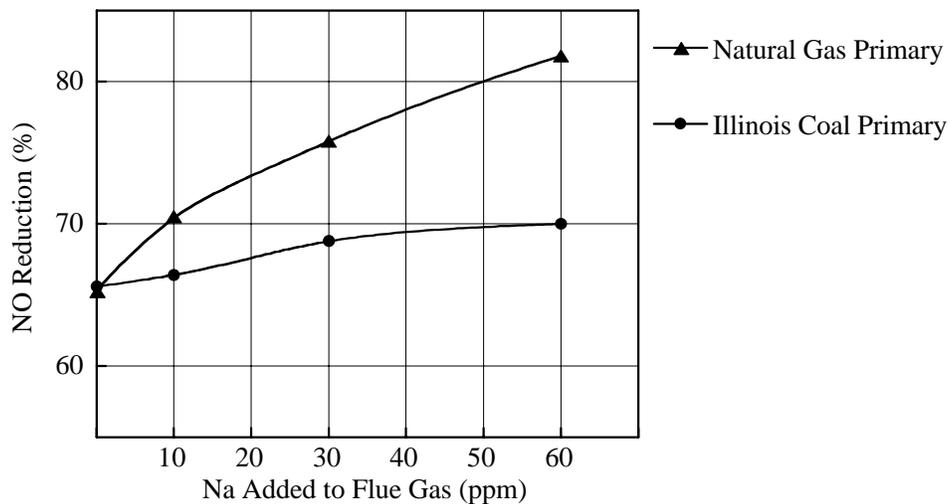


Figure 5.2. Furniture pellets promoted AR-Lean performance.

## 5.2 AR-Rich Test Results

AR-Rich tests were then conducted in which the N-agent was injected into the fuel rich reburning zone. Both furniture pellets and willow wood were tested. Test variables included additive injection temperature, NSR, and sodium promoter concentration. Figure 5.3 shows results of furniture pellets AR-rich tests. Urea was injected at 1390 and 1510 K, and OFA was injected at 1310 K. Performance was slightly better at the lower injection temperature. Maximum NO reduction achieved was 65%.

AR-Rich performance was characterized as a function of NSR with both furniture pellets and willow wood. Urea injection temperature was 1370 K. As shown in Fig. 5.4, performance was generally similar for the two biomass fuels. Maximum NO reduction was 68% for willow wood AR-Rich at an NSR of 1.6.

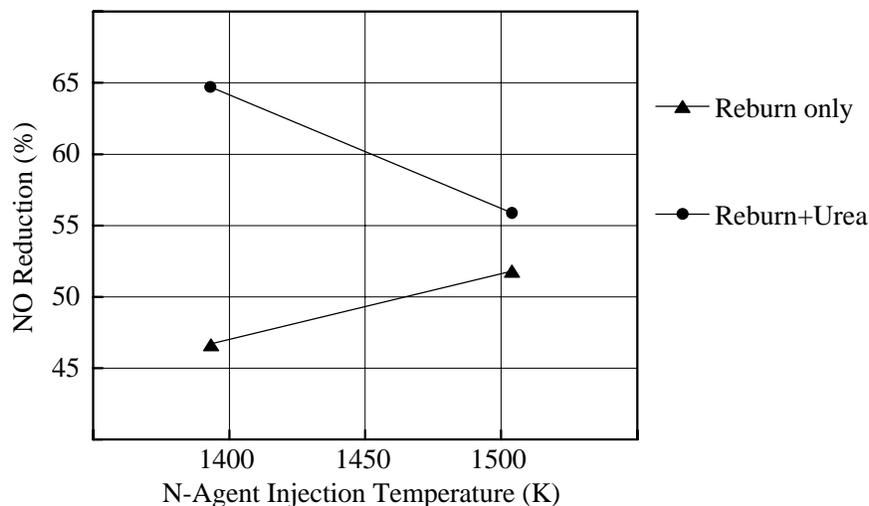


Figure 5.3. Furniture pellets AR-Rich results with Illinois coal primary.

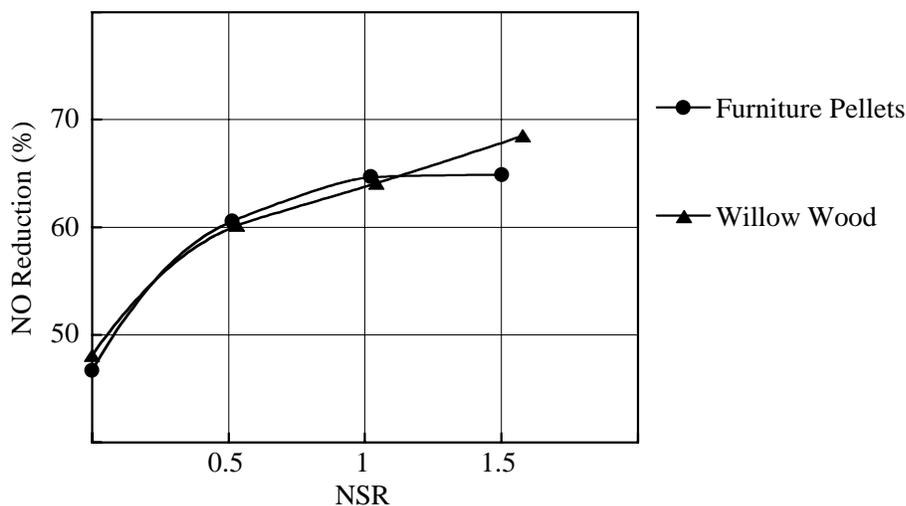


Figure 5.4. AR-Rich results as a function of NSR with Illinois coal primary.

### 5.3 Reburning + SNCR Tests

Tests were conducted in which the N-agent was added downstream of the OFA. Test variables included reburning fuel type (furniture pellets and willow wood), NSR, and N-agent injection temperature. Figure 5.5 shows willow wood reburning + SNCR test results as a function of urea injection temperature. Reburning heat input was 10%, and OFA was injected at 1450 K. Reburning alone gave about 40% NO reduction. With urea injection, the optimum injection temperature was found to be 1330 K, at which condition NO reduction was 77%.

Reburning + SNCR performance was characterized as a function of NSR with both furniture pellets and willow wood. Urea injection temperature was 1310 K. As shown in Figure 5.6, with both fuels NO reduction increased with increasing NSR. Better performance was achieved with willow wood

than with furniture pellets. Maximum NO reduction was 83% for willow wood at an NSR of 1.45. This is the highest NO reduction obtained for any of the AR test conditions.

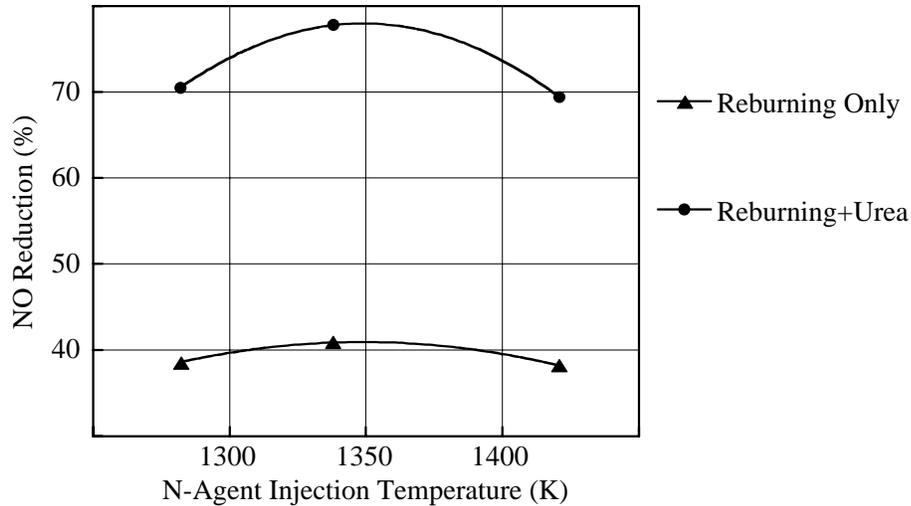


Figure 5.5. Willow wood reburning+SNCR performance with Illinois coal primary.

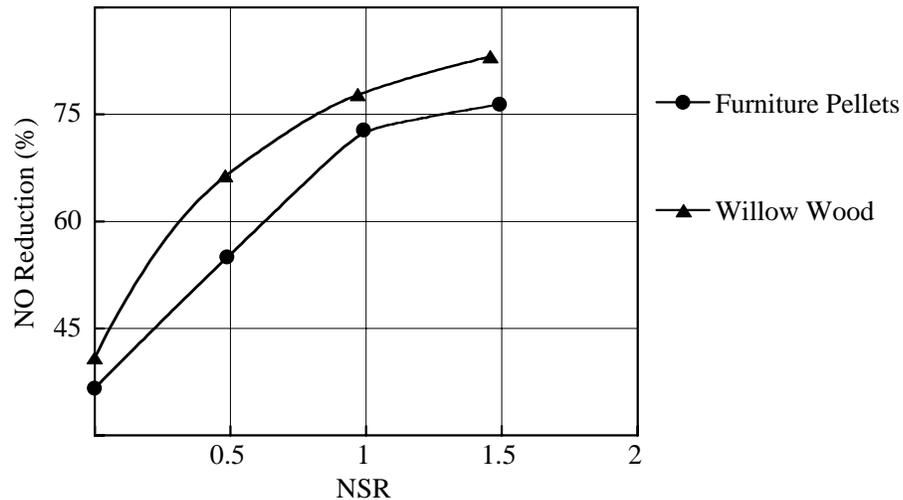


Figure 5.6. Biomass reburning+SNCR performance with Illinois coal primary.

In general, despite the fact that the willow wood had a larger particle size distribution, it provided somewhat higher NO control than did furniture pellets at each of the AR test conditions. The willow wood contains slightly higher volatiles and more alkaline components than the furniture pellets. It was also observed that while sodium promoter was somewhat effective with natural gas as the main fuel, it had smaller effect with Illinois coal as the main fuel. This is attributed to two effects. First, the relatively high inherent alkaline concentrations in the biomass fuels minimize the benefits of adding additional sodium. Second, the sulfur and fly ash generated by the coal might partially react with and deactivate the sodium.

## 6.0 Kinetic Modeling of Biomass Reburning

[DOE Task 1]

Experimental data demonstrated that  $\text{NO}_x$  reduction performance of different biomass fuels was quite different. Since test conditions for all fuels were similar, these differences most likely were due to differences in chemical composition. The purpose of kinetic modeling was to identify factors that control the efficiency of biomass as a reburning fuel to be able to predict  $\text{NO}_x$  reduction based on fuel analysis. The approach taken was to combine detailed kinetic modeling of the processes in the gas phase with a one-dimensional representation of mixing that has proved to provide a realistic description of the reburning process with natural gas (*Zamansky and Lissianski, 1999*). The kinetic mechanism (Appendix 1) includes 447 reactions of 65 C-H-O-N species (*Glarborg et al., 1998*) and 23 reactions of 4 Na species (*Zamansky et al., 1999*). Thermodynamic data are presented in Appendix 2.

The following sections describe the modeling approach used to describe reburning and Advanced Reburning of biomass.

### 6.1 Modeling of Biomass Reburning

The following sections describe the approach to represent biomass composition, model setup and modeling results.

#### 6.1.1 Representation of Biomass Composition

Experimental data for furniture pellets and willow wood show that for particles of small size the process efficiency does not depend on particle size. This result suggests that the time scale of biomass gasification under these test conditions was smaller than the characteristic time of the mixing process in the reburning zone. Since the selected biomass fuels all have high volatile content, it was further assumed that the contribution of char combustion to  $\text{NO}_x$  reduction was less significant than that of gas phase reactions. Thus, in modeling the biomass fuels were represented as gasification products, i.e. it was assumed that fuel gasification is instantaneous and complete. The fuel oxygen was presented in the form of CO. A mixture of  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  represented the remaining hydrocarbon component. The composition of biomass gasification products corresponds to the ultimate analysis and is shown in Table 6.1.

This approach to represent biomass gasification products has been used previously (*Chen et al., 1999; Williams et al., 1999*) and is often used in CFD (*Williams et al., 1999*) modeling where simplification of biomass gasification chemistry is a requirement. The approach assumes that primary products of biomass gasification are highly reactive and at high temperatures quickly decompose to produce less reactive hydrocarbons.

The concentration of N in the tested biomass fuels (about 0.5% by weight) is less than that usually found in coals (1-2%). However, this amount of fuel-N can contribute to  $\text{NO}_x$  production at large heat inputs of the reburning fuel. It was assumed that fuel-N was present in gasification products in the form of HCN. Modeling with representation of fuel-N as  $\text{NH}_3$  showed similar results.

Ash analysis shows that biomass contains many elements (Na, Fe, K, P, S and others) that can affect the reburning process. For example, it is known that alkali metals (*Zamansky et al., 1997; Dasappa et al., 1999*) and iron-containing compounds (*Zamansky et al., 2000*) added to the reburning zone can increase  $\text{NO}_x$  reduction. Comparison of K and Fe content in different biomass fuels (Table 4.1)

shows that they do not differ significantly from fuel to fuel. Also, concentrations of these metals in biomass are similar or lower than that found in coals. Thus, the presence of Fe and K in biomass can not explain differences in the performances of the biomass fuels observed in tests.

TABLE 6.1 ASSUMED COMPOSITION OF BIOMASS GASIFICATION PRODUCTS (vol%)

Component	Furniture pellets	Willow wood	Walnut Shells
CO	68.86	74.8	74.54
C <sub>2</sub> H <sub>6</sub>	27.40	–	–
C <sub>2</sub> H <sub>4</sub>	2.60	15.0	23.20
C <sub>2</sub> H <sub>2</sub>	–	9.0	1.50
HCN	1.10	1.2	0.70
NaOH	0.14	–	0.06

The concentration of Na in biomass, however, significantly differs from one fuel to another and can be higher than that found in coals. It was shown (*Zamansky et al., 1997*) that Na-containing additives can improve the efficiency of the reburning process if co-injected with NH<sub>3</sub>. Since the amount of Na found in ash of furniture pellets is significant, the presence of Na can affect the performance of this fuel.

Reactions of Na with components of flue gas have been studied (*Perry and Miller, 1996; Zamansky et al., 1997, 1999*) in connection with reduction of NO and N<sub>2</sub>O emissions in SNCR and reburning processes. Since the chemistry of NaOH decomposition and reactions with C-H-O-N species at high temperatures is relatively well defined (*Zamansky et al., 1997*), it can be easily incorporated into the kinetic model. Reactions of Na species (*Zamansky et al., 1997*) were added to the reaction mechanism (*Glarborg et al., 1998*) used to describe biomass reburning. The model includes 470 reactions of 69 chemical species.

The important question is in what form Na is present in biomass. The mineral composition of biomass fuel is generally complex and difficult to determine quantitatively. It was found (*Hald, 1994*) that in straw most alkali metals are present in a water soluble form (in the form of NaCl or ionically linked to the surface) and only small amounts are in a water insoluble form (mostly silicates). However, the distribution between forms of Na may be different for different biomass fuels. *Dayton and Milne, 1995* found that some biomass fuels release alkali metals during combustion in the form of chlorides, while others release significant amounts of alkali vapor in the form of hydroxides and cyanates. *Chenevert and Kramlich, 1999* showed that fuels with high chlorine content release alkali metals to the gas phase in the form of chlorides, while fuels with low chlorine content release metals in the form of sulfates and carbonates. However, the available information does not allow one to identify concentrations of different alkali-containing species released from the biomass studied in this work to the gas phase. Since Na<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·(SiO<sub>2</sub>)<sub>2</sub>, commonly found in biomass ash, is insoluble and stable at reburning temperatures (*Hald, 1994*), it was assumed in the current model that most sodium found in ash is present in the form of silicate. The amount of sodium present in the form of silicate was calculated based on the biomass ash analysis (Table 4.1) and the amount of silicate (Al<sub>2</sub>O<sub>3</sub>·(SiO<sub>2</sub>)<sub>2</sub>) present. Remaining sodium was assumed to be present in the form of NaOH since a previous study (*Zamansky et al., 1999*) showed that this form of Na is the most stable at high temperatures and flue gas compositions. The effect of variation in Na concentration in the gas phase during combustion of furniture pellets is discussed later.

### 6.1.2 Model Setup

The chemical kinetic code ODF (*Kau et al., 1987*), for “One Dimensional Flame” was employed to model experimental data. ODF treats a system as a series of one-dimensional reactors. Each reactor may be perfectly mixed (well-stirred) or unmixed (plug-flow). Each ODF reactor may be assigned a variety of thermodynamic characteristics, including adiabatic, isothermal, or specified profiles of temperature or heat flux, and/or pressure. Process streams may be added over any interval of the plug flow reactor, with arbitrary mixing profiles along the reactor length. The flexibility in model setup allows for many different chemical processes to be simulated under a wide variety of mixing conditions.

The approach adopted in this work is similar to that used (*Zamansky and Lissianski, 1999*) to describe natural gas reburning. The reburning process was treated as series of four plug-flow reactors. Each reactor described one of the physical and chemical processes occurring in a boiler: addition of the reburning fuel, NO<sub>x</sub> reduction as a result of reaction with the reburning fuel, addition of overfire air, and oxidation of partially oxidized products.

The following features of the mixing process were incorporated into the modeling:

- Injected gases are available for reaction over a certain period of time (mixing time) rather than instantaneously.
- Injection of reburning fuel results in mixture stratification such that mixture composition in the mixing area is not uniform.

The mixing was always described by adding flue gas to the injecting stream (inverse mixing) over mixing time. For example, mixing in the reburning zone was described by adding flue gas to the flow of natural gas; mixing of OFA was described by adding flue gas to the OFA.

The mixing time in the reburning zone was an adjustable parameter. For the reburning fuel jet, the mixing time was adopted to be 200 ms for all biomass fuels. The value 200 ms was chosen because it gave the best description of experimental data. This time is considerably longer than the mixing time for natural gas injection (120 ms) estimated for similar conditions using a model of single jet in cross flow (*Zamansky and Lissianski, 1999*). This increase in mixing time was introduced to take into account the longer heating times of biomass particles. Modeling showed that the value of the mixing time has a relatively small effect on the efficiency of NO<sub>x</sub> reduction. For example, a twofold increase in mixing time results in about 30% improvement in the reburning efficiency. For the overfire air jet, the mixing time was estimated (*Zamansky and Lissianski, 1999*) using a model of single jet in cross flow to be 120 ms.

### 6.1.3 Modeling Results

Modeling of reburning with willow wood and furniture pellets was conducted after obtaining experimental data. The model was used then to select another biomass fuel with high NO<sub>x</sub> reduction potential. Walnut shells were selected, and experiments validated model predictions.

#### *Willow Wood and Furniture Pellets*

Figure 6.1 shows comparison of modeling predictions with experimental data for willow wood. The model predicts that willow wood is a less effective reburning fuel than natural gas. The model quantitatively agrees with experiments within the scatter of experimental data.

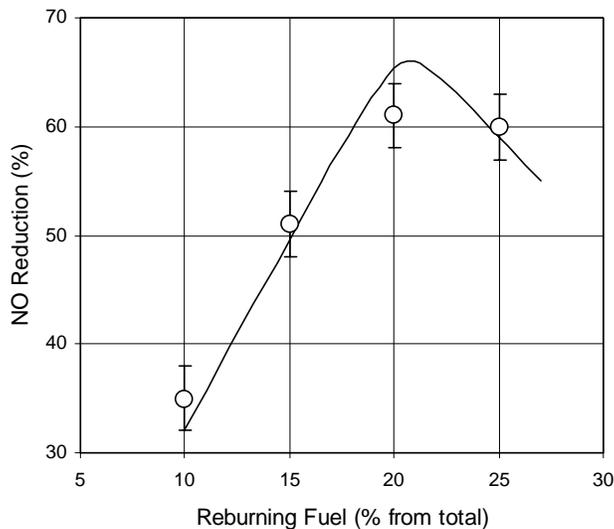


Figure 6.1 Performance of willow wood reburning. Symbols are experiments, line represents calculations.

Agreement of modeling predictions with experimental data for furniture pellets is qualitative (Fig. 6.2). The solid line in Fig. 6.2 represents calculations with the amount of NaOH in decomposition products calculated as discussed above. These calculations underestimated the efficiency of  $\text{NO}_x$  reduction by furniture pellets. The dashed line in Fig. 6.2 represents calculations made under the assumption that all Na found in biomass is present in the gas phase in the form of NaOH. These calculations gave better agreement with experimental data. While the amount of Na present in the gas phase during combustion of biomass is uncertain, modeling clearly shows that minerals present in ash can improve efficiency of biomass as reburning fuel by promoting reactions in the reburning zone. Modeling predicts high efficiency of furniture pellets at low heat inputs of the reburning fuel. A decrease in efficiency at large heat inputs is also predicted.

The fact that the model agrees with experimental data suggests that contribution of heterogeneous reactions to  $\text{NO}_x$  reduction is not significant and  $\text{NO}_x$  reduction at the test conditions is mainly determined by reactions in the gas phase.

#### *Walnut Shells*

The model developed in this work makes it possible to select effective biomass fuels based on their chemical composition and predict their performances relative to other fuels. Modeling shows that there are several factors that determine the reburning efficiency of biomass. At low heat inputs, fuels with a higher concentration of minerals show  $\text{NO}_x$  reduction efficiencies similar or better than that of natural gas. At high heat inputs, fuels with high fuel-N content show degradation in the reburning efficiency.

These conclusions can be used to estimate efficiencies of different types of biomass as potential reburning fuels. To demonstrate this, a number of biomass fuels with known composition were considered. Walnut shells were selected as a promising reburning fuel. As shown in Table 4.1,

walnut shells have low fuel-N and high Na in ash content. Modeling predicts that performance of walnut shells as a reburning fuel is comparable with that of natural gas.

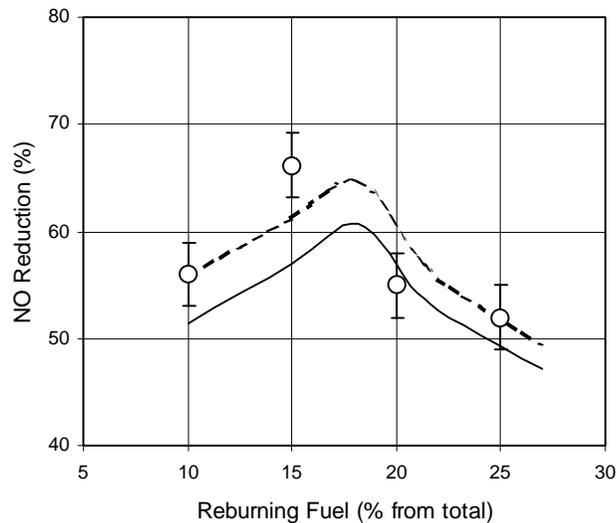


Figure 6.2. Performance of furniture pellets reburning. Symbols are experiments. Solid line represents calculations with biomass composition from Table 6.1, dashed line represents calculations assuming all Na is present in the form of NaOH.

To verify this prediction, the performance of walnut shells was tested in BSF under the same conditions as for furniture pellets and willow wood. Tests confirmed modeling predictions that walnut shells are an effective reburning fuel (Fig. 6.3). Their performance was slightly better than that of natural gas at lower reburning heat inputs, and worse than natural gas at higher reburning heat inputs. The walnut shells provided a maximum of 65% NO reduction at 20% reburning. Figure 6.3 shows comparison of modeling predictions with experimental data for walnut shells.

## 6.2 Modeling of Advanced Biomass Reburning

Three AR processes investigated via modeling were: AR-Lean, AR-Rich, and reburning + SNCR. With AR-Lean the nitrogen agent (urea) was co-injected along with the secondary air. With AR-Rich the nitrogen agent was injected into fuel-rich reburning zone. With reburning + SNCR the nitrogen agent was injected downstream of the OFA.

Initial concentration of NO in flue gas was 416 ppm, reburning fuel was injected at 1700 K. Modeling was done assuming that natural gas was the main fuel, while most experimental data available for comparison were obtained for Illinois coal as the main fuel. Differences in main fuels accounts for some disagreements between modeling predictions and experimental data.

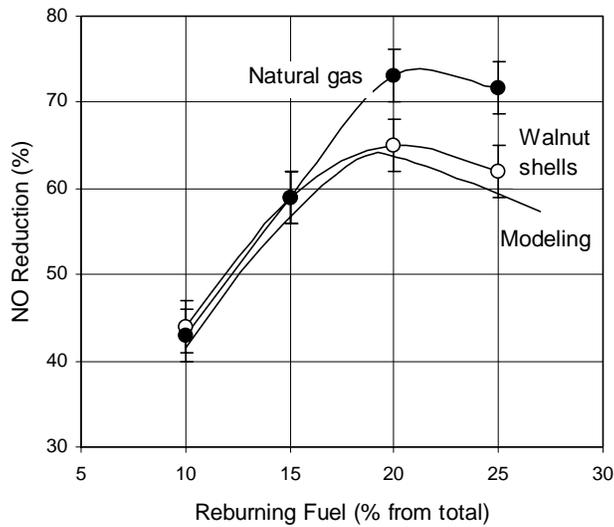


Figure 6.3. Performance of walnut shells reburning. Symbols are experiments, line represents calculations.

### 6.2.1 Modeling of AR-Lean Process

Comparison of modeling predictions and experimental data on AR-Lean process is shown in Figs. 6.4-6.7. The Figures compare promotional effects (above baseline reburning) achieved via injection of N-agent and sodium under different process conditions. Both furniture pellets and willow wood were investigated. Parameters under investigation included urea injection temperature, NSR, and sodium promoter concentration.

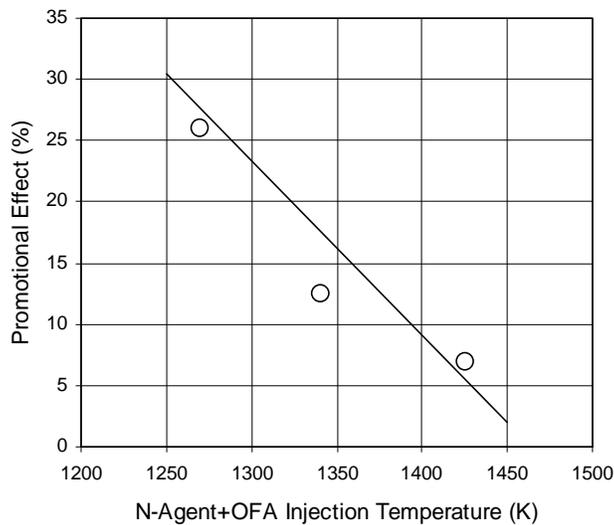


Figure 6.4. Comparison of modeling predictions with experimental data for AR-Lean process. Reburning fuel is furniture pellets. NSR = 0.75. Symbols are experiments, line represents calculations.

Figure 6.4 shows effect of N-agent and OFA injection temperature on NO reduction. Promotional effect is defined as difference in NO reduction between AR-Lean and basic reburning processes. Without urea, variation of OFA injection temperature has small effect on NO reduction. When urea is co-injected with OFA, NO reduction is more significant and increases as injection temperature decreases. This observation can be explained by changing main pathways by which  $\text{NH}_2$  radicals generated by urea react with flue gas. At high temperatures they are mostly oxidized to NO. At low temperatures  $\text{NH}_2$  radicals react with NO and reduce it to  $\text{N}_2$ .

Willow wood shows similar trends in AR-Lean process (Fig. 6.5): urea co-injection with OFA increases efficiency of NO reduction.

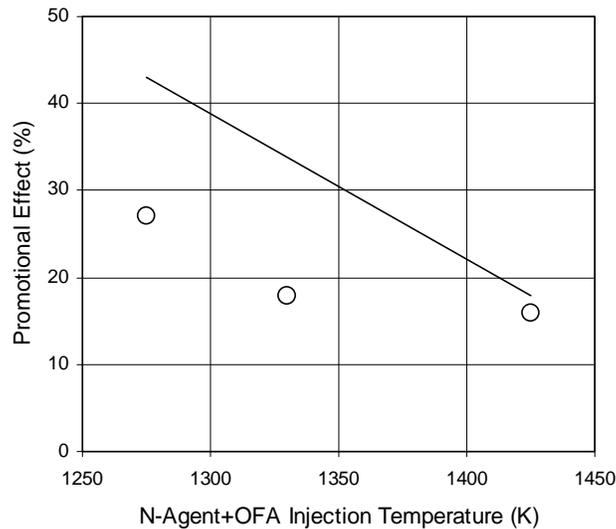


Figure 6.5. Comparison of modeling predictions with experimental data for willow wood. Urea is co-injected with OFA (AR-Lean). NSR = 0.75. Symbols are experiments, line represents calculations.

Figure 6.6 shows the effect of NSR on NO reduction. NO reduction increases with increasing NSR. Modeling shows that the relative promotion effect of the N-agent on NO reduction decreases as the amount of N-agent increases. This observation can be explained by the fact that as amount of N-agent increases, relative contribution of urea to NO production due to urea oxidation also increases and outweighs the benefit of NO reduction by urea.

Addition of sodium promoter in modeling practically does not affect NO reduction (Fig. 6.7). This result is in contradiction with experimental data that show significant increase in NO reduction as the amount of sodium promoter increases. This observation can be explained by incompleteness of the Na kinetic sub-model. Indeed, it was observed (*Zamansky et al., 1999*) that at temperatures higher than 1250 K modeling underpredicts the effect of sodium promoter on SNCR process. Since kinetic mechanism of promoter influence in SNCR is similar in nature to that in AR-Lean, disagreement between modeling and experimental data in Fig. 6.7 is not a surprise. The kinetic model has to be improved to give a closer description of the experiments.

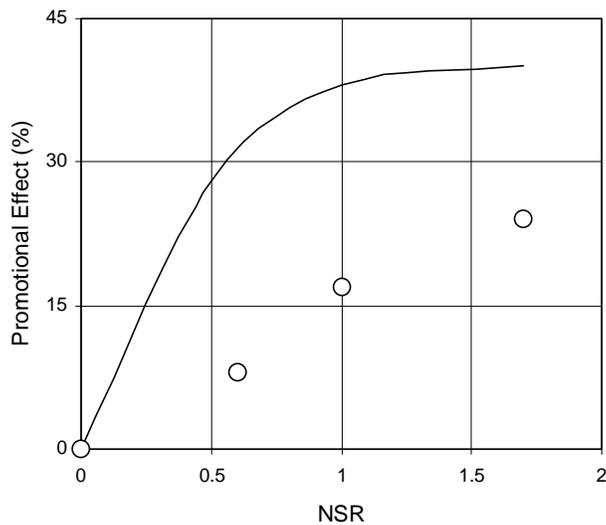


Figure 6.6. Effect of NSR on NO reduction in AR-Lean. Reburning fuel is willow wood. Urea and OFA are injected at 1310 K. Symbols are experiments, line represents calculations.

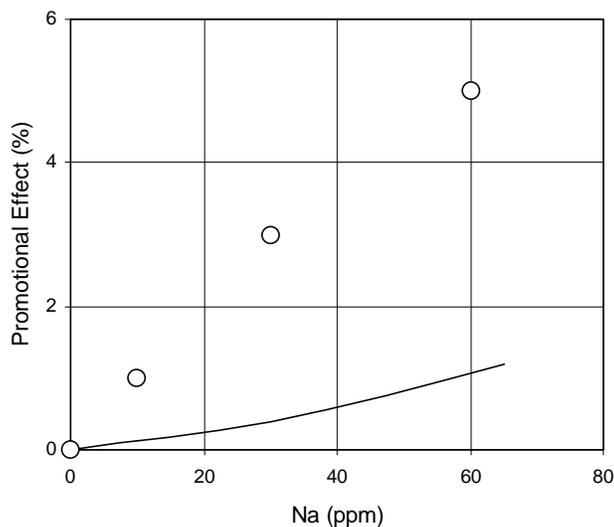
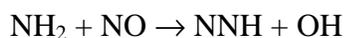
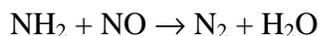


Figure 6.7 Effect of sodium promoter addition on NO reduction in AR-Lean. Urea and  $\text{Na}_2\text{CO}_3$  are co-injected with OFA at 1310 K. Reburning fuel is furniture pellets. NSR = 1.0. Symbols are experiments, line represents calculations.

Since most important Na reactions in the Na kinetic mechanism already have rate coefficient values close to the gas kinetic limit, further increase in the predicted promotional effect can not be achieved simply by varying rate coefficient expressions for sodium reactions; rather reactions that involve new Na species have to be suggested. It will require introduction of new species currently not present in the model, for example NaH.

## 6.2.2 Modeling of AR-Rich Process

Modeling shows (and supported by experimental data) that injection of urea into the reburning zone results in an increase of NO reduction. Performance is slightly better at lower injection temperatures (Fig. 6.8). Promotional effect of urea addition into the reburning zone on NO reduction is explained by reactions of  $\text{NH}_2$  radicals generated by urea decomposition with NO:



Mixture in the reburning zone is fuel-rich. However, some amount of oxygen is still present in flue gas since mixing of the reburning fuel with flue gas is not ideal and results in formation of areas with higher than average concentrations of  $\text{O}_2$ . Injection of urea at higher temperatures (i.e. at higher local  $\text{O}_2$  concentration) results in partial oxidation of N-agent and decreases the efficiency of the process. Injection of urea at lower temperatures provides longer time available for mixing of the reburning fuel with flue gas and thus results in lower local  $\text{O}_2$  concentration. This process is well described by the model.

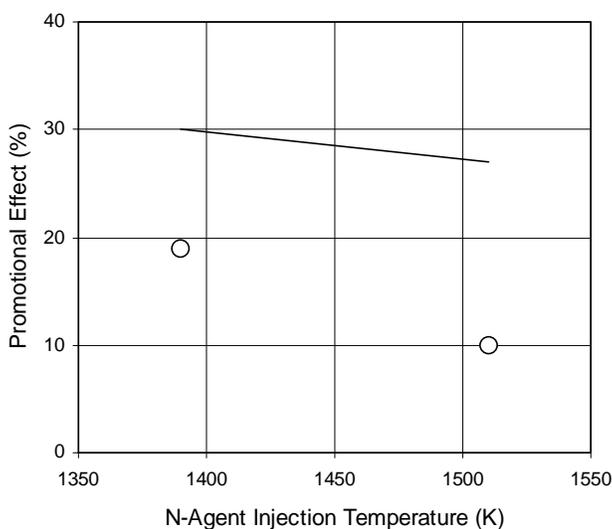


Figure 6.8. Comparison of modeling predictions (lines) with experimental data (symbols) for AR-Rich process. Reburning fuel is furniture pellets. NSR = 1.0. OFA is injected at 1310 K.

An increase in the amount of N-agent results in an increase of NO reduction (Fig. 6.9) both for furniture pellets and willow wood. Modeling shows that willow wood is more efficient reburning fuel in AR-Rich than furniture pellets. This observation is explained by difference in Na content of reburning fuels (see table 4.1).

Modeling overpredicts the effect of urea addition in AR-Rich on NO reduction. This observation can be explained by uncertainties of the mixing process in experiments and difficulties to describe it adequately in modeling.

### 6.2.3 Modeling of Reburning + SNCR

This process represents synergistic combination of two well-established industrial  $\text{NO}_x$  control methods: reburning and injection of N-agent (SNCR). The mixture injected into the SNCR zone in SNCR stand alone application react with flue gas which is rich in oxygen, while in the reburning + SNCR process flue gas entering SNCR zone has low  $\text{O}_2$  and high CO content. These differences (along with others) may account for higher efficiency of NO reduction in the combined reburning + SNCR process in comparison with that of reburning and SNCR-stand alone.

Figure 6.10 shows that injection of N-agent in the OFA zone results in an increase of NO reduction. Efficiency of this process increases as the amount of N-agent increases and reaches 80% NO reduction at  $\text{NSR} = 1.4$ . In agreement with experiments, modeling shows that furniture pellets have slightly better performance in the reburning + SNCR process than willow wood.

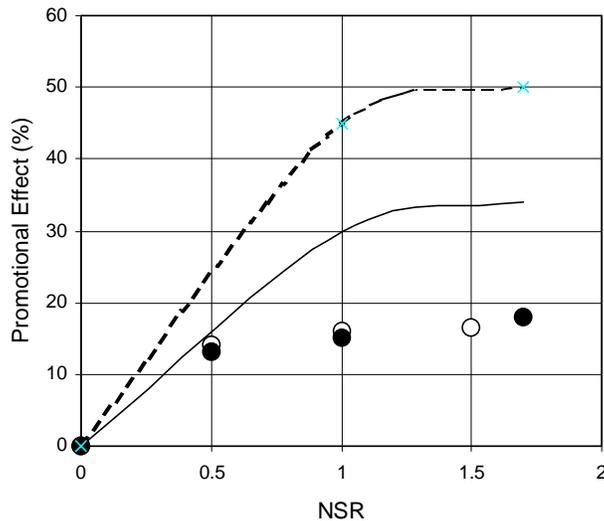


Figure 6.9. Effect of NSR on NO reduction in AR-Rich. Lines represent calculations, symbols experiments. Solid line and open symbols correspond to furniture pellets, dashed line and filled symbols to willow wood. Urea injection temperature is 1370 K, OFA is injected at 1310 K.

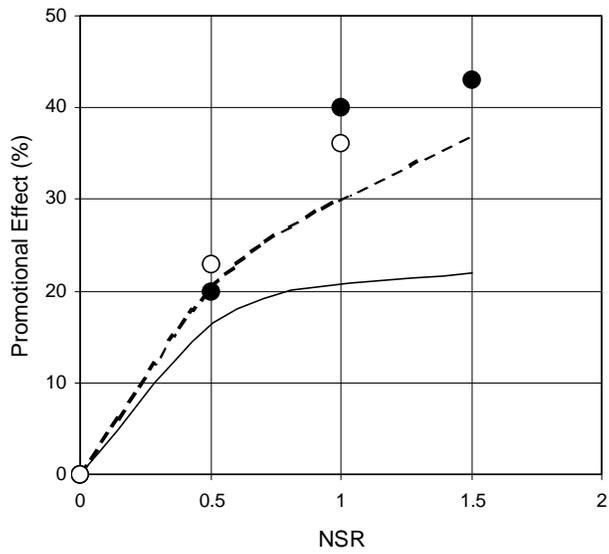


Figure 6.10. Comparison of modeling predictions with experimental data for reburning + SNCR. Lines represent calculations, symbols experimental data. Solid line and open symbols correspond to furniture pellets, dashed line and filled symbols to willow wood. OFA is injected at 1450 K, urea at 1310 K.

## 7.0 Physical Modeling

### [DOE Task 3]

EER developed a methodology for the scale up and application of reburning technologies to coal-fired boilers. This methodology has been successfully used for design of reburning systems employing natural gas and coal as the reburning fuel. One of the objectives of EER's biomass reburning studies is to adapt this methodology to the design of a reburning system using biomass as the reburning fuel. This methodology will ultimately be used to design a full-scale system for a coal-fired boiler in a demonstration of the technology.

The initial plan for this task called for the physical modeling of a boiler operated by the Niagra Mohawk power utility. Before this task was conducted, however, Niagra Mohawk withdrew from the proposed demonstration agreement following a change in ownership. As a result, no specific site was identified for the demonstration phase of the project. To complete the program objectives, the physical flow modeling studies were performed on a typical coal-fired boiler. A tangentially-fired boiler which has previously been studied for reburning retrofit was selected as the basis for the present study.

### 7.1 Preliminary Process Design

The boiler selected for the scale-up studies is a tangentially fired boiler manufactured by Combustion Engineering and has a Maximum Continuous Rating (MCR) capacity of 170 MW (gross). The unit was designed to burn and presently fires Eastern bituminous coal with a nominal heating value of 12,381 Btu/lb. At full load firing pulverized coal, the unit has a gross heat input of 1,427 MMBtu/hr. The unit is equipped with low-NO<sub>x</sub> burners and close-coupled overfire air ports (CCOFA). There are four coal nozzles in the burners. One mill provides coal to the four nozzles located on the furnace corners at each elevation. Flue gas from the flames passes from the lower furnace into the upper furnace and then into the rear convective pass.

The biomass composition used for physical flow modeling studies is similar to that of pulverized furniture waste used in earlier pilot scale studies under this program. The composition parameters which were used as the basis for physical flow modeling are shown in Table 8.1 for both the coal used in this boiler and the biomass.

Results of experimental studies of biomass reburning (Section 4) suggest that for reburn systems using biomass similar to this furniture waste, the optimum basic reburn fuel heat input could be as low as 15%. This is lower than the 20% which is typical for reburning systems based on other fuel types. For the purposes of preliminary design studies, two cases within this range of basic reburning heat input were selected for the physical modeling study. As shown in Table 7.2, the first case is reburning with 19% of the fuel heat input from biomass, and the second is 15% biomass reburning. The other parameters in the table describe the injection parameters for these cases. 19% reburning corresponds to a reburn zone stoichiometric ratio (SR) of 0.90, the value typically chosen for other types of reburn fuel. 15% reburning, which may provide better performance for some biomass types as previously noted, corresponds to a reburn zone SR of 0.95.

TABLE 7.1. FUEL ANALYSIS

Ultimate Analysis (Wet)

		Coal <sup>1</sup>	Biomass <sup>2</sup>
C	wt. %	72.750	49.865
H	wt. %	4.330	5.615
N	wt. %	1.380	0.518
S	wt. %	0.780	0.028
O	wt. %	5.580	35.260
Cl	wt. %	0.000	1.212
Ash	wt. %	8.710	0.176
H <sub>2</sub> O	wt. %	6.470	7.327
Total	wt. %	100.000	100.000
Higher HV	Btu/lb	12,381	7,884

<sup>1</sup> Eastern Bituminous coal currently fired at example plant.

<sup>2</sup> Furniture Waste used in earlier experimental studies

These SR's assume that the carrier gas used to inject biomass into the furnace has a relatively low oxygen content, otherwise larger amounts of reburning fuel would be required to achieve the same reburn zone chemistry. For this reason, the preliminary process design is based on Flue Gas Recirculation (FGR) as a readily available source of low-oxygen gas. The relative amount of FGR, 6 to 7% of the total flue gas flow rate, was selected based on the mass flow and velocity requirements calculated for good mixing of the biomass-laden fuel jet. For both cases, the FGR would mix with the biomass to a temperature of about ~170°F, and take the biomass reburn fuel from the mill to the boiler in 4–15 inch I.D. pipes with a transport velocity of approximately 4,800 ft/min. At the boiler, the available pressure in the line would be used to neck down to the nozzle size and obtain the required injection velocity. The maximum nozzle pressure loss will be on the order of 12 in wg so the required pressure would be the 12 in wg plus the line losses. The mass ratio of FGR to biomass, 2.5 to 3.7 for the cases studied, is comparable to that employed in typical reburning systems using other types of solid fuel such as coal. The requirements for good transport of biomass within the carrier lines are an issue for future development of this technology.

TABLE 7.2. REBURNING CASES STUDIED

Case #	% Reburn	% FGR	FGR/BioMass Ratio	Reburn Fuel Jet Vel (ft/s)	HP-OFA Jet Vel (ft/s)	LP-OFA Jet Vel (ft/s)
1	19	6	2.46	191	146	119
2	15	7	3.70	222	146	83

EER has identified a preliminary approach for locating basic and advanced biomass reburning injectors for the subject unit. In both processes, the reburning fuel would be injected at an elevation above the main burners, and the OFA would be injected at an elevation selected to provide the maximum reburning zone residence time within the furnace constraints. As shown in Figure 7.1, the reburning fuel injectors would be located approximately eight feet above the CCOFA, which represents the upper part of the primary zone injectors. This elevation is chosen to provide sufficient separation between the main flames and the reburning zone to ensure good reburning performance. OFA injectors for the burnout zone (not to be confused with the primary burner's CCOFA) would be located on the furnace corners at an elevation approximately ten feet above the reburning fuel injectors. The OFA system design must provide for good control over carbon monoxide emissions and burnout of the biomass and coal particles.

The reburning fuel injectors would be installed on each corner of the furnace to promote mixing of the reburning fuel. For the use of biomass as a reburning fuel, preliminary calculations suggest that the use of a total of four injectors would result in effective mixing of the reburning fuel with the furnace gases. Each injector consists of a single reburning fuel nozzle with a diameter of approximately 9.5 inches. Injection velocities in the range of 190-220 feet/sec were calculated to achieve good mixing of the reburning fuel in the range of 19 to 15% reburn fuel heat input, with lower velocities required at the higher reburn fuel flow rate.

The OFA injection system would consist of four dual-compartment OFA injectors installed at each corner of the furnace. They can also be used for injection of N-agent (ammonia or urea) if the system is operated in the AR mode. The dual-compartment OFA injectors consist of a constant velocity inlet and a modulating velocity inlet. This feature permits individual tuning of the OFA injectors to bias flow conditions according to furnace flow patterns, and the capability of operating over a wider range of reburning conditions. The design which was studied employed a modulated low-pressure air inlet immediately above the high-pressure, constant velocity inlet. A velocity of about 146 ft/s was calculated for the constant velocity port, with the modulating zone velocity increased from 83 to 119 ft/s as reburn heat input increased from 15 to 19%.

Material balances for this unit with and without reburning are shown in Table 7.3 through 7.5. The baseline material balance in Table 7.3 represents current operation without reburning. The biomass reburning mass balances are based on Maximum Continuous Rating (MCR) operation, 170 MW for this unit. The primary excess air level in the burners would be lowered from 20% to 10% in order to minimize the amount of reburning fuel needed to achieve a specific NO<sub>x</sub> emissions target. Sufficient overfire air would be added to bring the boiler up to its normal operating excess air level of 20%. The material balances shown for 19% reburning are shown in Table 7.4, and for 15% reburning in Table 7.5.

## **7.2 Physical Flow Modeling Results**

Physical flow modeling provides a way to visualize and quantify the mixing performance of a reburning injection system. Since reburning performance is strongly dependent on local stoichiometry and on residence time, rapid and uniform mixing of reburning and burnout air (OFA) jets is critical to optimized NO<sub>x</sub> control.

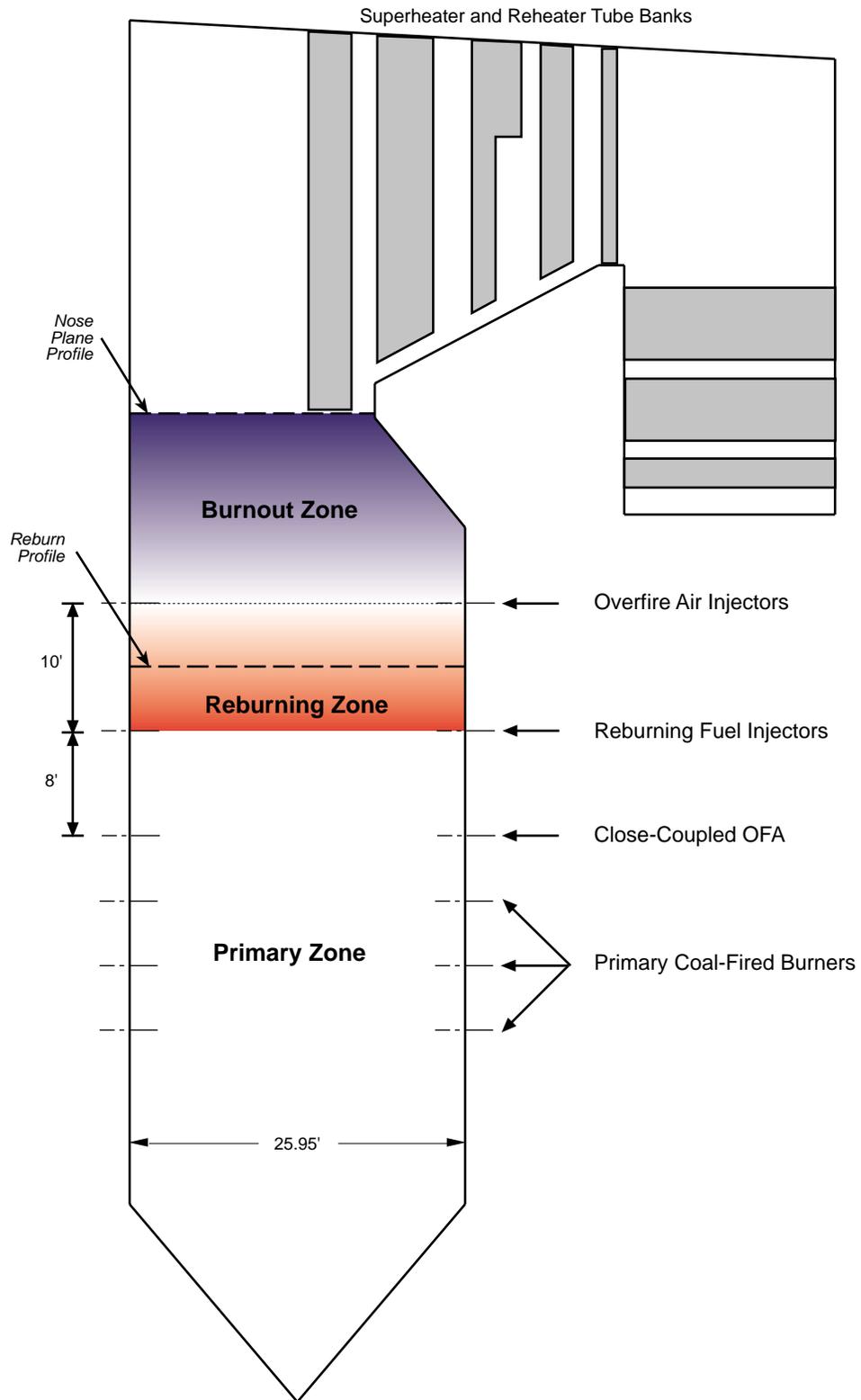


Figure 7.1. Injection locations for reburning study.

TABLE 7.3. MATERIAL BALANCE SUMMARY FOR BASELINE OPERATION AT 100% MCR.

SR: 1.20									
DESCRIPTION	Primary Fuel: Coal	Coal Combustion Air	Reburning Fuel: Biomass	Reburning Fuel Transport	Overfire Air	Boiler Bottom Ash	Economizer Hopper Ash	ESP Ash	Flue Gas to Stack
<b>GAS SIDE:</b>									
Air (lbs/hr), dry		1,304,111							
Flue Gas (lbs/hr)									1,409,310
SO2 (lbs/hr)									1,796
<b>SOLID SIDE:</b>									
H2O From Fuel (lb/hr)	7,456								
H2O From H2 Comb. (lb/hr)	44,593								
Total H2O (lbs/hr)	52,049	0							52,049
Primary Fuel (lbs/hr)	115,236								
Fuel Inerts (lbs/hr)	10,037					2,509	502	7,026	
Total Waste Solids (lbs/hr)	10,037					2,509	502	7,026	

TABLE 7.4. MATERIAL BALANCE SUMMARY FOR 19% BIOMASS REBURNING (CASE 1).

DESCRIPTION	Primary Fuel: Coal	Coal Combustion Air	Reburning Fuel: Biomass	Reburning Fuel Transport	Overfire Air	Boiler Bottom Ash	Economizer Hopper Ash	ESP Ash	Flue Gas to Stack	SR:			
										SR1: 1.10	SR2: 0.90	SR3: 1.20	
<b>GAS SIDE:</b>													
Air (lbs/hr), dry		981,310		0	331,524								
Flue Gas (lbs/hr)				85,955					1,432,579				
SO2 (lbs/hr)									1,469				
<b>SOLID SIDE:</b>													
H2O From Fuel (lb/hr)	6,018		2,556										
H2O From H2 Comb. (lb/hr)	35,996		17,507										
Total H2O (lbs/hr)	42,014	0	20,064		0				62,078				
Primary Fuel (lbs/hr)	93,019		34,890										
Fuel Inerts (lbs/hr)	8,102		61			2,041	408	5,714					
Total Waste Solids (lbs/hr)	8,102		61			2,041	408	5,714					

TABLE 7.5. MATERIAL BALANCE SUMMARY FOR 15% BIOMASS REBURNING (CASE 2).

DESCRIPTION	Primary Fuel: Coal	Coal Combustion Air	Reburning Fuel: Biomass	Reburning Fuel Transport	Overfire Air	Boiler Bottom Ash	Economizer Hopper Ash	ESP Ash	Flue Gas to Stack	SR:		
										SR1: 1.10	SR2: 0.95	SR3: 1.20
<b>GAS SIDE:</b>												
Air (lbs/hr), dry		1,034,375		0	276,275							
Flue Gas (lbs/hr)				99,897					1,427,103			
SO <sub>2</sub> (lbs/hr)									1,543			
<b>SOLID SIDE:</b>												
H <sub>2</sub> O From Fuel (lb/hr)	6,344		1,978									
H <sub>2</sub> O From H <sub>2</sub> Comb. (lb/hr)	37,942		13,544									
Total H <sub>2</sub> O (lbs/hr)	44,286	0	15,521		0				59,807			
Primary Fuel (lbs/hr)	98,049		26,991									
Fuel Inerts (lbs/hr)	8,540		47			2,147		6,011				
Total Waste Solids (lbs/hr)	8,540		47			2,147	429	6,011				

In a physical flow modeling study, the first step is to construct a subscale isothermal flow model of the host boiler. The physical model is typically 1:12 geometric scale and includes all of the important features of the host site furnace. The model will simulate the region along the combustion flow path from the burners to the first few tube banks of the convective pass. The present study focused on a boiler which had previously been modeled for reburning, so a physical flow model was already available and needed only some adjustments to simulate the proposed biomass reburning injection system.

Initially, the furnace flow field was visually assessed. The model is constructed of transparent material to facilitate visual observation. Smoke injection through selected inlets provides a visual indicator of the mixing behavior of those inlets in the overall furnace flow. These observations were used to assess the preliminary design and ensure that the injection design is basically operating correctly, prior to conducting more time-consuming quantitative measurements.

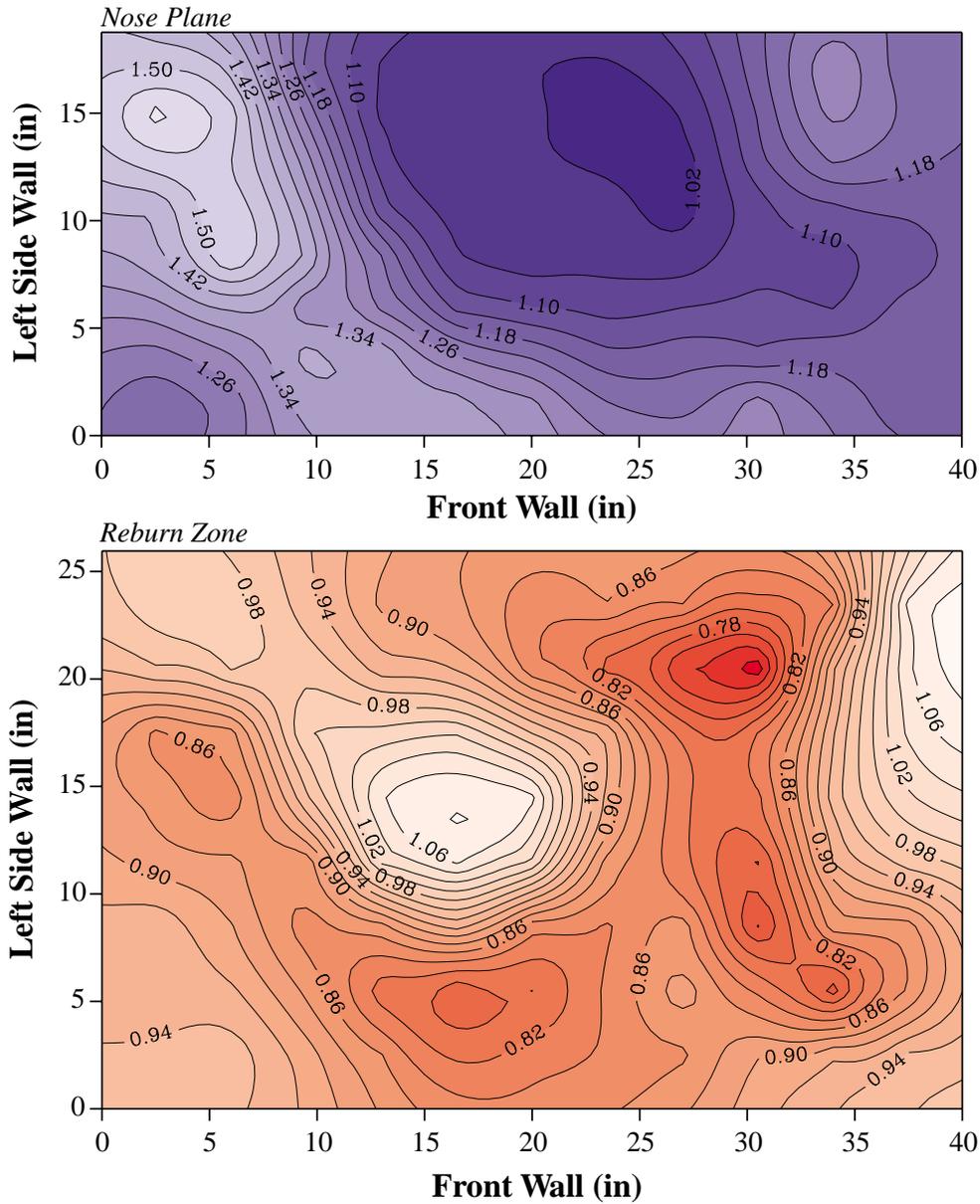
The proposed injection systems were then evaluated by conducting tracer dispersion measurements. In this technique, a small amount of a tracer gas such as SF<sub>6</sub> is added to the jets which represent reburning fuel or overfire air. The tracer concentration profiles are measured downstream of the injection system. These measurements provide a map of the effectiveness of the system in dispersing the tracer. The tracer concentrations are used to calculate the corresponding local stoichiometries which would be encountered in the actual system. The map of local stoichiometries can be used to compare the effectiveness of different injection systems in mixing the reburning fuel, overfire air, and N-agent for the AR mode, as an aid for assessing the relative impacts on NO<sub>x</sub> reduction.

Figures 7.2 and 7.3 show the dispersion profiles for the two cases of biomass reburning that were tested using the isothermal flow model. The two cases presented previously in Table 2, represent 15 percent (SR<sub>2</sub>~0.95) and 19 percent (SR<sub>2</sub>~0.90) reburning. For each case, two dispersion profiles were performed. The reburn zone profile is performed at about the mid-point between the reburn fuel injectors and the overfire air injectors. The overfire air profile is performed at the nose plane. The measured data is then converted to stoichiometric ratio, statistically analyzed, and present in the contour plots shown on the figures. The contours are labeled by the calculated local stoichiometric ratio, which may be compared to the mean stoichiometric ratio for the region. As shown in the figure legends, the mean SR for the reburn zone is 0.90 for Figure 7.2 (19% reburn) and 0.95 for Figure 7.3 (15 % reburn), and the mean SR for the burnout zone (nose plane) is 1.20 for both cases.

The following observations were made based on these results:

- The 19 percent reburning case shows spotty coverage around a center swirling core that is typical of tangentially fired boilers. The reburn fuel profile shows the typical four low stoichiometric regions where the concentration of the reburn fuel jets is highest. Those four regions surround the center of the cyclone where the stoichiometric ratios are relatively high because of the difficulty in penetrating this highly cyclonic region. This profile is consistent with results obtained during the gas reburning modeling study conducted previously for this same unit.
- The 19 percent overfire air case shows a large low stoichiometric region near the back wall. The front right and rear right OFA injectors typically cover this area. In this case, it appears that poor coverage of this area is due to the overfire air jets entraining into the main cyclone and bypassing this region. This was not observed during the gas reburning case, but it seems

Boiler Load	Full	<b>OFA Jet Parameters</b>	
Reburn Heat Input	19.3 %	No. of Jets	4
SR (Burners)	1.10	Inner Jet Flow	45 %
SR (Reburn)	0.90	<i>HP OFA</i>	
SR (Final)	1.20	Jet Velocity	146 ft/s
FGR	6.00 %	Velocity Head	2.50 "WG
RF Transport Medium	FGR	<i>LP OFA</i>	
RF Transport Temp.	170 °F	Jet Velocity	119 ft/s
RF Boost	None	Velocity Head	1.65 "WG
<b>Reburn Fuel Jet Parameters</b>		<b>Test Results</b>	
Number of Jets	4	RF COV.	0.48
Jet Diameter	9.5 in	OFA COV.	0.46
Jet Velocity	191 ft/s		
Velocity Head	9.8 in wg		



Boiler Load	Full	<b>OFA Jet Parameters</b>	
Reburn Heat Input	14.9 %	No. of Jets	4
SR (Burners)	1.10	Inner Jet Flow	54 %
SR (Reburn)	0.95	<i>HP OFA</i>	
SR (Final)	1.20	Jet Velocity	146 ft/s
FGR	7.00 %	Velocity Head	2.49 "WG
RF Transport Medium	FGR	<i>LP OFA</i>	
RF Transport Temp.	170 °F	Jet Velocity	83 ft/s
RF Boost	None	Velocity Head	0.80 "WG
<b>Reburn Fuel Jet Parameters</b>		<b>Test Results</b>	
Number of Jets	4	RF COV.	0.48
Jet Diameter	9.5 in	OFA COV.	0.41
Jet Velocity	222 ft/s		
Velocity Head	12.0 in wg		

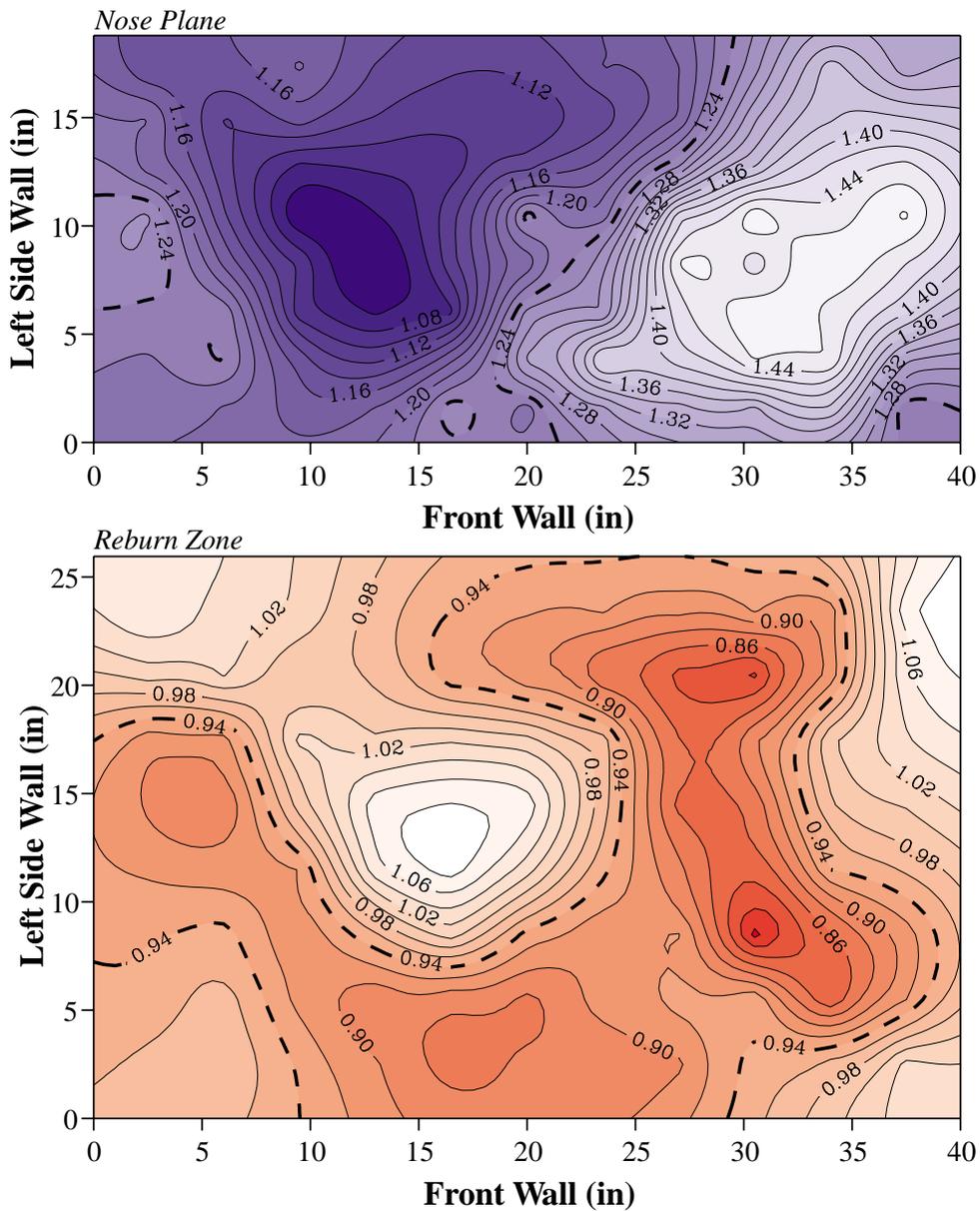


Figure 7.3. 15% biomass reburn - dispersion profiles.

to be caused by slight changes in the flow field caused by the high mass flow added in the reburning zone. This assessment was confirmed by turning off the reburning flow and observing the behavior and the coverage provided by the right side jets.

- The 15 percent reburning mixing case is almost identical to the 19 percent case. This was by design and it is the reason for raising the % FGR from 6 to 7 percent and the nozzle conditions from 191 ft/s to 222 ft/s.
- The OFA profile for 15% reburning case shows that the low stoichiometric zone has shifted to the left side of the boiler. Again, the sensitivity of the jets to the flow field is causing some regions to show nonideal distribution.

The Coefficient of Variance (COV) for each stoichiometry profile is listed in the legend for each figure. The values obtained for these cases are within the range of acceptable, but not optimized, operation. Although these profiles are not optimized, it appears that additional modeling work could result in improved mixing and dispersion of the reburning fuel and overfire air. There are several parameters which could be adjusted to improve mixing performance including jet inlet dimensions, quantity of carrier gas, and jet velocities. Detailed optimization studies are necessarily specific to the particular installation, and the additional effort is not justified in this generic design study. However, the present results indicate that once a specific host is identified, that this methodology may be used in designing an effective biomass reburning system.

## 8.0 Economic Analysis of Biomass Reburn Technologies

[USDA Task 4]

This analysis will be finalized once biomass preparation economics are available from DOE NETL R&D Group (DOE Task 4). The following is a summary of EER's Phase I economic analysis which will be updated using the new cost figures.

### 8.1 Summary of Economic Analysis

The economic study was conducted to determine the cost effectiveness of biomass as a reburning fuel for large, coal fired boilers. The following is a summary of the results of the Phase I study, based on the figures available in 1996 when that study was conducted. The Phase I study consisted of two parts.

One part, called the Fuel Comparison Study, addressed the issue of the relative advantages of using biomass pyrolysis gas versus micronization for direct solids injection. The study evaluated three fuels: natural gas, micronized coal, and biomass (gasified and micronized) using a computer-based computational methodology developed in the earlier EER Spouted Bed Market Study. The study identified the most cost effective boiler size as greater than 200 MW's. A 300 MW boiler was selected for detailed cost effectiveness comparisons and generally supports the following conclusions:

- The capital costs of biomass gasification and micronization are nominally the same and similar to those of micronized coal reburning.
- The choice between biomass and coal is primarily driven by the relative cost of the two fuels and the degree of control required.
- The low capital cost of natural gas reburning is offset by the higher cost of purchased fuel and generally makes it the least attractive option for large boilers.
- There are some 118 coal fired boilers in states with intensive biomass products industries which are potential candidates for biomass reburning.

The objectives for Phase II are based on further examination of micronization as the fuel preparation technology of choice for biomass, based on lower initial capital expense compared to gasification, and the wider existing availability of micronization equipment among electric utilities. Therefore, gasification will be mentioned only in passing in the following discussion.

The second part, called the Technology Comparison Study, was performed after the combustion tests and evaluated four technologies with varying levels of NO<sub>x</sub> control and their cost effectiveness:

- Basic reburning (BR) with the three previously evaluated fuels,
- Advanced reburning with the three previously evaluated fuels,
- Selective Catalytic Reduction (SCR) with NH<sub>3</sub> as the reducing agent, and
- Selective Non-Catalytic Reduction (SNCR) with NH<sub>3</sub> as the reducing agent.

The Technology Comparison Study was based on the selection of a 200 MW coal fired plant and the use of the Electric Power Research Institute Technology Assessment Guide (EPRI TAG)

Methodology (EPRI, 1987) for comparison of the above technologies. This analysis has confirmed biomass as the best reburning fuel and the superiority of advanced reburning over SCR when deep NO<sub>x</sub> control is required. The results are sensitive to the cost and type of fuel. The following are significant conclusions:

- Biomass reburning cost effectiveness can be as low as 55 \$/ton NO removed as compared to coal at 235 \$/ton.
- Advanced biomass reburning provides reductions which exceed SCR with a significantly improved cost effectiveness, 191 versus 776 \$/ton NO removed.

### 8.1.1 Biomass Cost

Biomass costs for application in power plants may range from negative, if a tipping fee for landfill of waste products is required, to about \$3/MBtu for dedicated biomass crops. The cost depends on a variety of factors, such as type of biomass, soil quality, climate, season, transportation expenses, etc. The value of emission credits is another factor. The proposed emission credits for CO<sub>2</sub> - \$50/ton of fossil carbon avoided - would provide dramatic economic benefit for biomass co-firing with coal and reburning. An energy production payment for "closed loop" biomass fired power is 1.5 cents/kWhr. Credits for SO<sub>2</sub> and NO<sub>x</sub> reduction are also under consideration. The use of biomass for co-firing and reburning can be economically feasible in those regions of the country where there is potential for low cost biomass production.

Woodwaste and agricultural waste have lowest cost. These products include construction/demolition wood, furniture industry residues, railroad ties, sawdust, agricultural residues and byproducts, etc.

Another potential low cost feedstock is energy crops. Several federal programs support biomass-to-energy conversion in general and production of cost competitive energy crops in particular. In 1991, the U.S. DOE formed the National Biomass Power Program to help establish a sustainable biomass-to-energy conversion. This Program has partnered with the U.S. Department of Agriculture on the Biomass Power for Rural Development initiative to develop cost-competitive renewable biomass power systems that spur rural economic development. Another DOE program is the Biofuel Feedstock Development Program which helps to facilitate the commercialization of energy crops. DOE is supporting eleven feasibility projects which examine integrated systems for producing energy from biomass (*Craig and Reed, 1996*). A number of feedstocks are under consideration: switchgrass, willow, alfalfa, pine, sugarcane, corn, poplar, etc. These studies demonstrate that various biomass systems may be economically competitive with other energy options. Furthermore, in most cases, a feedstock supply system may not only be feasible but may result in substantial economic and environmental benefits to the areas surrounding the projected installations.

Although dedicated biomass feedstocks were not presently competitive with fossil fuels as of 1996, several demonstration programs have been conducted on biomass co-firing with coal in utility boilers. Successful results were recently presented at the Seventh National Bioenergy Conference (*Bioenergy'96*). A list of utilities which presented results on these programs at the Conference include: New York State Electric and Gas Corp. (NYSEG), Niagara Mohawk Power Corp., Tennessee Valley Authority (TVA), Madison Gas and Electric Co., and Pennsylvania Electric Co. These companies' plans were to use local production of specific biomass feedstocks

to cover 3-20% of power plant energy input. For example, co-firing a 100 MW power plant with 10 MW of willow biomass in New York would require nearly 10,000 acres (*White et al., 1996*). This acreage would account for less than 1% of the area in a 50 mile transport radius surrounding the power plant. Several presenters claimed that in their regions they will be able to buy or produce biomass at a similar or lower price than coal. The estimated cost of willow biomass crops in New York is expected to be \$1.75/MBtu. In some regions available waste wood is priced at less than \$1.00/MBtu. For instance, the 108 MW Greenidge Station of NYSEG has been cofiring wood chips with coal since June 1996. The cost of the biomass feedstock is \$8/ton which corresponds to \$0.45/MBtu.

Reburning and AR provide effective NO<sub>x</sub> control, and therefore, these options are value-added applications in comparison with biomass co-firing. Consequently, benefits of biomass reburning will be always greater than those of co-firing. The utility companies which successfully demonstrate biomass co-firing, also need effective NO<sub>x</sub> control; they are potential EER partners for commercialization of the biomass reburning technology.

### **8.1.2 Fuel Comparison Study**

The objective of the Phase I study was to evaluate concepts for preparing biomass for injection into a boiler with acceptable operational and cost impacts. Specific objectives were to:

- Define an economic scale for a coal-fired boiler reburning application.
- Quantify the relative performance of both solid and gas phase injection.
- Evaluate the effects of biomass fuel price and cost differentials relative to more conventional coal and gas reburn systems.
- Scope the number of potential applications.

Previous parametric studies of gas reburning indicate a cost effectiveness sensitivity to the size of the boiler. The following options were therefore evaluated at 100 through 300 MW scale to determine the boiler size needed to support a cost-effective biomass implementation.

- Micronized, bone dried biomass using equipment similar to that proposed for coal reburning.
- Gasified biomass, as is, using a spouted bed reactor or equivalent technology.

Existing data bases from EER and other sources, provide support to the analysis. Cost effectiveness was established by using systematic assumptions across both scenarios and using the same methodology developed in earlier market studies (*EER, 1994*). The general procedure was to develop capital and operating cost data for a 200 MW reference plant, and then apply scaling rules for establishing cost-effectiveness from 100 to 300 MW. Other consistently applied assumptions include the availability of biomass with specific heating value and moisture content, other operating parameters, and cost parameters including fuel prices and capital recovery factors.

Comparisons of micronized and gasifier biomass preparation plant cost and performance details are made on the basis of the same equivalent BTU delivery at the boiler. The economics for a conventional natural gas reburning system have similarly been calculated for comparative purposes. The results of the parametric study generally confirm the following:

- Biomass is more cost effective than gas at prices below about 20 \$/ton, dry basis.

- Biomass is more cost effective than coal at prices below about 30 \$/ton, dry basis.
- Micronized and gasified biomass have similar economics on a \$/ton basis.

As the scale of the project increases above 300 MW's, both coal and biomass economics improve over natural gas because of the returns to scale of the capital investment, but their relative standings should not change appreciably as they require about the same capital investments.

### 8.1.3 Technology Comparison Study

This study was conducted after evaluating micronized biomass in Phase I pilot-scale experiments to confirm assumptions regarding NO<sub>x</sub> control performance. Test results demonstrated that basic reburning with natural gas and micronized biomass as reburn fuels have similar performance. However, advanced reburning with biomass was more effective than with natural gas. A comparative study of different NO<sub>x</sub> control concepts was conducted to confirm superior economics of biomass reburning over commercialized and emerging technologies.

Table 8.1 summarizes the technology options which were evaluated. Four technologies were compared:

- Basic reburning (BR) with the three previously evaluated fuels,
- Advanced reburning with the three previously evaluated fuels,
- SCR with NH<sub>3</sub> as the reducing agent, and
- SNCR with NH<sub>3</sub> as the reducing agent.

The technologies were applied to a 200 MW coal fired plant firing a coal with SO<sub>2</sub> emission potential of 1.2 lb/10<sup>6</sup> Btu and a delivered cost of 1.75 \$/10<sup>6</sup> Btu. This analysis assumed that natural gas and biomass reburning reduce NO<sub>x</sub> emissions by 60 percent while coal reburning achieved only 50 percent. These assumptions were based upon test results and the EER database.

The analysis utilized the Electric Power Research Institute (EPRI) Technology Assessment Guide (TAG) methodology for comparison of the above technologies. This involves levelizing the capital costs over the life of the equipment and adding the annual operating cost. The annual NO<sub>x</sub> reduction divided by the total annual cost is the NO<sub>x</sub> control cost (\$/ton).

Figure 8.1 shows the results of this analysis. The technologies can be roughly divided into two groups: moderate NO<sub>x</sub> control (SNCR and Basic Reburning) and deep NO<sub>x</sub> control (Advanced Reburning and SCR). For both groups, the Biomass technologies produce the highest NO<sub>x</sub> reduction and the lowest cost on a \$/ton basis. The results are sensitive to the biomass fuel cost. The higher cost of 1.75 \$/10<sup>6</sup> Btu is the same as the base coal fuel. Even at this high cost, the biomass technologies are favored. If the biomass can be obtained at a discount (1.25 \$/10<sup>6</sup> Btu), the cost of NO<sub>x</sub> control drops substantially. In some cases, biomass may be available at even lower costs or for a tipping fee. In these cases, the cost of NO<sub>x</sub> control via biomass will drop to very low values.

TABLE 8.1. COMPARISON OF NO<sub>x</sub> CONTROL TECHNOLOGIES

Technology	NO <sub>x</sub> Reduction, (%)	Capital Cost (\$/kw)	Reburn. Fuel Cost (\$/10 <sup>6</sup> Btu)
SNCR	40.0	5	
Reburning			
Gas	60.0	15	2.50
Coal	50.0	35	1.75
Biomass	60.0	35	1.25-1.75
Advanced Reburning			
Gas	85.0	25	2.50
Coal	83.5	45	1.75
Biomass	90.0	45	1.25-1.75
SCR	80.0	80	

SCR - Selective Cat. Reduction	SNCR - Selective Non-Cat. Reduction
GR - Gas Reburning	AGR - Advanced Gas Reburning
CR - Coal Reburning	ACR - Advanced Coal Reburning
BR - Biomass Reburning	ABR - Advanced Biomass Reburning

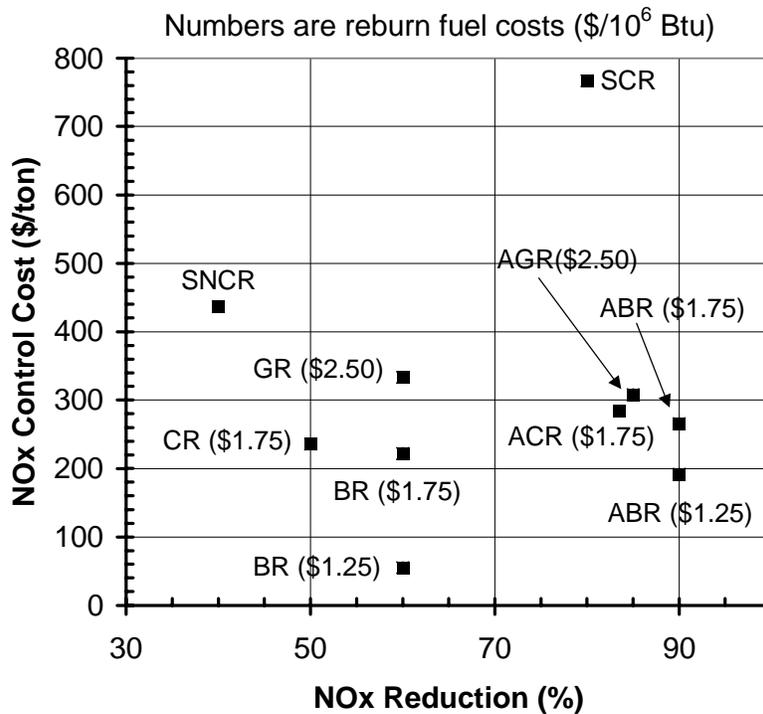


Figure 8.1. Comparison of Cost effectiveness for different NO<sub>x</sub> Control Technologies.

### 8.1.5 Potential Market Size

The potential market for biomass gas reburning will be governed by a number of parameters, the most significant of which are:

- Demographics, the number, size, and location of large coal fired boilers in large biomass waste sheds.
- Regulatory drivers, state/federal, for acid (NO<sub>x</sub>/SO<sub>x</sub>) and green house (CO<sub>2</sub>/CH<sub>4</sub>) gases.
- Price differentials between the evaluated fuels.

To some degree the demographic issue can be addressed through a knowledge of the number and locations of large coal fired boilers. There are some 285 boilers greater than 300 (average of 500) MW's comprising some 74 percent of the coal fired power generation capacity.

Waste sheds are more difficult to quantitatively define as they are diverse and sometimes competed for by other industries, but typically are located as follows:

- Where there are intensive forest products industries such as saw and primary paper mills, although substantial wood waste is typically used on site
- In metropolitan areas where there are large landfills receiving green and demolition wood wastes
- In agricultural areas with several growing seasons, e.g., the sunbelt states

The preferred waste sheds are those that are large and homogeneous such as at forest products industry. Other waste sheds are more diverse, difficult to access, and potentially increase problems with plant operations, particularly micronization which requires a dry, clean product. Gasifiers should be more forgiving and would probably be the preferred technology for wet, heterogeneous wastes. One hundred eighteen boilers found in states with large biomass production and forest industries have been extracted from the industry database, summarized in Table 8.2, comprising some 71,000 MW's or 40% of the large boiler population.

TABLE 8.2. PROFILE OF STATES WITH LARGE COAL FIRED BOILERS AND SIGNIFICANT BIOMASS PRODUCT INDUSTRIES

Region	State	<300 MW		>300 MW	
		Number	MW	Number	MW
South East	Florida	10	1555	17	8748
	Georgia	18	2586	15	10333
Gulf	Lousiana	0	0	6	3320
Great Lakes	Wisconsin	17	1857	11	4691
	Illinois	36	4662	22	11914
	Ohio	58	7854	21	14386
North East	New Jersey	12	1850	4	1635
	New York	21	2377	1	655
	Pennsylvania	32	4645	19	13974
West	Washington			2	1380
Total		204	27386	118	71036
Average			134		602

## 9.0 Design Methodology and Application

[USDA Task 5]

### 9.1 Approach

EER has developed a methodology for the scale up and application of reburning technologies to coal-fired boilers. This methodology has been successfully used for design of reburning systems employing natural gas and coal as the reburning fuel. One of the objectives of EER's biomass reburning studies is to adapt this methodology to the design of a reburning system using biomass as the reburning fuel. This methodology will then be used to design a full-scale system for a coal-fired boiler in a demonstration of the technology.

The initial plan for this task called for the process design to be conducted on a candidate demonstration boiler operated by the Niagra Mohawk power utility. Before this task was conducted, however, Niagra Mohawk withdrew from the proposed demonstration agreement following a change in ownership. As a result, no specific site was identified for the demonstration phase of the project. To complete the program objectives, the scale up studies were performed on a typical coal-fired boiler. A tangentially-fired boiler which has previously been studied for reburning retrofit was selected as the basis for the present study.

In considering the use of biomass as a reburning fuel for reburning and advanced reburning technologies, a number of important questions need to be addressed:

1. What design specifications are needed to ensure effective mixing of the biomass particles with the furnace flue gases?
2. How does biomass reburning and advanced biomass reburning impact the boiler thermal performance and efficiency?
3. How does biomass particle size impact carbon burnout?
4. What is the best approach for injecting reagent in advanced biomass reburning?

Each of these issues can impact the performance and costs for applying biomass reburning technologies to a specific unit.

As a first step in addressing these issues, EER has developed a conceptual design for the application of biomass reburning and advanced biomass reburning technologies to a typical coal-fired boiler selected from an internal database on coal-fired boilers. The conceptual design is the basis for a more detailed analysis to address the specific issues identified above. The conceptual design was first developed by performing a review of the boiler characteristics to define a potential approach for installing reburning technologies to the unit. This approach was then used to develop a preliminary conceptual design for reburning and advanced reburning systems using biomass, and to project the NO<sub>x</sub> control performance that might be achievable.

The following section includes a brief description of the reburning and advanced reburning process, EER's recommended approach for applying biomass reburning technologies to the unit, and preliminary NO<sub>x</sub> control projections.

## 9.2 Biomass Reburning and Advanced Biomass Reburning Technologies

EER has completed pilot-scale studies of biomass reburning. These studies have been summarized in previous sections. A number of pulverized biomass fuels were tested, including willow wood (23% through 200 mesh), walnut shells (55% through 200 mesh), and furniture waste (48% through 200 mesh for most tests). Common conditions for the experiments were a primary zone stoichiometric ratio (SR) of 1.10, a final SR of 1.15, and reburn fuel injected at a combustion gas temperature of about 1700 K. Performance on the basis of percent  $\text{NO}_x$  reduction improved as the level of initial  $\text{NO}_x$  increased. Basic reburning performance improved with increased reburn fuel heat input, except for furniture waste biomass when injected with inert carrier gas (which showed peak performance at 15% heat input). However, this performance peak did not reflect most biomass fuels tested and also disappeared for furniture waste when air was used as the carrier gas, which is more reflective of the type of carrier anticipated in actual practice (that is, containing some amount of oxygen). Performance improved as the reburn zone residence time increased and overfire air injection temperature correspondingly decreased; in practice the OFA injection temperature needs to be set at a practical level to achieve good mixing and burnout of rich reburning flue gas within the furnace.

For experiments in which N-agents were introduced (Advanced Reburning or Reburning+SNCR), good performance was found for NSR of about 1.5. The maximum  $\text{NO}_x$  performance of all conditions tested was 83% for Reburn+SNCR with Willow wood at an SNCR of 1.45, after OFA injection at 1450 K and urea injection at 1310 K. Under similar conditions, Reburn+SNCR using furniture waste provided about 76%  $\text{NO}_x$  reduction.

A number of factors can influence the performance of reburning and advanced reburning on a particular utility boiler. The boiler design impacts the locations where reburning fuel injectors and overfire air ports can be installed, and ultimately dictates the reburning zone residence time and thermal environment, both of which have a first order impact on reburning performance. The boiler design also largely controls the characteristics of the gas flow path in the furnace, which determines how effectively and how fast the reburning process streams can be mixed into the bulk furnace flow. The firing configuration of the boiler also influences the process, since it determines the  $\text{NO}_x$  levels and the temperature of the gases entering the reburning zone. In general, the  $\text{NO}_x$  control performance of reburning increases as the level of  $\text{NO}_x$  emissions entering the process and the gas temperatures at the point of reburning fuel introduction increases. Application of Advanced Reburning to a specific boiler requires a very site-specific analysis to assess furnace flow fields and temperature profiles for optimum location and design of the reagent injectors.

## 9.3 Reburning Application

The boiler selected for the scale-up studies is a tangentially fired boiler manufactured by Combustion Engineering and has a rated capacity of 170 MW (gross). The unit was designed to burn and presently fires Eastern bituminous coal with a nominal heating value of 12,381 Btu/lb. At full load firing pulverized coal, the unit has a gross heat input of 1,427 MMBtu/hr. As shown in Figure 9.1, the unit is equipped with low- $\text{NO}_x$  burners and close-coupled overfire air ports (CCOFA). There are four coal nozzles in the burners. One mill provides coal to the four nozzles located on the furnace corners at each elevation. Flue gas from the flames passes from the lower furnace into the upper furnace and then into the rear convective pass.

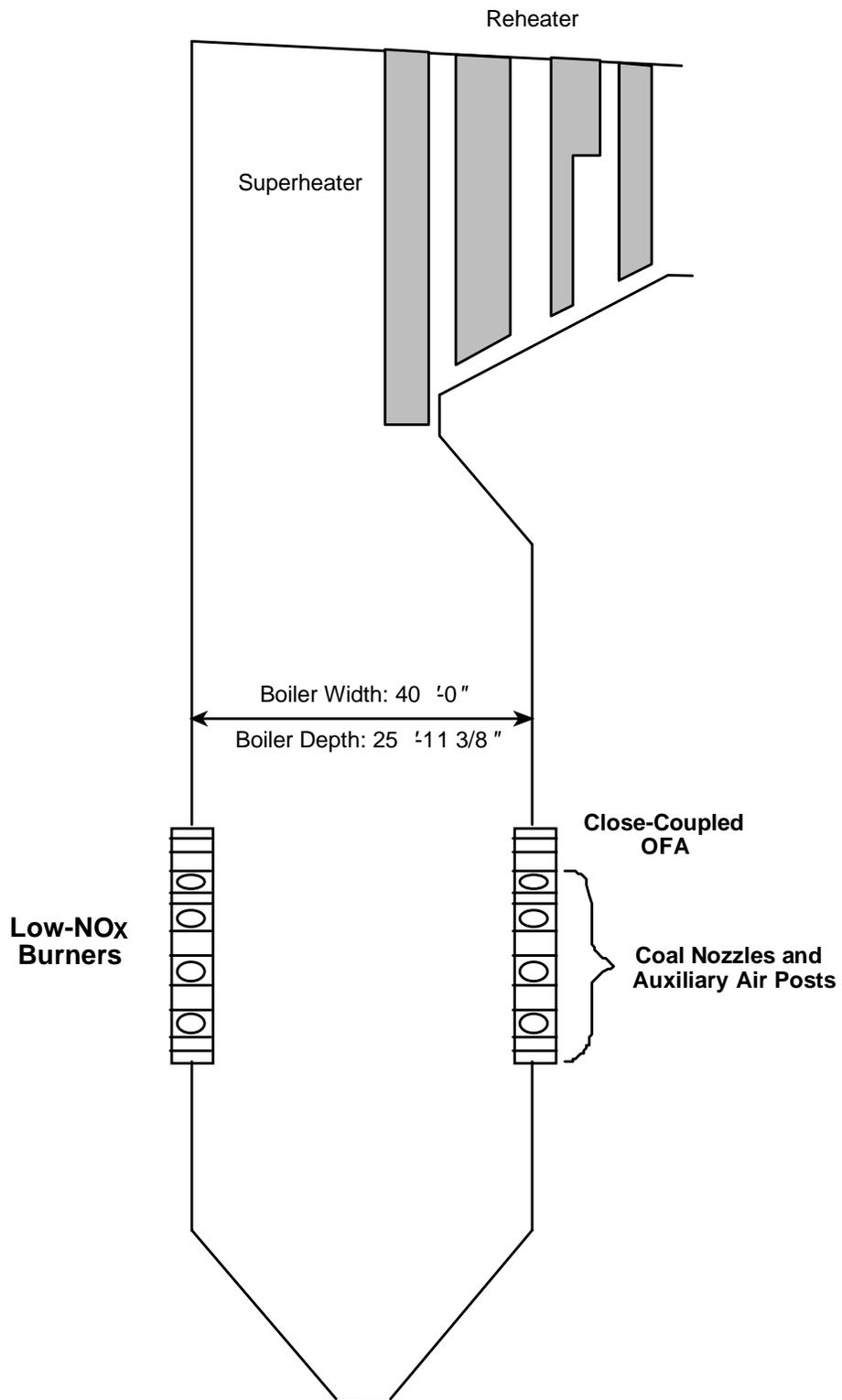


Figure 9.1. Sideview of a typical tangentially fired boiler.

At full load, NO<sub>x</sub> emissions vary from 0.28 to 0.38 lb/MMBtu, depending upon specific operating and burner settings. Average NO<sub>x</sub> emissions are 0.32 lb/MMBtu. As load is reduced, NO<sub>x</sub> emissions are reduced and reach 0.27 lb/MMBtu at 50% load. The normal excess air level of the unit at full load is approximately 20%. Carbon-in-ash levels are typically in the range of 5 to 10%.

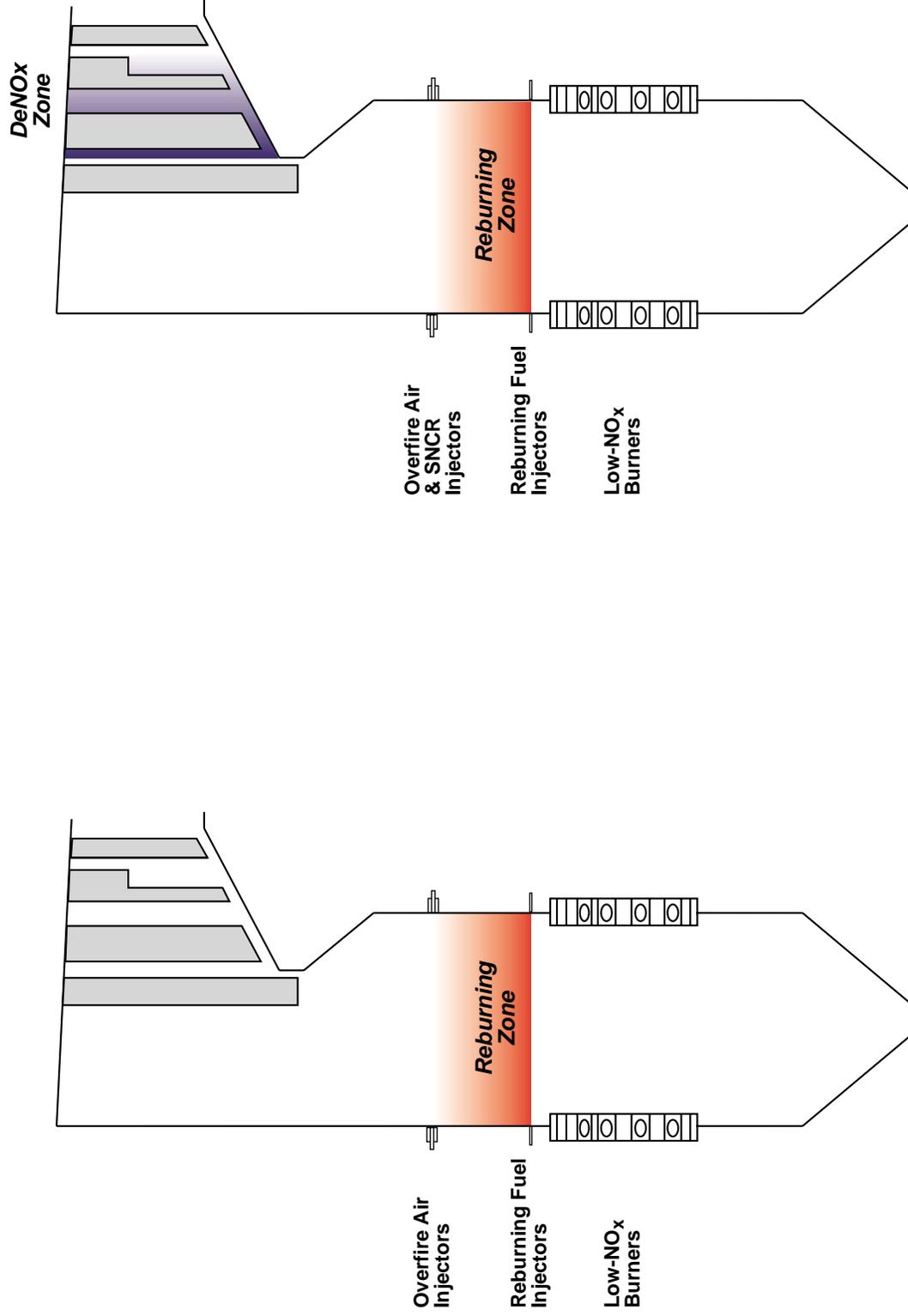
The biomass composition used for conceptual design studies is similar to that of pulverized furniture waste used in earlier pilot scale studies under this program. The composition parameters which entered into the current analysis (ultimate analysis and heating value) are shown in Table 9.1 for both the coal used in this boiler and the biomass.

EER has identified a preliminary approach for applying biomass and advanced biomass reburning to the unit as illustrated in Figure 9.2. In both processes, the reburning fuel would be injected at an elevation above the main burners, and the overfire air would be injected at an elevation selected to provide the maximum reburning zone residence time within the furnace constraints. As shown in Figure 9.2, the reburning fuel injectors would be located approximately eight feet above the upper coal nozzles on the furnace corners. This elevation is above the burners, and should provide sufficient separation between the main flames and the reburning zone to ensure good reburning performance. Overfire air injectors would be located on the furnace corners at an elevation approximately ten feet above the reburning fuel injectors. The overfire air system would be designed to provide good control over carbon monoxide emissions and burnout of the biomass and coal particles. For this unit, EER would install the reagent injectors within the overfire air injectors. The droplet size would be optimized to permit delivery of reagent into the proper temperature window. Based upon the above, the conceptual design described below was developed.

TABLE 9.1. FUEL ANALYSIS

Parameter	Units	Coal*	Furniture Waste
<u>Ultimate analysis</u>			
Carbon	% dry	77.78	53.81
Hydrogen	% dry	4.63	6.06
Nitrogen	% dry	1.48	0.56
Sulfur	% dry	0.83	0.03
Oxygen (difference)	% dry	5.97	38.05
Ash	% dry	9.31	1.31
Chlorine	% dry	--	0.19
Moisture	% as fired	6.47	7.33
Higher Heating Value	Btu/lb dry	13,237	8,507

\* Eastern Bituminous coal currently fired at example plant.



(a) Biomass reburning.

(a) Advanced biomass reburning.

Figure 9.2. Application of biomass reburning technologies to a typical tangentially fired boiler.

The reburning fuel injectors would be installed on each corner of the furnace to promote mixing of the reburning fuel. For the use of biomass as a reburning fuel, preliminary calculations suggest that the use of a total of four injectors would result in effective mixing of the reburning fuel with the furnace gases. Each injector would consist of a single reburning fuel nozzle with a diameter of between 10 to 15 inches depending upon the mill and transport requirements. Injection velocities in the range of 150 feet/sec are expected to be required to achieve good mixing of the reburning fuel. The injection velocity is linked to the amount of transport gas (air or recycled flue gas) that is required by the biomass mill and to transport the biomass from milling/storage to the injection location. The effect of these coupled parameters should be evaluated further in future studies. Physical flow modeling studies based on nominal values of these parameters are summarized in Section 7.

The overfire injection system would consist of four dual-compartment OFA injectors installed at each corner of the furnace. The dual-compartment OFA injectors consist of a constant velocity zone and a modulating velocity zone. This feature permits individual tuning of the OFA injectors to bias flow conditions according to furnace flow patterns, and the capability of operating over a wider range of reburning conditions. In general, sufficient mixing should be attainable using the existing windbox pressure. Physical flow modeling studies in Section 7 evaluate the effectiveness of OFA mixing under conditions estimated to provide acceptable mixing. However, this is also a parameter that should be evaluated in further studies.

For implementation of advanced reburning, a preliminary analysis suggests that the most cost-effective approach would be to locate the reagent injectors within the overfire air ports. This approach would minimize the retrofit costs and should provide good SCNR performance. The size distribution of the reagent spray would need to be optimized to deliver the reagent within the proper window. Future studies should evaluate the specific droplet size requirements and their impacts on  $\text{NO}_x$  reduction.

Preliminary process flow diagrams for the application of biomass reburning and advanced biomass reburning to the unit are shown in Figures 9.3 and 9.4. Material balances corresponding to these two process flow diagrams are shown in Tables 9.2 and 9.3. For biomass reburning (Table 9.2), the system would be sized for operation at 170 MW. The primary excess air level in the burners would be lowered from 20% to 10% in order to minimize the amount of reburning fuel needed to achieve a specific  $\text{NO}_x$  emissions target. Sufficient overfire air would be added to bring the boiler up to its normal operating excess air level of 20%. In the reburning zone, the target is to achieve an overall stoichiometric ratio of 0.90, which is optimal for  $\text{NO}_x$  reduction when using biomass. For these criteria, the reburning fuel represents approximately 20 percent of the total boiler heat input (based upon the use of recycled flue gas as the reburning fuel transport and injection medium). This material balance is very similar to the one presented earlier in Table 7.4, representing 19% heat input from reburning fuel. That condition was studied using physical flow modeling techniques as presented in Section 7.

It is possible to reduce the amount of reburning fuel used to achieve a specific  $\text{NO}_x$  target by lowering the burner excess air level below 10%. The potential to lower the burner excess air level and its impacts on operation of the lower furnace and carbon loss need to be evaluated in a more detailed assessment. For advanced reburning, the operation of the reburning system would be similar to that described above. The design point for the reagent injection system would be to achieve a nitrogen stoichiometric ratio (NSR) of 1.5. A preliminary mass balance for advanced reburning, with virtually no adjustment of the fuel or air flow rates compared to the 20%

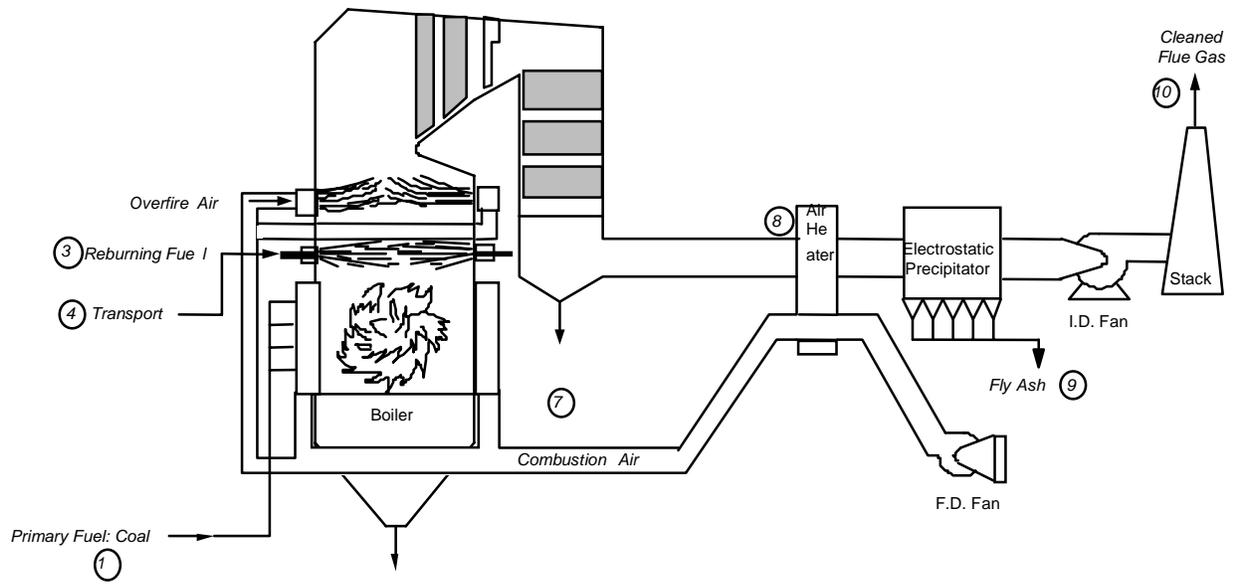


Figure 9.3. Process flow diagram for biomass reburning application.

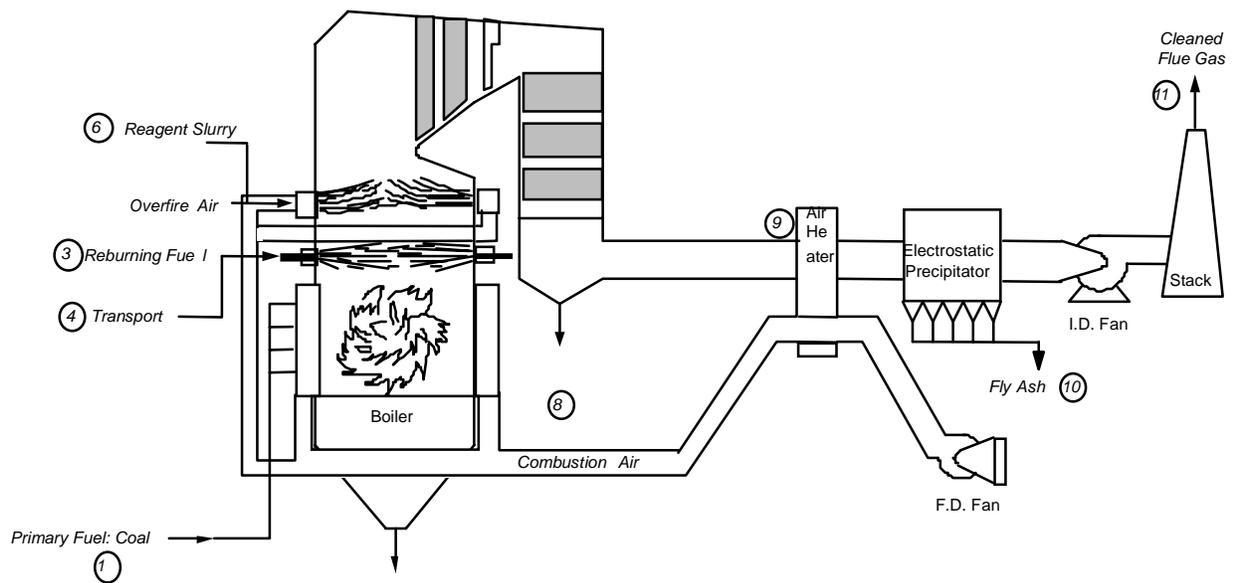


Figure 9.4. Process flow diagram for advanced biomass reburning application.

TABLE 9.2. REBURNING MATERIAL BALANCE

STREAM NUMBER	1	2	3	4	5	6	7	8	9	10
DESCRIPTION	Primary Fuel: Coal	Coal Combustion Air	Reburning Fuel: Biomass	Reburning Fuel Transport	Overfire Air	Boiler Bottom Ash	Economizer Hopper Ash	Air Heater Leakage	ESP Ash	Flue Gas to Stack
<b>GAS SIDE:</b>										
Air (lbs/hr)		981,642			331,636					
Air (SCFM)		213,586			72,158					
Reburn Fuel (lbs/hr)			34,841							
Flue Gas (lbs/hr)				85,984						1,433,065
Flue Gas (SCFM)										287,757
<b>SOLID SIDE:</b>										
Primary Fuel (lbs/hr)	93,050									
Fuel Inerts (lbs/hr)	8,105		61			2,042	408		5,716	
Total Waste Solids (lbs/hr)	8,105		61			2,042	408		5,716	

TABLE 9.3. ADVANCED REBURNING MATERIAL BALANCE

STREAM NUMBER	DESCRIPTION	1	2	3	4	5	6	7	8	9	10	11
	Primary Fuel: Coal											
	Coal Combustion Air		981,642									
	Air (lbs/hr)					331,636						
	Air (SCFM)		213,586			72,158						
	Reburn Fuel (lbs/hr)			34,841								
	Flue Gas (lbs/hr)				86,306							1,438,429
	Flue Gas (SCFM)											289,516
	Reagent (lbs/hr)						268					
	Reagent Type: CO(NH <sub>2</sub> ) <sub>2</sub>						5,096					
	H <sub>2</sub> O (lbs/hr)											
	Primary Fuel (lbs/hr)	93,050										
	Fuel Inerts (lbs/hr)	8,105		61				2,042	408		5,716	
	Total Waste Solids (lbs/hr)	8,105		61				2,042	408		5,716	

reburning case, is shown in Table 9.3. In the physical flow modeling study described in Section 7, a case was considered in which the reburning fuel heat input was reduced to 15%, representative of the type of change which might be considered in conjunction with a more detailed advanced reburn design study.

#### **9.4 NO<sub>x</sub> Control Performance**

A preliminary projection of the impacts of reburning and advanced reburning with biomass on NO<sub>x</sub> emissions from the tangentially fired boiler has been developed. The projected emissions performance curves are shown in Figure 9.5.

The emissions performance curves are based on the range of performance trends seen for different biomass fuels studied in the experimental program. They do not include the peak in performance at about 15% reburning heat input which was seen only for furniture waste, and only with nitrogen as the carrier gas. (Depending on economic considerations, the preferred carrier gas could be either air, which is easy to handle but reduces NO<sub>x</sub> reduction performance, or recirculated flue gas, which gives better performance but requires higher capital costs.) Even though the composition used in process design calculations was that of furniture waste, the projections here are designed to be more generally applicable to a variety of biomass fuels. Fuel-specific issues will be considered further in later studies.

At full load, it is expected that biomass reburning should be capable of reducing NO<sub>x</sub> emissions from a baseline of 0.32 lb/MMBtu to 0.19 lb/MMBtu, which represents a 40 percent reduction in NO<sub>x</sub> emissions. This level of NO<sub>x</sub> emissions should be achievable with approximately 20 percent of the boiler heat input supplied by the reburning fuel, depending upon the acceptable burner excess air level. A preliminary estimate of the application of advanced biomass reburning to the tangentially fired boiler indicates that NO<sub>x</sub> emissions levels of 0.17 or below could potentially be reached.

These estimates of the potential NO<sub>x</sub> control levels achievable with reburning and advanced reburning should be considered preliminary pending a more detailed analysis of the furnace gas temperatures, residence times, and flow patterns.

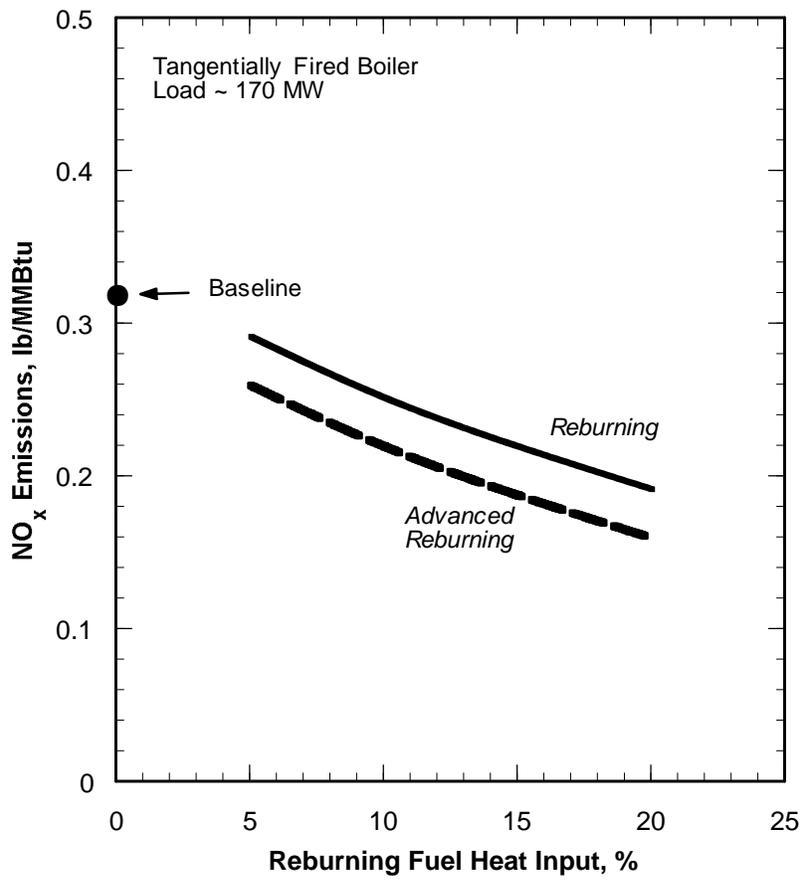


Figure 9.5. Projected performance for reburning and advanced reburning with biomass.

## 10.0 Summary and Conclusions

### 10.1 Experimental Results

Furniture pellets and walnut shells provided similar NO<sub>x</sub> control as that of natural gas in basic reburning at low heat inputs and performed worse at high ones. Maximum NO<sub>x</sub> reduction achieved with walnut shell and furniture pellets was 65% and 58% respectively. Performance of willow wood was worse than that of natural gas at all heat inputs with maximum NO<sub>x</sub> reduction of 50%.

Optimum heat input for furniture waste is about 15%, and for other biomass fuels about 20%.

With furniture waste, NO<sub>x</sub> reduction increases with decreasing biomass particle size. With willow wood, NO<sub>x</sub> reduction decreases slightly with decreasing particle size.

Efficiency of biomass as a reburning fuel depends on a nature of the primary fuel and is higher for natural gas than for coal. Biomass reburning with Illinois and Ohio coals as primary fuels showed about the same efficiencies.

Efficiency of biomass increases when N-agent is injected into reburning and/or burnout zones, or along with OFA (Advanced Reburning). Co-injection of Na<sub>2</sub>CO<sub>3</sub> with N-agent further increases efficiency of NO<sub>x</sub> reduction. Maximum NO<sub>x</sub> reduction achieved with furniture pellets and willow wood in Advanced Reburning was 83% and 78% respectively.

### 10.2 Kinetic Modeling Results

The kinetic model of biomass reburning agrees with experimental data for a wide range of initial conditions and thus correctly represents main features of the reburning process.

Modeling suggests that the most important factors that provide high efficiency of biomass in reburning are low fuel-N content and high content of alkali metals in ash. This conclusion allows to predict the efficiency of biomass as a reburning fuel based on its ultimate, proximate, and ash analysis.

### 10.3 Physical Modeling Results

The validated methodology for reburning system design has been applied to biomass reburning in a typical coal-fired boiler. This methodology includes the use of physical flow models to assess the mixing performance of reburn fuel and overfire air jets, which is of paramount importance in achieving target NO<sub>x</sub> control performance. The current study assessed the performance of the reburning system for two operating scenarios. The dispersion profiles of both the reburning zone and the overfire are zone were assessed to quantitatively determine the quality of mixing within each zone. The two preliminary cases studied showed potential as candidate reburning designs, and demonstrated that similar mixing performance could be achieved in operation with different quantities of reburning fuel. Refinement of the reburning system to achieve optimum performance is deferred until later studies on an actual host unit.

## **10.4 Process Design Results**

Based upon this preliminary evaluation, EER believes that reburning and advanced reburning technologies can be successfully applied using biomass. Pilot-scale studies on biomass reburning conducted by EER have indicated that biomass is an excellent reburning fuel. A preliminary conceptual design has been developed for a typical coal-fired boiler. Preparation for an actual installation would warrant additional design studies to evaluate the potential to achieve good mixing of the reburning fuel, overfire air, and reagent within the boiler under evaluation and the potential impacts of reburning and advanced reburning on boiler performance. This information will provide guidance for the application of biomass and advanced biomass reburning technologies in a coal-fired boiler.

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## Appendix A. Kinetic Mechanism Used in Modeling

Reactions are presented in Chemkin format (*Kee, et al., 1991*), where  $k = AT^n \exp(-E/RT)$  / cm; mol; s; K.

### A.1. Reactions Containing only C, H, O, N

	A	n	E
REACTIONS			
2O+M<=>O2+M	1.200E+17	-1.000	.00
H2/ 2.40/ H2O/15.40/ CH4/ 2.00/ CO/ 1.75/ CO2/ 3.60/ C2H6/ 3.00/ AR/ .83/			
O+H+M<=>OH+M	5.000E+17	-1.000	.00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
O+H2<=>H+OH	5.000E+04	2.670	6290.00
O+HO2<=>OH+O2	2.000E+13	.000	.00
O+H2O2<=>OH+HO2	9.630E+06	2.000	4000.00
O+CH<=>H+CO	5.700E+13	.000	.00
O+CH2<=>H+HCO	8.000E+13	.000	.00
O+CH2(S)<=>H2+CO	1.500E+13	.000	.00
O+CH2(S)<=>H+HCO	1.500E+13	.000	.00
O+CH3<=>H+CH2O	8.430E+13	.000	.00
O+CH4<=>OH+CH3	1.020E+09	1.500	8600.00
O+CO+M<=>CO2+M	6.020E+14	.000	3000.00
H2/2.00/ O2/6.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/3.50/ C2H6/3.00/ AR/ .50/			
O+HCO<=>OH+CO	3.000E+13	.000	.00
O+HCO<=>H+CO2	3.000E+13	.000	.00
O+CH2O<=>OH+HCO	3.900E+13	.000	3540.00
O+CH2OH<=>OH+CH2O	1.000E+13	.000	.00
O+CH3O<=>OH+CH2O	1.000E+13	.000	.00
O+CH3OH<=>OH+CH2OH	3.880E+05	2.500	3100.00
O+CH3OH<=>OH+CH3O	1.300E+05	2.500	5000.00
O+C2H<=>CH+CO	5.000E+13	.000	.00
O+C2H2<=>H+HCCO	1.020E+07	2.000	1900.00
O+C2H2<=>OH+C2H	4.600E+19	-1.410	28950.00
O+C2H2<=>CO+CH2	1.020E+07	2.000	1900.00
O+C2H3<=>H+CH2CO	3.000E+13	.000	.00
O+C2H4<=>CH3+HCO	1.920E+07	1.830	220.00
O+C2H5<=>CH3+CH2O	1.320E+14	.000	.00
O+C2H6<=>OH+C2H5	8.980E+07	1.920	5690.00
O+HCCO<=>H+2CO	1.000E+14	.000	.00
O+CH2CO<=>OH+HCCO	1.000E+13	.000	8000.00
O+CH2CO<=>CH2+CO2	1.750E+12	.000	1350.00
O2+CO<=>O+CO2	2.500E+12	.000	47800.00
O2+CH2O<=>HO2+HCO	1.000E+14	.000	40000.00
H+O2+M<=>HO2+M	2.800E+18	-.860	.00
O2/ .00/ H2O/ .00/ CO/ .75/ CO2/1.50/ C2H6/1.50/ N2/ .00/ AR/ .00/			
H+2O2<=>HO2+O2	3.000E+20	-1.720	.00
H+O2+H2O<=>HO2+H2O	9.380E+18	-.760	.00
H+O2+N2<=>HO2+N2	3.750E+20	-1.720	.00
H+O2+AR<=>HO2+AR	7.000E+17	-.800	.00
H+O2<=>O+OH	8.300E+13	.000	14413.00
2H+M<=>H2+M	1.000E+18	-1.000	.00
H2/ .00/ H2O/ .00/ CH4/2.00/ CO2/ .00/ C2H6/3.00/ AR/ .63/			
2H+H2<=>2H2	9.000E+16	-.600	.00
2H+H2O<=>H2+H2O	6.000E+19	-1.250	.00
2H+CO2<=>H2+CO2	5.500E+20	-2.000	.00

H+OH+M<=>H2O+M	2.200E+22	-2.000	.00
H2/ .73/ H2O/3.65/ CH4/2.00/ C2H6/3.00/ AR/ .38/			
H+HO2<=>O+H2O	3.970E+12	.000	671.00
H+HO2<=>O2+H2	2.800E+13	.000	1068.00
H+HO2<=>2OH	1.340E+14	.000	635.00
H+H2O2<=>HO2+H2	1.210E+07	2.000	5200.00
H+H2O2<=>OH+H2O	1.000E+13	.000	3600.00
H+CH<=>C+H2	1.100E+14	.000	.00
H+CH2(+M)<=>CH3(+M)	2.500E+16	-.800	.00
LOW / 3.200E+27	-3.140	1230.00/	
TROE/ .6800	78.00	1995.00	5590.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
H+CH2(S)<=>CH+H2	3.000E+13	.000	.00
H+CH3(+M)<=>CH4(+M)	1.270E+16	-.630	383.00
LOW / 2.477E+33	-4.760	2440.00/	
TROE/ .7830	74.00	2941.00	6964.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
H+CH4<=>CH3+H2	6.600E+08	1.620	10840.00
H+HCO(+M)<=>CH2O(+M)	1.090E+12	.480	-260.00
LOW / 1.350E+24	-2.570	1425.00/	
TROE/ .7824	271.00	2755.00	6570.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
H+HCO<=>H2+CO	7.340E+13	.000	.00
H+CH2O(+M)<=>CH2OH(+M)	5.400E+11	.454	3600.00
LOW / 1.270E+32	-4.820	6530.00/	
TROE/ .7187	103.00	1291.00	4160.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/			
H+CH2O(+M)<=>CH3O(+M)	5.400E+11	.454	2600.00
LOW / 2.200E+30	-4.800	5560.00/	
TROE/ .7580	94.00	1555.00	4200.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/			
H+CH2O<=>HCO+H2	2.300E+10	1.050	3275.00
H+CH2OH(+M)<=>CH3OH(+M)	1.800E+13	.000	.00
LOW / 3.000E+31	-4.800	3300.00/	
TROE/ .7679	338.00	1812.00	5081.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/			
H+CH2OH<=>H2+CH2O	2.000E+13	.000	.00
H+CH2OH<=>OH+CH3	1.200E+13	.000	.00
H+CH2OH<=>CH2(S)+H2O	6.000E+12	.000	.00
H+CH3O(+M)<=>CH3OH(+M)	5.000E+13	.000	.00
LOW / 8.600E+28	-4.000	3025.00/	
TROE/ .8902	144.00	2838.00	45569.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/			
H+CH3O<=>H+CH2OH	3.400E+06	1.600	.00
H+CH3O<=>H2+CH2O	2.000E+13	.000	.00
H+CH3O<=>OH+CH3	3.200E+13	.000	.00
H+CH3O<=>CH2(S)+H2O	1.600E+13	.000	.00
H+CH3OH<=>CH2OH+H2	1.700E+07	2.100	4870.00
H+CH3OH<=>CH3O+H2	4.200E+06	2.100	4870.00
H+C2H(+M)<=>C2H2(+M)	1.000E+17	-1.000	.00
LOW / 3.750E+33	-4.800	1900.00/	
TROE/ .6464	132.00	1315.00	5566.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
H+C2H2(+M)<=>C2H3(+M)	5.600E+12	.000	2400.00
LOW / 3.800E+40	-7.270	7220.00/	
TROE/ .7507	98.50	1302.00	4167.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			

H+C2H3(+M)<=>C2H4(+M)	6.080E+12	.270	280.00
LOW / 1.400E+30	-3.860	3320.00/	
TROE/	.7820	207.50	2663.00 6095.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
H+C2H3<=>H2+C2H2	3.000E+13	.000	.00
H+C2H4(+M)<=>C2H5(+M)	1.080E+12	.454	1820.00
LOW / 1.200E+42	-7.620	6970.00/	
TROE/	.9753	210.00	984.00 4374.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
H+C2H4<=>C2H3+H2	1.325E+06	2.530	12240.00
H+C2H5(+M)<=>C2H6(+M)	5.210E+17	-.990	1580.00
LOW / 1.990E+41	-7.080	6685.00/	
TROE/	.8422	125.00	2219.00 6882.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
H+C2H5<=>H2+C2H4	2.000E+12	.000	.00
H+C2H6<=>C2H5+H2	1.150E+08	1.900	7530.00
H+HCCO<=>CH2(S)+CO	1.000E+14	.000	.00
H+CH2CO<=>HCCO+H2	5.000E+13	.000	8000.00
H+CH2CO<=>CH3+CO	1.130E+13	.000	3428.00
H+HCCOH<=>H+CH2CO	1.000E+13	.000	.00
H2+CO(+M)<=>CH2O(+M)	4.300E+07	1.500	79600.00
LOW / 5.070E+27	-3.420	84350.00/	
TROE/	.9320	197.00	1540.00 10300.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
OH+H2<=>H+H2O	2.160E+08	1.510	3430.00
2OH(+M)<=>H2O2(+M)	7.400E+13	-.370	.00
LOW / 2.300E+18	-.900	-1700.00/	
TROE/	.7346	94.00	1756.00 5182.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
2OH<=>O+H2O	3.570E+04	2.400	-2110.00
OH+HO2<=>O2+H2O	2.900E+13	.000	-500.00
OH+H2O2<=>HO2+H2O	1.750E+12	.000	320.00
DUPLICATE			
OH+H2O2<=>HO2+H2O	5.800E+14	.000	9560.00
DUPLICATE			
OH+C<=>H+CO	5.000E+13	.000	.00
OH+CH<=>H+HCO	3.000E+13	.000	.00
OH+CH2<=>H+CH2O	2.000E+13	.000	.00
OH+CH2<=>CH+H2O	1.130E+07	2.000	3000.00
OH+CH2(S)<=>H+CH2O	3.000E+13	.000	.00
OH+CH3(+M)<=>CH3OH(+M)	6.300E+13	.000	.00
LOW / 2.700E+38	-6.300	3100.00/	
TROE/	.2105	83.50	5398.00 8370.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/			
OH+CH3<=>CH2+H2O	5.600E+07	1.600	5420.00
OH+CH3<=>CH2(S)+H2O	2.501E+13	.000	.00
OH+CH4<=>CH3+H2O	1.000E+08	1.600	3120.00
OH+CO<=>H+CO2	4.760E+07	1.228	70.00
OH+HCO<=>H2O+CO	5.000E+13	.000	.00
OH+CH2O<=>HCO+H2O	3.430E+09	1.180	-447.00
OH+CH2OH<=>H2O+CH2O	5.000E+12	.000	.00
OH+CH3O<=>H2O+CH2O	5.000E+12	.000	.00
OH+CH3OH<=>CH2OH+H2O	1.440E+06	2.000	-840.00
OH+CH3OH<=>CH3O+H2O	6.300E+06	2.000	1500.00
OH+C2H<=>H+HCCO	2.000E+13	.000	.00
OH+C2H2<=>H+CH2CO	2.180E-04	4.500	-1000.00
OH+C2H2<=>H+HCCOH	5.040E+05	2.300	13500.00

OH+C2H2<=>C2H+H2O	3.370E+07	2.000	14000.00
OH+C2H2<=>CH3+CO	4.830E-04	4.000	-2000.00
OH+C2H3<=>H2O+C2H2	5.000E+12	.000	.00
OH+C2H4<=>C2H3+H2O	3.600E+06	2.000	2500.00
OH+C2H6<=>C2H5+H2O	3.540E+06	2.120	870.00
OH+CH2CO<=>HCCO+H2O	7.500E+12	.000	2000.00
2HO2<=>O2+H2O2	1.300E+11	.000	-1630.00
DUPLICATE			
2HO2<=>O2+H2O2	4.200E+14	.000	12000.00
DUPLICATE			
HO2+CH2<=>OH+CH2O	2.000E+13	.000	.00
HO2+CH3<=>O2+CH4	1.000E+12	.000	.00
HO2+CH3<=>OH+CH3O	2.000E+13	.000	.00
HO2+CO<=>OH+CO2	1.500E+14	.000	23600.00
HO2+CH2O<=>HCO+H2O2	1.000E+12	.000	8000.00
C+O2<=>O+CO	5.800E+13	.000	576.00
C+CH2<=>H+C2H	5.000E+13	.000	.00
C+CH3<=>H+C2H2	5.000E+13	.000	.00
CH+O2<=>O+HCO	3.300E+13	.000	.00
CH+H2<=>H+CH2	1.107E+08	1.790	1670.00
CH+H2O<=>H+CH2O	1.713E+13	.000	-755.00
CH+CH2<=>H+C2H2	4.000E+13	.000	.00
CH+CH3<=>H+C2H3	3.000E+13	.000	.00
CH+CH4<=>H+C2H4	6.000E+13	.000	.00
CH+CO(+M)<=>HCCO(+M)	5.000E+13	.000	.00
LOW / 2.690E+28 -3.740 1936.00/			
TROE/ .5757 237.00 1652.00 5069.00 /			
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
CH+CO2<=>HCO+CO	3.400E+12	.000	690.00
CH+CH2O<=>H+CH2CO	9.460E+13	.000	-515.00
CH+HCCO<=>CO+C2H2	5.000E+13	.000	.00
CH2+O2<=>OH+HCO	1.320E+13	.000	1500.00
CH2+H2<=>H+CH3	5.000E+05	2.000	7230.00
2CH2<=>H2+C2H2	3.200E+13	.000	.00
CH2+CH3<=>H+C2H4	4.000E+13	.000	.00
CH2+CH4<=>2CH3	2.460E+06	2.000	8270.00
CH2+CO(+M)<=>CH2CO(+M)	8.100E+11	.500	4510.00
LOW / 2.690E+33 -5.110 7095.00/			
TROE/ .5907 275.00 1226.00 5185.00 /			
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
CH2+HCCO<=>C2H3+CO	3.000E+13	.000	.00
CH2(S)+N2<=>CH2+N2	1.500E+13	.000	600.00
CH2(S)+AR<=>CH2+AR	9.000E+12	.000	600.00
CH2(S)+O2<=>H+OH+CO	2.800E+13	.000	.00
CH2(S)+O2<=>CO+H2O	1.200E+13	.000	.00
CH2(S)+H2<=>CH3+H	7.000E+13	.000	.00
CH2(S)+H2O(+M)<=>CH3OH(+M)	2.000E+13	.000	.00
LOW / 2.700E+38 -6.300 3100.00/			
TROE/ .1507 134.00 2383.00 7265.00 /			
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/			
CH2(S)+H2O<=>CH2+H2O	3.000E+13	.000	.00
CH2(S)+CH3<=>H+C2H4	1.200E+13	.000	-570.00
CH2(S)+CH4<=>2CH3	1.600E+13	.000	-570.00
CH2(S)+CO<=>CH2+CO	9.000E+12	.000	.00
CH2(S)+CO2<=>CH2+CO2	7.000E+12	.000	.00
CH2(S)+CO2<=>CO+CH2O	1.400E+13	.000	.00
CH2(S)+C2H6<=>CH3+C2H5	4.000E+13	.000	-550.00

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CH3+O2<=>O+CH3O          2.675E+13      .000    28800.00
CH3+O2<=>OH+CH2O          3.600E+10      .000     8940.00
CH3+H2O2<=>HO2+CH4        2.450E+04      2.470     5180.00
2CH3(+M)<=>C2H6(+M)        2.120E+16      -.970     620.00
    LOW / 1.770E+50   -9.670   6220.00/
    TROE/ .5325  151.00  1038.00  4970.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
2CH3<=>H+C2H5              4.990E+12      .100    10600.00
CH3+HCO<=>CH4+CO          2.648E+13      .000      .00
CH3+CH2O<=>HCO+CH4        3.320E+03      2.810     5860.00
CH3+CH3OH<=>CH2OH+CH4     3.000E+07      1.500     9940.00
CH3+CH3OH<=>CH3O+CH4      1.000E+07      1.500     9940.00
CH3+C2H4<=>C2H3+CH4       2.270E+05      2.000     9200.00
CH3+C2H6<=>C2H5+CH4       6.140E+06      1.740    10450.00
HCO+M<=>H+CO+M            1.870E+17      -1.000    17000.00
H2/2.00/ H2O/ 11.20/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
HCO+O2<=>HO2+CO           7.600E+12      .000     400.00
CH2OH+O2<=>HO2+CH2O       1.800E+13      .000     900.00
CH3O+O2<=>HO2+CH2O        4.280E-13      7.600    -3530.00
C2H+O2<=>HCO+CO           5.000E+13      .000     1500.00
C2H+H2<=>H+C2H2           4.070E+05      2.400     200.00
C2H3+O2<=>HCO+CH2O        3.980E+12      .000    -240.00
C2H4(+M)<=>H2+C2H2(+M)     8.000E+12      .440    88770.00
    LOW / 7.000E+50   -9.310  99860.00/
    TROE/ .7345  180.00  1035.00  5417.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
C2H5+O2<=>HO2+C2H4        8.400E+11      .000     3875.00
HCCO+O2<=>OH+2CO          1.600E+12      .000     854.00
2HCCO<=>2CO+C2H2          1.000E+13      .000      .00
! *** NH3 Reactions ***
!
NH3+M = NH2+H+M           2.2E16    0    93470 ! a
NH3+H = NH2+H2            6.4E05   2.39  10171 ! a
NH3+O = NH2+OH            9.4E06   1.94   6460 ! a
NH3+OH = NH2+H2O          2.0E06   2.04    566 ! a
NH3+HO2 = NH2+H2O2        3.0E11    0   22000 ! a
!
! *** NH2 Reactions ***
!
NH2+H = NH+H2             4.0E13    0    3650 ! a
NH2+O = HNO+H             6.6E14  -0.5     0 ! a
NH2+O = NH+OH             6.8E12    0     0 ! a
NH2+OH = NH+H2O           4.0E06   2.0   1000 ! a
NH2+HO2 = H2NO+OH         5.0E13    0     0 ! a
NH2+HO2 = NH3+O2          1.0E13    0     0 ! a
H2NO+O = NH2+O2           2.0E14    0     0 ! c
NH2+NH2= N2H2+H2          8.5E11    0     0 ! a
NH2+NH2= NH3+NH           5.0E13    0  10000 ! a
NH2+NH2(+M)=N2H4(+M)      1.5E13    0     0 ! a
    LOW/1.0E18  0  0/
    N2/2.5/  H2O/5/  NH3/10/
NH2+NH = N2H2+H           5.0E13    0     0 ! a
NH2+N = N2+2H             7.0E13    0     0 ! a
NH2+NO = NNH+OH           8.9E12  -0.35    0 ! c
NH2+NO = N2+H2O           1.3E16  -1.25    0 ! a
DUP
NH2+NO = N2+H2O           -8.9E12  -0.35    0 ! c

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DUP
NH2+NO2 = N2O+H2O          3.2E18 -2.2      0 ! a
NH2+NO2 = H2NO+NO          3.5E12   0      0 ! b
!
! *** NH and N Reactions ***
!
NH+H = N+H2                 3.0E13   0      0 ! a
NH+O = NO+H                 9.2E13   0      0 ! a
NH+OH = HNO+H              2.0E13   0      0 ! a
NH+OH = N+H2O              5.0E11  0.5    2000 ! a
NH+O2 = HNO+O              4.6E05  2.0    6500 ! a
NH+O2 = NO+OH              1.3E06  1.5     100 ! a
NH+N = N2+H                 3.0E13   0      0 ! a
NH+NH = N2+2H              2.5E13   0      0 ! a
NH+NO = N2O+H              2.9E14 -0.4     0 ! a
DUP
NH+NO = N2O+H              -2.2E13 -0.23    0 !
DUP
NH+NO = N2+OH              2.2E13 -0.23    0 ! a
NH+NO2 = N2O+OH           1.0E13   0      0 ! a
N+OH = NO+H                3.8E13   0      0 ! a
N+O2 = NO+O                6.4E09  1.0    6280 ! a
N+NO = N2+O                3.3E12  0.3     0 ! a
!
! *** NO Reactions ***
!
NO+O+M = NO2+M             7.5E19 -1.41    0 ! b
      N2/1.7/ O2/1.5/ H2O/10/
NO+OH+M = HONO+M          5.0E23 -2.51 -68 ! b
      N2/1.0/ H2O/5.0/
NO+HO2 = NO2+OH           2.1E12   0    -480 ! a
!
! *** Consumption of NO2 ***
!
NO2+H = NO+OH              8.4E13   0      0 ! b
NO2+O = NO+O2              3.9E12   0    -238 ! b
NO2+O(+M) = NO3(+M)        1.3E13  0.00    0 ! b
      LOW/1.0E28 -4.08 2470/
      N2/1.5/ O2/1.5/ H2O/18.6/
NO2+NO2 = NO+NO+O2         1.6E12   0    26123 ! b
NO2+NO2 = NO3+NO           9.6E09  0.73  20900 ! b
!
! *** Reactions of HNO, HONO, H2NO, NO3 ***
!
HNO+M = H+NO+M             1.5E16   0    48680 ! a
      H2O/10/ O2/2/ N2/2/ H2/2/
HNO+H = NO+H2              4.4E11  0.72   650 ! a
HNO+O = NO+OH              1.0E13   0      0 ! a
HNO+OH = NO+H2O            3.6E13   0      0 ! a
HNO+O2 = NO+HO2            1.0E13   0    25000 ! a
HNO+NH2= NO+NH3            2.0E13   0    1000 ! a
HNO+NO = N2O+OH            2.0E12   0    26000 ! a
HNO+NO2 = HONO+NO          6.0E11  0.00   2000 ! b
HNO+HNO = N2O+H2O          4.0E12   0    5000 ! a
HONO+H = NO2+H2            1.2E13  0.0   7350 ! b
HONO+O = NO2+OH            1.2E13  0.0   6000 ! b
HONO+OH = NO2+H2O          4.0E12   0      0 ! b

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HONO+NH = NH2+NO2	1.0E13	0	0	!	b
HONO+NH2 = NH3+NO2	5.0E12	0	0	!	b
HONO+HONO=NO+NO2+H2O	2.3E12	0	8400	!	b
H2NO+M = HNO+H+M	2.5E16	0	50000	!	c
H2NO+H = HNO+H2	3.0E07	2.0	2000	!	a
H2NO+H = NH2+OH	5.0E13	0	0	!	a
H2NO+O = HNO+OH	3.0E07	2.0	2000	!	a
H2NO+OH = HNO+H2O	2.0E07	2.0	1000	!	a
H2NO+NO = HNO+HNO	2.0E07	2.0	13000	!	a
H2NO+NH2 = HNO+NH3	3.0E12	0	1000	!	a
H2NO+NO2 = HONO+HNO	6.0E11	0.00	2000	!	b
NO3+H = NO2+OH	6.0E13	0.0	0	!	b
NO3+O = NO2+O2	1.0E13	0.0	0	!	b
NO3+OH = NO2+HO2	1.4E13	0.0	0	!	b
NO3+HO2 = NO2+O2+OH	1.5E12	0.0	0	!	b
NO3+NO2 = NO+NO2+O2	5.0E10	0.00	2940	!	b
!					
! *** N2-amine Subset ***					
!					
N2H4+H = N2H3+H2	1.3E13	0	2500	!	a
N2H4+O = N2H2+H2O	8.5E13	0	1200	!	a
N2H4+OH = N2H3+H2O	4.0E13	0	0	!	b
N2H4+NH2 = N2H3+NH3	3.9E12	0	1500	!	a
N2H3+M = N2H2+H+M	3.5E16	0	46000	!	a
N2H3+H = NH2+NH2	1.6E12	0	0	!	a
N2H3+O = N2H2+OH	5.0E12	0	5000	!	a
N2H3+O = NH2+HNO	1.0E13	0	0	!	a
N2H3+OH = N2H2+H2O	1.0E13	0	1000	!	a
N2H3+OH = NH3+HNO	1.0E12	0	15000	!	a
N2H3+NH = N2H2+NH2	2.0E13	0	0	!	a
N2H2+M = NNH+H+M	5.0E16	0	50000	!	a
H2O/15.0/ H2/2.0/ N2/2.0/ O2/2.0/					
N2H2+H = NNH+H2	5.0E13	0	1000	!	a
N2H2+O = NH2+NO	1.0E13	0	1000	!	a
N2H2+O = NNH+OH	2.0E13	0	1000	!	a
N2H2+OH = NNH+H2O	1.0E13	0	1000	!	a
N2H2+NH = NNH+NH2	1.0E13	0	1000	!	a
N2H2+NH2= NNH+NH3	1.0E13	0	1000	!	a
N2H2+NO = N2O+NH2	3.0E12	0	0	!	a
NNH = N2+H	1.0E07	0	0	!	c
NNH+H = N2+H2	1.0E14	0	0	!	a
NNH+O = N2O+H	1.0E14	0	0	!	a
NNH+O = NH+NO	5.0E13	0	0	!	b
NNH+OH = N2+H2O	5.0E13	0	0	!	a
NNH+O2 = N2+HO2	2.0E14	0	0	!	c
NNH+O2 = N2+H+O2	5.0E13	0	0	!	c
NNH+NH = N2+NH2	5.0E13	0	0	!	a
NNH+NH2 = N2+NH3	5.0E13	0	0	!	a
NNH+NO = N2+HNO	5.0E13	0	0	!	a
!					
! *** N2O Subset ***					
!					
N2O+M = N2+O+M	4.0E14	0	56100	!	a
N2/1.7/ O2/1.4/ CO2/3.0/ H2O/12/				!	
N2O+H = N2+OH	3.3E10	0	4729	!	b
DUP					
N2O+H = N2+OH	4.4E14	0	19254	!	

DUP

N2O+O = NO+NO	2.9E13	0	23150 ! a
N2O+O = N2+O2	1.4E12	0	10800 ! a
N2O+OH = N2+HO2	2.0E12	0	40000 ! b

## A.2. Reactions Containing Na

Reaction	A	n	E
NA+N2O=NAO+N2	1.69E+14	0.00	3159.
NAO+H2O=NAOH+OH	1.32E+13	0.00	0.
NAO+O=NA+O2	2.23E+14	0.00	0.
NAO+NO=NA+NO2	9.04E+13	0.00	0.
NAO+H2=NAOH+H	1.25E+13	0.00	0.
NA+O2+M=NAO2+M	1.74E+21	-1.30	0.
H2O/5/ CO2/3/ CO/2/ H2/2/			
NA+OH+M=NAOH+M	1.82E+21	-1.00	0.
NAO+OH=NAOH+O	2.00E+13	0.00	0.
NAO+HO2=NAOH+O2	5.00E+13	0.00	0.
NAO+H2=NA+H2O	3.13E+12	0.00	0.
NAO+CO=NA+CO2	1.00E+14	0.00	0.
H+NAO2=HO2+NA	2.00E+14	0.00	0.
NAO+H=NA+OH	2.00E+14	0.00	0.
NAO+OH=NA+HO2	3.00E+13	0.00	0.
NA+HO2=NAOH+O	1.00E+14	0.00	0.
NAO2+H=NAO+OH	5.00E+13	0.00	0.
NAO+HO2=NAO2+OH	5.00E+13	0.00	0.
NAO2+H=NAOH+O	1.00E+14	0.00	0.
NAO2+CO=NAO+CO2	1.00E+14	0.00	0.
NAO2+O=NAO+O2	1.00E+14	0.00	0.
NAO+NH3=NAOH+NH2	1.00E+13	0.00	0.
NAOH+H=NA+H2O	1.07E+13	0.00	1967.
NAO2+OH=NAOH+O2	8.00E+13	0.00	0.

## Appendix B. Thermodynamic Data Used in Modeling

Thermodynamic data is presented here in the Chemkin thermodynamic coefficient format (*Kee, et al., 1991*), which is similar to that of the NASA coefficient format (*Gordon and McBride, 1973*).

### B.1. Species Containing only C, H, O, N, Ar

ELEMENTS

O H C N AR

SPECIES

NH3 O2 NO H2O CO2 N2  
H2 H O OH HO2 H2O2  
C CH CH2 CH2(S) CH3 CH4 CO  
HCO CH2O CH2OH CH3O CH3OH C2H C2H2 C2H3  
C2H4 C2H5 C2H6 HCCO CH2CO HCCOH  
N NH NH2 NNH N2H2 N2H3 N2H4  
HNO HONO NO3 H2NO N2O NO2  
AR

THERMO

300.000	1500.000	5000.000								
O	L 1/900	1	00	00	00G	200.000	3500.000	1000.000		1
	2.56942078E+00	-8.59741137E-05	4.19484589E-08	-1.00177799E-11	1.22833691E-15					2
	2.92175791E+04	4.78433864E+00	3.16826710E+00	-3.27931884E-03	6.64306396E-06					3
	-6.12806624E-09	2.11265971E-12	2.91222592E+04	2.05193346E+00	6.72540300E+03					4
O2	TPIS890	2	00	00	00G	200.000	3500.000	1000.000		1
	3.28253784E+00	1.48308754E-03	-7.57966669E-07	2.09470555E-10	-2.16717794E-14					2
	-1.08845772E+03	5.45323129E+00	3.78245636E+00	-2.99673416E-03	9.84730201E-06					3
	-9.68129509E-09	3.24372837E-12	-1.06394356E+03	3.65767573E+00	8.68010400E+03					4
H	L 7/88H	1	00	00	00G	200.000	3500.000	1000.000		1
	2.50000001E+00	-2.30842973E-11	1.61561948E-14	-4.73515235E-18	4.98197357E-22					2
	2.54736599E+04	-4.46682914E-01	2.50000000E+00	7.05332819E-13	-1.99591964E-15					3
	2.30081632E-18	-9.27732332E-22	2.54736599E+04	-4.46682853E-01	6.19742800E+03					4
H2	TPIS78H	2	00	00	00G	200.000	3500.000	1000.000		1
	3.33727920E+00	-4.94024731E-05	4.99456778E-07	-1.79566394E-10	2.00255376E-14					2
	-9.50158922E+02	-3.20502331E+00	2.34433112E+00	7.98052075E-03	-1.94781510E-05					3
	2.01572094E-08	-7.37611761E-12	-9.17935173E+02	6.83010238E-01	8.46810200E+03					4
OH	RUS 780	1H	1	00	00G	200.000	3500.000	1000.000		1
	3.09288767E+00	5.48429716E-04	1.26505228E-07	-8.79461556E-11	1.17412376E-14					2
	3.85865700E+03	4.47669610E+00	3.99201543E+00	-2.40131752E-03	4.61793841E-06					3
	-3.88113333E-09	1.36411470E-12	3.61508056E+03	-1.03925458E-01	8.81310600E+03					4
H2O	L 8/89H	20	1	00	00G	200.000	3500.000	1000.000		1
	3.03399249E+00	2.17691804E-03	-1.64072518E-07	-9.70419870E-11	1.68200992E-14					2
	-3.00042971E+04	4.96677010E+00	4.19864056E+00	-2.03643410E-03	6.52040211E-06					3
	-5.48797062E-09	1.77197817E-12	-3.02937267E+04	-8.49032208E-01	9.90409200E+03					4
HO2	L 5/89H	10	2	00	00G	200.000	3500.000	1000.000		1
	4.01721090E+00	2.23982013E-03	-6.33658150E-07	1.14246370E-10	-1.07908535E-14					2
	1.11856713E+02	3.78510215E+00	4.30179801E+00	-4.74912051E-03	2.11582891E-05					3
	-2.42763894E-08	9.29225124E-12	2.94808040E+02	3.71666245E+00	1.00021620E+04					4
H2O2	L 7/88H	20	2	00	00G	200.000	3500.000	1000.000		1
	4.16500285E+00	4.90831694E-03	-1.90139225E-06	3.71185986E-10	-2.87908305E-14					2
	-1.78617877E+04	2.91615662E+00	4.27611269E+00	-5.42822417E-04	1.67335701E-05					3
	-2.15770813E-08	8.62454363E-12	-1.77025821E+04	3.43505074E+00	1.11588350E+04					4
C	L11/88C	1	00	00	00G	200.000	3500.000	1000.000		1
	2.49266888E+00	4.79889284E-05	-7.24335020E-08	3.74291029E-11	-4.87277893E-15					2
	8.54512953E+04	4.80150373E+00	2.55423955E+00	-3.21537724E-04	7.33792245E-07					3

-7.32234889E-10	2.66521446E-13	8.54438832E+04	4.53130848E+00	6.53589500E+03	4				
CH	TPIS79C	1H	1	00	00G	200.000	3500.000	1000.000	1
2.87846473E+00	9.70913681E-04	1.44445655E-07	-1.30687849E-10	1.76079383E-14	2				
7.10124364E+04	5.48497999E+00	3.48981665E+00	3.23835541E-04	-1.68899065E-06	3				
3.16217327E-09	-1.40609067E-12	7.07972934E+04	2.08401108E+00	8.62500000E+03	4				
CH2	L S/93C	1H	2	00	00G	200.000	3500.000	1000.000	1
2.87410113E+00	3.65639292E-03	-1.40894597E-06	2.60179549E-10	-1.87727567E-14	2				
4.62636040E+04	6.17119324E+00	3.76267867E+00	9.68872143E-04	2.79489841E-06	3				
-3.85091153E-09	1.68741719E-12	4.60040401E+04	1.56253185E+00	1.00274170E+04	4				
CH2(S)	L S/93C	1H	2	00	00G	200.000	3500.000	1000.000	1
2.29203842E+00	4.65588637E-03	-2.01191947E-06	4.17906000E-10	-3.39716365E-14	2				
5.09259997E+04	8.62650169E+00	4.19860411E+00	-2.36661419E-03	8.23296220E-06	3				
-6.68815981E-09	1.94314737E-12	5.04968163E+04	-7.69118967E-01	9.93967200E+03	4				
CH3	L11/89C	1H	3	00	00G	200.000	3500.000	1000.000	1
2.28571772E+00	7.23990037E-03	-2.98714348E-06	5.95684644E-10	-4.67154394E-14	2				
1.67755843E+04	8.48007179E+00	3.67359040E+00	2.01095175E-03	5.73021856E-06	3				
-6.87117425E-09	2.54385734E-12	1.64449988E+04	1.60456433E+00	1.03663400E+04	4				
CH4	L 8/88C	1H	4	00	00G	200.000	3500.000	1000.000	1
7.48514950E-02	1.33909467E-02	-5.73285809E-06	1.22292535E-09	-1.01815230E-13	2				
-9.46834459E+03	1.84373180E+01	5.14987613E+00	-1.36709788E-02	4.91800599E-05	3				
-4.84743026E-08	1.66693956E-11	-1.02466476E+04	-4.64130376E+00	1.00161980E+04	4				
CO	TPIS79C	1O	1	00	00G	200.000	3500.000	1000.000	1
2.71518561E+00	2.06252743E-03	-9.98825771E-07	2.30053008E-10	-2.03647716E-14	2				
-1.41518724E+04	7.81868772E+00	3.57953347E+00	-6.10353680E-04	1.01681433E-06	3				
9.07005884E-10	-9.04424499E-13	-1.43440860E+04	3.50840928E+00	8.67100000E+03	4				
CO2	L 7/88C	1O	2	00	00G	200.000	3500.000	1000.000	1
3.85746029E+00	4.41437026E-03	-2.21481404E-06	5.23490188E-10	-4.72084164E-14	2				
-4.87591660E+04	2.27163806E+00	2.35677352E+00	8.98459677E-03	-7.12356269E-06	3				
2.45919022E-09	-1.43699548E-13	-4.83719697E+04	9.90105222E+00	9.36546900E+03	4				
HCO	L12/89H	1C	1O	1	00G	200.000	3500.000	1000.000	1
2.77217438E+00	4.95695526E-03	-2.48445613E-06	5.89161778E-10	-5.33508711E-14	2				
4.01191815E+03	9.79834492E+00	4.22118584E+00	-3.24392532E-03	1.37799446E-05	3				
-1.33144093E-08	4.33768865E-12	3.83956496E+03	3.39437243E+00	9.98945000E+03	4				
CH2O	L 8/88H	2C	1O	1	00G	200.000	3500.000	1000.000	1
1.76069008E+00	9.20000082E-03	-4.42258813E-06	1.00641212E-09	-8.83855640E-14	2				
-1.39958323E+04	1.36563230E+01	4.79372315E+00	-9.90833369E-03	3.73220008E-05	3				
-3.79285261E-08	1.31772652E-11	-1.43089567E+04	6.02812900E-01	1.00197170E+04	4				
CH2OH	GUNL93C	1H	3O	1	00G	200.000	3500.000	1000.000	1
3.69266569E+00	8.64576797E-03	-3.75101120E-06	7.87234636E-10	-6.48554201E-14	2				
-3.24250627E+03	5.81043215E+00	3.86388918E+00	5.59672304E-03	5.93271791E-06	3				
-1.04532012E-08	4.36967278E-12	-3.19391367E+03	5.47302243E+00	1.18339080E+04	4				
CH3O	121686C	1H	3O	1	00G	300.00	3000.00	1000.000	1
0.03770799E+02	0.07871497E-01	-0.02656384E-04	0.03944431E-08	-0.02112616E-12	2				
0.12783252E+03	0.02929575E+02	0.02106204E+02	0.07216595E-01	0.05338472E-04	3				
-0.07377636E-07	0.02075610E-10	0.09786011E+04	0.13152177E+02		4				
CH3OH	L 8/88C	1H	4O	1	00G	200.000	3500.000	1000.000	1
1.78970791E+00	1.40938292E-02	-6.36500835E-06	1.38171085E-09	-1.17060220E-13	2				
-2.53748747E+04	1.45023623E+01	5.71539582E+00	-1.52309129E-02	6.52441155E-05	3				
-7.10806889E-08	2.61352698E-11	-2.56427656E+04	-1.50409823E+00	1.14352770E+04	4				
C2H	L 1/91C	2H	1	00	00G	200.000	3500.000	1000.000	1
3.16780652E+00	4.75221902E-03	-1.83787077E-06	3.04190252E-10	-1.77232770E-14	2				
6.71210650E+04	6.63589475E+00	2.88965733E+00	1.34099611E-02	-2.84769501E-05	3				
2.94791045E-08	-1.09331511E-11	6.68393932E+04	6.22296438E+00	1.04544720E+04	4				
C2H2	L 1/91C	2H	2	00	00G	200.000	3500.000	1000.000	1
4.14756964E+00	5.96166664E-03	-2.37294852E-06	4.67412171E-10	-3.61235213E-14	2				
2.59359992E+04	-1.23028121E+00	8.08681094E-01	2.33615629E-02	-3.55171815E-05	3				
2.80152437E-08	-8.50072974E-12	2.64289807E+04	1.39397051E+01	1.00058390E+04	4				
C2H3	L 2/92C	2H	3	00	00G	200.000	3500.000	1000.000	1
3.01672400E+00	1.03302292E-02	-4.68082349E-06	1.01763288E-09	-8.62607041E-14	2				
3.46128739E+04	7.78732378E+00	3.21246645E+00	1.51479162E-03	2.59209412E-05	3				
-3.57657847E-08	1.47150873E-11	3.48598468E+04	8.51054025E+00	1.05750490E+04	4				
C2H4	L 1/91C	2H	4	00	00G	200.000	3500.000	1000.000	1
2.03611116E+00	1.46454151E-02	-6.71077915E-06	1.47222923E-09	-1.25706061E-13	2				

4.93988614E+03	1.03053693E+01	3.95920148E+00	-7.57052247E-03	5.70990292E-05	3					
-6.91588753E-08	2.69884373E-11	5.08977593E+03	4.09733096E+00	1.05186890E+04	4					
C2H5	L12/92C	2H	5	00	00G	200.000	3500.000	1000.000	1	
1.95465642E+00	1.73972722E-02	-7.98206668E-06	1.75217689E-09	-1.49641576E-13	2					
1.28575200E+04	1.34624343E+01	4.30646568E+00	-4.18658892E-03	4.97142807E-05	3					
-5.99126606E-08	2.30509004E-11	1.28416265E+04	4.70720924E+00	1.21852440E+04	4					
C2H6	L 8/88C	2H	6	00	00G	200.000	3500.000	1000.000	1	
1.07188150E+00	2.16852677E-02	-1.00256067E-05	2.21412001E-09	-1.90002890E-13	2					
-1.14263932E+04	1.51156107E+01	4.29142492E+00	-5.50154270E-03	5.99438288E-05	3					
-7.08466285E-08	2.68685771E-11	-1.15222055E+04	2.66682316E+00	1.18915940E+04	4					
CH2CO	L 5/90C	2H	20	1	00G	200.000	3500.000	1000.000	1	
4.51129732E+00	9.00359745E-03	-4.16939635E-06	9.23345882E-10	-7.94838201E-14	2					
-7.55105311E+03	6.32247205E-01	2.13583630E+00	1.81188721E-02	-1.73947474E-05	3					
9.34397568E-09	-2.01457615E-12	-7.04291804E+03	1.22156480E+01	1.17977430E+04	4					
HCCO	SRIC91H	1C	20	1	00G	300.00	4000.00	1000.000	1	
0.56282058E+01	0.40853401E-02	-0.15934547E-05	0.28626052E-09	-0.19407832E-13	2					
0.19327215E+05	-0.39302595E+01	0.22517214E+01	0.17655021E-01	-0.23729101E-04	3					
0.17275759E-07	-0.50664811E-11	0.20059449E+05	0.12490417E+02		4					
HCCOH	SRI91C	2O	1H	2	00G	300.000	5000.000	1000.000	1	
0.59238291E+01	0.67923600E-02	-0.25658564E-05	0.44987841E-09	-0.29940101E-13	2					
0.72646260E+04	-0.76017742E+01	0.12423733E+01	0.31072201E-01	-0.50866864E-04	3					
0.43137131E-07	-0.14014594E-10	0.80316143E+04	0.13874319E+02		4					
N	J 3/61N	1	0	0	0G	300.000	5000.000	1000.000	01	
2.50104420E+00	0.00000000E+00	0.00000000E+00	0.00000000E+00	0.00000000E+00	2					
5.61038356E+04	4.17481974E+00	2.50104420E+00	0.00000000E+00	0.00000000E+00	3					
0.00000000E+00	0.00000000E+00	5.61038356E+04	4.17481974E+00		4					
NH	melius/91	N	1H	1	0	0G	300.000	5000.000	1368.000	01
2.71207542E+00	1.33555860E-03	-3.70230207E-07	4.57845270E-11	-2.13216798E-15	2					
4.24170243E+04	6.21142965E+00	3.49617412E+00	-2.58512197E-04	8.00229766E-07	3					
-3.18729027E-10	3.76580317E-14	4.21181588E+04	1.91107205E+00		4					
NO	J 6/63N	1O	1	0	0G	300.000	5000.000	1397.000	01	
3.30616438E+00	1.05880379E-03	-3.35101565E-07	4.84712126E-11	-2.66276333E-15	2					
9.80488610E+03	6.14537840E+00	3.18302768E+00	1.26159588E-03	-4.40480253E-07	3					
6.32411494E-11	-1.29137488E-15	9.85926748E+03	6.84194428E+00		4					
N2	J 9/65N	2	0	0	0G	300.000	5000.000	1651.000	01	
2.99595342E+00	1.23650804E-03	-3.70307892E-07	5.05346628E-11	-2.62980307E-15	2					
-9.13275945E+02	5.68044094E+00	3.26021755E+00	5.91317615E-04	2.24046981E-07	3					
-1.95572855E-10	3.61873253E-14	-9.99926028E+02	4.27471775E+00		4					
NH2	L 9/81N	1H	2	0	0G	300.000	5000.000	1379.000	01	
2.81084081E+00	3.24676780E-03	-1.05043681E-06	1.56667098E-10	-8.82503591E-15	2					
2.19519093E+04	6.57719920E+00	4.10811911E+00	-1.25157496E-03	4.38306028E-06	3					
-2.62867774E-09	5.10376771E-13	2.16908327E+04	2.01299833E-01		4					
HNO	WA/93	H	1N	1O	1	0G	300.000	5000.000	1671.000	01
3.78577430E+00	2.86062728E-03	-1.02423922E-06	1.64463139E-10	-9.77943616E-15	2					
1.14004149E+04	3.87180712E+00	3.33656431E+00	2.67682939E-03	5.61801303E-07	3					
-1.11362279E-09	2.84076438E-13	1.16664200E+04	6.71330606E+00		4					
NO2	J 9/64N	1O	2	0	0G	300.000	5000.000	1502.000	01	
5.25702679E+00	1.59120496E-03	-5.75149303E-07	9.26518589E-11	-5.51558940E-15	2					
1.98171367E+03	-2.31252539E+00	2.83832558E+00	6.42094110E-03	-3.71675448E-06	3					
7.13464440E-10	2.36187798E-14	2.88065438E+03	1.09303839E+01		4					
NNH	Melius93N	2H	1	0	0G	300.000	5000.000	1571.000	01	
4.16742317E+00	2.46673021E-03	-8.65307320E-07	1.36642746E-10	-8.02228303E-15	2					
2.83839159E+04	2.06116000E+00	3.73530535E+00	1.00340348E-03	3.26619841E-06	3					
-2.89569645E-09	6.96522384E-13	2.87981268E+04	5.28804396E+00		4					
N2O	J12/64N	2O	1	0	0G	300.000	5000.000	1389.000	01	
5.34204014E+00	1.90604176E-03	-6.74838906E-07	1.07237509E-10	-6.32392655E-15	2					
7.86113134E+03	-5.23705883E+00	2.69094434E+00	8.36738233E-03	-6.74046569E-06	3					
2.71424228E-09	-4.38174973E-13	8.74933506E+03	8.89673234E+00		4					
NH3	J 9/65N	1H	3	0	0G	300.000	5000.000	1389.000	01	
2.97970284E+00	5.36649578E-03	-1.72269060E-06	2.55767504E-10	-1.43684720E-14	2					
-6.74869189E+03	4.46279267E+00	3.24695599E+00	3.11219422E-03	1.94311272E-06	3					
-1.94660247E-09	4.40577561E-13	-6.64082103E+03	3.66779173E+00		4					
H2NO	M/JB86	N	1H	2O	1	0G	300.000	5000.000	1398.000	01

4.26222939E+00	4.60071183E-03	-1.52686779E-06	2.32081624E-10	-1.32607907E-14	2					
6.26937941E+03	1.89523882E+00	2.62132814E+00	8.05594293E-03	-4.34199752E-06	3					
1.31067689E-09	-1.79413169E-13	6.89825870E+03	1.08768221E+01		4					
HONO	NBS	N	1H	10	2	OG	300.000	5000.000	1377.000	11
6.11754445E+00	3.00786121E-03	-1.06923897E-06	1.70344657E-10	-1.00625644E-14	2					
-1.17949476E+04	-6.16262788E+00	2.75201621E+00	1.05958045E-02	-7.62288678E-06	3					
2.77356136E-09	-4.14321183E-13	-1.05902472E+04	1.20246757E+01		4					
N2H2	J12/65N	2H	2	0	OG	300.000	5000.000	1391.000	01	
4.17789510E+00	4.56480666E-03	-1.41875536E-06	2.10366577E-10	-1.19629007E-14	2					
2.33992310E+04	4.99620907E-01	1.86991331E+00	9.88823409E-03	-6.18682259E-06	3					
2.19505186E-09	-3.35933023E-13	2.42170286E+04	1.29348918E+01		4					
N2H3	J12/65N	2H	3	0	OG	300.000	5000.000	1408.000	01	
5.17455613E+00	6.20839945E-03	-2.04623019E-06	3.09591864E-10	-1.76333264E-14	2					
2.19580913E+04	-4.69414951E+00	1.55383758E+00	1.53873331E-02	-1.11813107E-05	3					
4.51731686E-09	-7.65249835E-13	2.31503729E+04	1.45063790E+01		4					
N2H4	J12/65N	2H	4	0	OG	300.000	5000.000	1399.000	11	
6.51535328E+00	7.45035248E-03	-2.52984543E-06	3.90697765E-10	-2.25791189E-14	2					
8.55432595E+03	-1.19149920E+01	8.18811840E-01	2.28521917E-02	-1.91832580E-05	3					
8.76414899E-09	-1.63696490E-12	1.03626512E+04	1.80013590E+01		4					
AR	L	5/66AR	1	0	0	OG	300.000	5000.000	1000.000	01
2.50104420E+00	0.00000000E+00	0.00000000E+00	0.00000000E+00	0.00000000E+00	2					
-7.45686328E+02	4.36103010E+00	2.50104420E+00	0.00000000E+00	0.00000000E+00	3					
0.00000000E+00	0.00000000E+00	-7.45686328E+02	4.36103010E+00		4					
NO3	121286N	10	3	G	0300.00	5000.00	1000.00	1		
0.07120307E+02	0.03246228E-01	-0.14316134E-05	0.02797053E-08	-0.02013007E-12	2					
0.05864479E+05	-0.12137301E+02	0.12210763E+01	0.01878797E+00	-0.13443212E-04	3					
0.12746013E-08	0.13540601E-11	0.07473144E+05	0.01840202E+03		4					

## B.2. Species Containing Na

NAO2	D=37.2NA	10	2	0	G	300.000	2000.000	1000.00	1	
.24373729D+01	.11708054D-01	-.12465450D-04	.60394798D-08	-.10877028D-11	2					
-.68349080D+04	.15175355D+02	.24373729D+01	.11708054D-01	-.12465450D-04	3					
.60394798D-08	-.10877028D-11	-.68349080D+04	.15175355D+02		4					
NAOH	J12/70NA	10	1H	100	OG	300.000	2000.000	1000.00	1	
.45711116D+01	.61346093D-02	-.76237353D-05	.43706135D-08	-.89064713D-12	2					
-.25359026D+05	-.95321963D-01	.45711116D+01	.61346093D-02	-.76237353D-05	3					
.43706135D-08	-.89064713D-12	-.25359026D+05	-.95321963D-01		4					
NA	L	4/93NA	100	000	000	OG	300.000	2000.000	1000.00	1
.25010442D+01	.00000000D+00	.00000000D+00	.00000000D+00	.00000000D+00	2					
.12157060D+05	.42385793D+01	.25010442D+01	.00000000D+00	.00000000D+00	3					
.00000000D+00	.00000000D+00	.12157060D+05	.42385793D+01		4					
NAO	J12/67NA	10	100	000	OG	300.000	2000.000	1000.00	1	
.36192660D+01	.29441938D-02	-.35206654D-05	.18827273D-08	-.36198896D-12	2					
.88821327D+04	.62033018D+01	.36192660D+01	.29441938D-02	-.35206654D-05	3					
.18827273D-08	-.36198896D-12	.88821327D+04	.62033018D+01		4					

## **Appendix C. Reburning vs. Cofiring Evaluation**

**[DOE Task 6]**

Attached is the Final Report of the Antares Subcontract. This report compares the economics of biomass reburning and biomass cofiring (DOE Task 6, Reburning vs. Cofiring Evaluation).

**Pre-feasibility Study of Reburn Options  
for Dunkirk Power Plant**

**Prepared for:**

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### REFERENCES

## EXECUTIVE SUMMARY

Existing legislation and pending regulations are applying considerable pressure on power generators to reduce air born emissions. This includes NO<sub>x</sub> which has emerged as a very hot issue especially in New York where Ozone transport issues are being highlighted by recent gubernatorial rhetoric. The net effect is that coal-fueled power plants are looking for technologies that will help them comply with a varying landscape of emission limitations. Reburn is emerging as a choice with considerable technical and economic merit especially if a low cost reburn fuel can be used. Given Dunkirk station's ongoing retrofit to cofire biomass fuels, this technology should be of special interest.

The reburning process is accomplished by routing part of the boiler's fuel, approximately 10-20%, to a point above the primary combustion zone. When properly designed and implemented, this technology can offer significant reductions in boiler NO<sub>x</sub> emissions (up to 85%).

Reburn fuels demonstrated on a utility scale include natural gas, coal, and orimulsion. Other fuels, including biomass have been demonstrated as effective for reburn on a pilot scale.

Biomass is an attractive choice for several reasons. It is a renewable fuel, low in sulfur, and can be obtained at a significant discount to coal or other fossil fuels. In addition, pilot scale reburn tests have indicated that under certain conditions it can outperform other fuels (including natural gas) in providing NO<sub>x</sub> reductions.

Beyond its potential for low cost, biomass may have other economic benefits. Several legislative initiatives have been undertaken to allow power providers using biomass as fuel to earn tax credits. In addition, green power markets may add value to power generated renewably, adding even more incentive for biomass-based generation.

The results of the economic analysis suggest that biomass reburn is economically attractive and can provide deep NO<sub>x</sub> control at while adding value to the plant's bottom line. The results also suggest that biomass reburn could be more economically attractive than biomass cofiring.

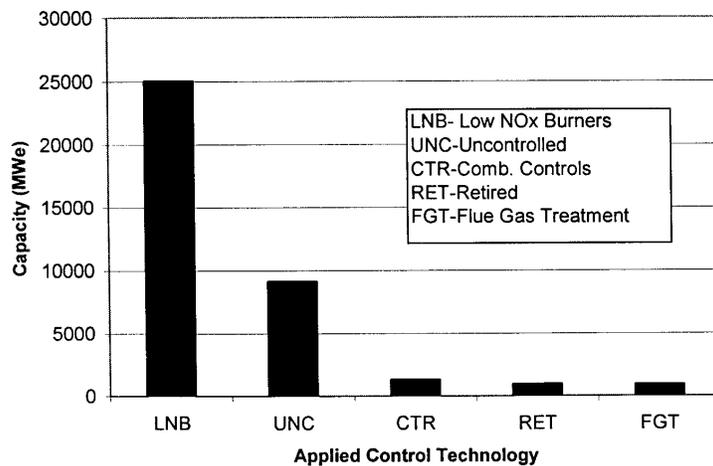
Based on the research and analysis documented in this report, Dunkirk Station is well positioned to capitalize on the opportunities presented by biomass reburn technology. The plant is already undergoing retrofits to cofire biomass, and much of the equipment needed to explore reburn is already on-site. Certainly, more in-depth analysis is required, but a biomass reburn demonstration project at Dunkirk should be seriously considered by the plant's management. The approach for a demonstration would include confirming NO<sub>x</sub> reductions experienced under current plans to cofire, detailed planning of retrofit requirements, and implementation of a testing protocol.

**1.0 INTRODUCTION**

Recently, many strategies have been adopted within the Ozone Transport Region (OTR) to meet the Clean Air Act (CAA) Title I and Title IV Phase II compliance orders. These technologies include low-NO<sub>x</sub> burners, flue gas treatment, selective catalytic and non-catalytic reduction, combustion controls, and repowering. Exhibit 1-1 outlines the application of these technologies for coal-fired boilers in the OTR. Low-NO<sub>x</sub> burners are unquestionably the most popular choice. Using this technology NO<sub>x</sub> can be reduced approximately 30-50% below uncontrolled emissions levels.

However, natural gas reburn is emerging as an important technologies for NO<sub>x</sub> reduction. Originally designed for cyclone boilers, reburn technologies is being applied to an expanding range of boilers including stokers and utility pulverized-coal units. Developers of reburn technology have received substantial assistance to demonstrate reburn systems at various energy production sites through the Clean Coal Technology Demonstration Program sponsored by the U.S. Department of Energy (DOE).

**Exhibit 1-1:**  
OTR Utility Coal-Fired Boiler  
Capacity by Applied Control Technology



*Taken from Status Report on NO<sub>x</sub> Control Technologies and Cost Effectiveness for Utility Boilers, NESCAUM, June 98.*

Reburning technology uses hydrocarbon radicals to convert nitric oxide (NO) to nitrogen (N<sub>2</sub>) and carbon monoxide (CO). In the boiler's primary combustion region, fuel is burned with lower than usual excess air. The reburning process is accomplished by routing part of the boiler's fuel, approximately 10-20%, to a point above the primary combustion zone, where it is injected to produce a slightly fuel-rich "reburn zone." The remaining combustion air is then injected to ensure that

all the reburn fuel and other combustibles completely burn out. In order to obtain the best results for NO<sub>x</sub> reduction, injection of the reburn fuel should be able to penetrate completely across the furnace and mix thoroughly with furnace gases. Reductions in NO<sub>x</sub> without the use of an injected reagent (advanced reburn) typically range between 58-77%.

As noted previously, low-NO<sub>x</sub> burners are the major retrofit used to comply with Phase I, Title IV obligations of the CAA Amendments of 1990. Although reburn technology can be applied to boilers already outfitted with low-NO<sub>x</sub> burners, it can also be applied to boilers that are not able to use standard low-NO<sub>x</sub> combustion modification techniques because of the need for high furnace temperatures - such as wet bottom boilers.

Currently, natural gas is the preferred reburn fuel because, in general, it generates the greatest NO<sub>x</sub> reduction per heat unit of injected fuel. Natural gas also produces negligible quantities of ash and sulfur, and requires no preparation. Micronized coal has also been used as a reburn fuel at some power facilities either by itself or blended with biomass. Micronized biomass, the focus of this report, is also being explored and tested as a reburn fuel on a pilot scale.

This report focuses on evaluating the economic feasibility of using micronized biomass as a reburn fuel at a tangentially fired pulverized coal facility like Dunkirk Steam Station. Reburn and advanced reburn options are discussed. Technical and economic performance data are based on information provided by the reburn project team. Specifically, Niagara Mohawk provided data on Dunkirk Station operations and cofiring retrofit costs; EER and the Federal Energy Technology Center (FETC) in Pittsburgh provided reburn performance data, MESA Reduction Engineering and Processing – a developer of biomass processing technologies – provided costs and performance data on micronizing biomass.

## **2.0 PILOT STUDY AND PRELIMINARY DATA**

### **2.1 Description of Reburn and Advanced Reburn Systems**

Low-NO<sub>x</sub> burners have dominated as the technology of choice for power plant operators to meet the Phase-I, Title IV NO<sub>x</sub> requirements of the Clean Air Act Amendments. However, the looming deadline for Phase-II/III reductions and the failure of low-NO<sub>x</sub> burners to live up to performance expectations at some sites has forced plant operators to look elsewhere. Reburn technologies are emerging as the potentially lowest cost choice for NO<sub>x</sub> controls in boilers with emission levels less than 0.6 lb/MMBtu. These technologies offer substantial NO<sub>x</sub> reductions (potentially in excess of 85% using advanced reburn) and can even help boilers with other underperforming NO<sub>x</sub> control technologies.

#### **2.1.1 *Reburn Systems***

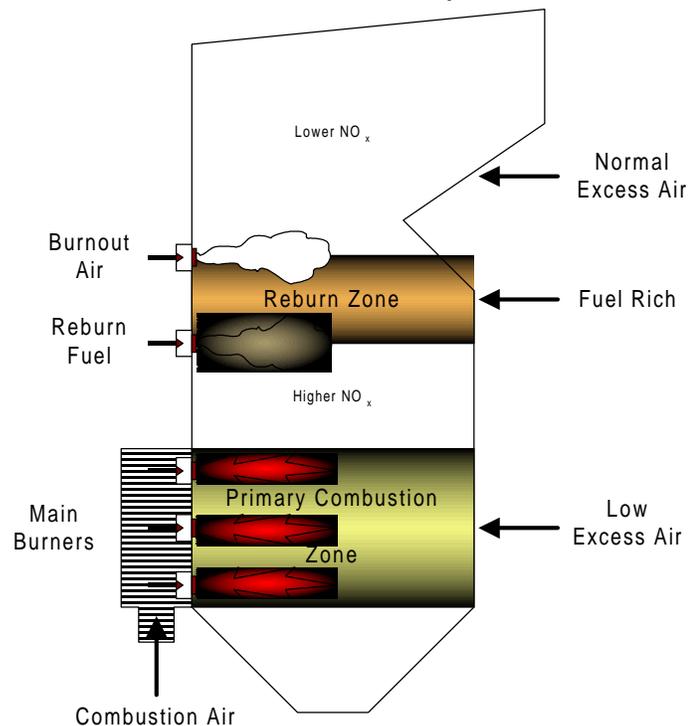
Exhibit 2-1 shows a schematic of a conventional reburn system. In the lower primary combustion zone, the main fuel (coal for the purposes of this report) is burned with lower than usual excess air. Combustion by-products including NO<sub>x</sub>, then move to the reburn zone. In the reburn zone, a hydrocarbon fuel is injected to produce a slightly fuel-rich mixture. In the upper part of the boiler, overfire air is added to ensure complete burnout of the reburn fuel and other combustibles. Reductions in NO<sub>x</sub> using conventional reburning technologies typically range between 58-77%.

No physical change to the main burners is required, but the burners are typically operated at the lowest excess air that maintains flame stability and with acceptable carbon losses, slag tapping, and ash deposition. Maximum NO<sub>x</sub> reduction is usually achieved with the reburn zone operating in the range of 90% theoretical air.

For best results, the reburn fuel injectors should be located close to the upper firing elevation to allow enough space above the main burners to complete the primary combustion process. The reburn fuel injectors are designed for rapid mixing and to allow the fuel to penetrate across the boiler depth.

The reburn fuel can be any hydrocarbon and site-specific economics will dictate the best choice. Natural gas, oil, micronized coal, orimulsion, and micronized biomass have all been shown to be effective reburn fuels. However, natural gas remains the preferred fuel for several reasons including: 1) it produces the greatest  $\text{NO}_x$  reduction per heat unit of injected fuel over the greatest range of heat input; 2) it has no ash or sulfur; and 3) it requires no fuel preparation. However, on a \$/MMBtu basis, natural gas remains a premium fuel.

**Exhibit 2-1: Reburn System**



Significant savings in fuel costs are part of the attraction that biomass fuels may offer to power plants pursuing biomass reburn. Biomass supplies can be obtained at prices as low as \$0.50/MMBtu, or about a fifth of the delivered cost of natural gas. Some additional processing will be required in most cases, but this provides the potential for substantial savings in fuel costs. Additionally, relative to natural gas, biomass may also offer some  $\text{NO}_x$  reduction benefits at lower heat input percentages. This advantage is discussed further in section 2.2.

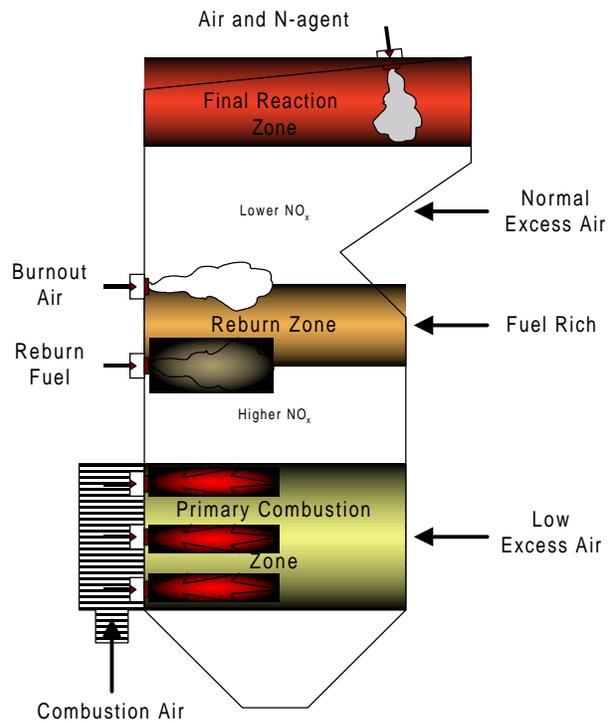
### 2.1.2 Advanced Reburn Systems

Exhibit 2-2 shows a schematic of an advanced reburn configuration. The advanced reburn (AR) option uses a nitrogen-rich compound or N-agent to provide even more  $\text{NO}_x$  control than conventional reburn systems. To date, most of the advanced reburn research has focused on using natural gas as the reburn fuel. Provided that demonstrations of biomass reburn technologies are successful, advanced reburn technologies may be pursued for this feedstock as well.

There are two approaches to advanced reburn configuration in coal boilers; synergistic and non-synergistic. For non-synergistic configurations, the N-agent is added downstream of the reburn system. This essentially represents a combination of reburn and selective non-catalytic reduction. For these configurations NO<sub>x</sub> reductions are expected to be on the order of 56-70% for a 10% heat input of natural gas.

For synergistic advanced reburn configurations, the N-agent is injected with the overfire air above the reburn zone. In this case combustion dynamics are customized to provide NO<sub>x</sub> control of up to 85% for 10% heat input of natural gas. Although limited in application by some boiler configurations, this approach allows greater flexibility in flue gas temperature resulting in better load following characteristics.

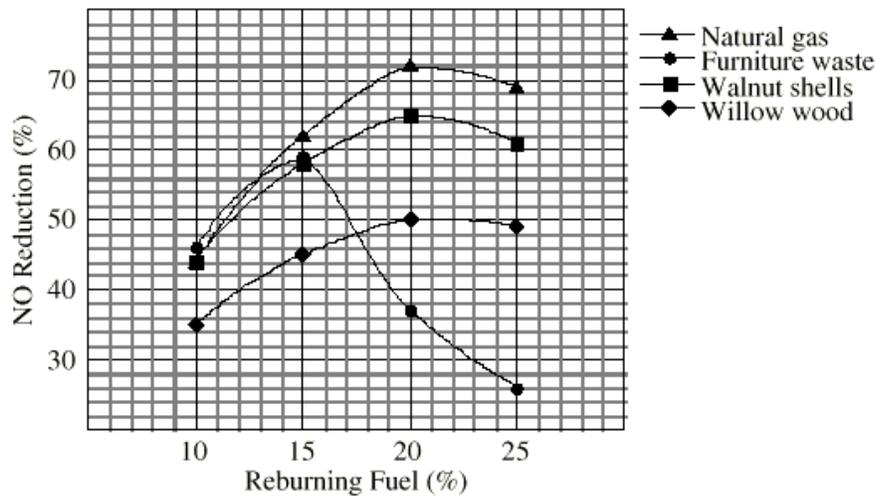
**Exhibit 2-2: Advanced Reburn System**



**2.2 Results of EER Biomass Reburn Studies**

Energy and Environmental Research Corporation (EER) has initiated a Small Business Innovation Research (SBIR) multi-phase development and demonstration program, funded by the U.S. Department of Agriculture. Phase-I of the program involved feasibility studies on

**EXHIBIT 2-3: Pilot Scale Reburn Test Results**



reburning and advanced reburning technologies using biomass as the reburn fuel. EER has also completed Phase-II of the program, which involved further development and optimization of these technologies. Results from pilot-scale demonstrations have been very promising.

For example, pilot-scale experimental testing has shown that furniture waste can yield comparable NO<sub>x</sub> reduction performance to natural gas at reburn heat input rates up to 15%. Exhibit 2-3 shows some of these results for biomass reburn. This is a significant development since biomass can often be obtained much less expensively than natural gas. EER has also developed an advanced biomass reburning technology that utilizes additives and has achieved 70-90% NO<sub>x</sub> control in pilot scale experiments.

### 2.3 List of EER Reburn Projects

GE/EER will have completed 10 reburn projects by the Fall of 1999. A list of projects is shown in Exhibit 2-4. The choice of reburn fuel for these projects has depended on site specific conditions and includes, coal, orimulsion, and natural gas. Although GE/EER is not the only vendor for reburn technologies retrofits, this list is sufficient to demonstrate the interest and the power sector's commitment in this technology.

**Exhibit 2-4:** List of GE/EER Reburn Projects

Utility Name	Plant	(MWe)	Configuration	Status
Illinois Power	Hennepin 1	71	Tan	Complete
City Water, Light & Power	Lakeside 7	33	Cyc	Complete
P.S. Company of Colorado	Cherokee 3	158	FW	Complete
New York State E&G	Greenidge 4	104	Tan	Complete
Ukraine	Ladyzhin	300	Opp	Complete
Eastman Kodak	Kodak Park 15	50	Cyc	Complete
Tennessee Valley Authority	Allen 1	330	Cyc	Complete
Baltimore Gas & Electric	Crane 1	205	Cyc	Complete
Baltimore Gas & Electric	Crane 2	205	Cyc	Complete
Conectiv	Edge Moor 4	160	Tan	Complete
Tennessee Valley Authority	Allen 2	330	Cyc	Summer '99
Tennessee Valley Authority	Allen 3	330	Cyc	Install Fall '99
Allegheny Power	Hatfield 2	595	Opp	Install Fall '99
Potomac Electric	Chalk Point 1	355	Opp	Install Spring '00
Potomac Electric	Chalk Point 2	355	Opp	Install Spring '00

### 3.0 DESCRIPTION OF MODELED SYSTEM

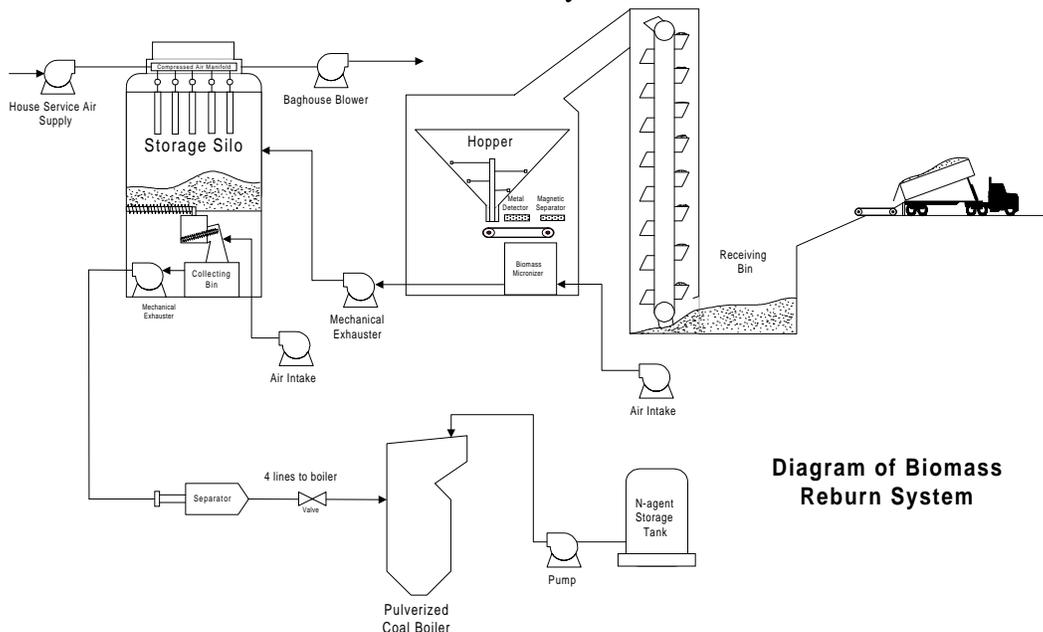
Dunkirk Station, a pulverized coal plant representative of the target market for reburn, is equipped with two 200 MW and two 100 MW Combustion Engineering tangentially fired boilers, circa 1950. The later units (Unit #1, #2) currently burn eastern bituminous coals and have been retrofitted with low-NO<sub>x</sub> burners and upgraded combustion control systems. Unit #1 has 16 burners located at four levels in the corners of the furnace. Coal is supplied to each level by a Raymond bowl mill and the unit has been retrofitted with a low-NO<sub>x</sub> burner system which incorporates a close-coupled overfire air system. This unit is currently undergoing retrofits to cofire biomass at heat input rates of up to 20 percent. Besides the addition of biomass handling and processing equipment, the boiler has already been modified to inject processed biomass through ports located between the second- and third-level coal nozzles.

Since Dunkirk Station is already undergoing retrofit for biomass combustion, the modifications required to use biomass as a reburn fuel are minimal. Newly installed receiving, primary handling, processing, and storage facilities are all adequate to handle the material for a reburn application. Modifications required beyond those considered for the cofiring retrofit will include:

- 1) Use of biomass micronizing equipment for secondary processing
- 2) Change in biomass flow for delivery to the boiler
- 3) Addition of injection ports in reburn zone
- 4) Urea injection and storage - *Advanced Reburn Option*

Exhibit 3-1 shows a possible configuration for conducting reburn and advanced reburn operations at Dunkirk.

**Exhibit 3-1: Reburn System Schematic**



**Diagram of Biomass Reburn System**

Although a substantial portion of Dunkirk's biomass processing train is useable in reburn application there are some fuel sizing requirements that need to be addressed. The current cofiring system is designed for a final biomass fuel particle sizes of 1/8" minus. This will allow complete burnout of the fuel when introduced into the boiler's primary combustion zone. However, based on discussions with various combustion and processing experts, a particle size of 1/16" minus may be required for reburn applications. Larger particle sizes may be acceptable, but this aspect of biomass reburn can only be quantified in full scale tests.

## **4.0 ECONOMIC MODEL**

As part of its efforts to evaluate renewable energy technologies, ANTARES has developed a number of specialized models. These include models for determining the economic and technical feasibility of different cofiring and reburn technologies. The model used in this efforts is composed of two main modules: power plant performance; and financial performance.

### **4.1 Model Description**

#### ***4.1.1 Power Plant Performance Module***

This module uses inputs based on typical values for utility-scale power plant operations to estimate net plant generation, emissions, and fuel requirements. Input parameters include gross plant power output, parasitic loads, gross plant efficiency, cofiring/reburn heat input, emissions profiles (lb/MMBtu), and operating schedules. These parameters are also used to estimate the required equipment sizes and staffing requirements. For this effort, many of the input parameters have been tailored to model the performance of Dunkirk Station while using biomass reburn.

#### ***4.1.2 Financial Performance Module***

This part of the model is used to calculate the production cost effects of cofiring/reburning based on the plant performance results. Inputs include the delivered cost of fuels (biomass and coal); the value of emission credits; tax incentives, green marketing incentives; and capital costs. The output of the module is the production cost effect on the plant for cofiring/reburning.

### **4.2 Key Input Data**

Input data used in the analysis was collected from the project partners. This included estimates of retrofit costs, boiler performance data, increased O&M data, and pilot- scale NO<sub>x</sub> reduction data.

#### ***4.2.1 Retrofit Costs***

Retrofit costs were based on estimates provided by Niagara Mohawk for biomass handling/processing equipment that is being secured to retrofit the station for cofiring. These requirements have been scaled, where appropriate, to accommodate the different heat input levels

for biomass reburn. Costs that are exclusive to the reburn or advanced reburn systems modeled were derived from estimates provided by EER. These included urea storage and injection system costs.

Specialty processing equipment (biomass micronizing train) costs were provided by an outside vendor. There are several vendors of such technology and most are similar to those used to finely process coal. Mesa Reduction Engineering and Processing has developed a milling technology that has been designed and tested on biomass feedstocks. For this reason, the specifications of this equipment have been used for this analysis. This technology reportedly has the ability to process incoming biomass feedstocks to the appropriate parameters in one pass, rather than requiring multiple hammer mills and feedback loops for oversized material. However, before specifying equipment for project deployment, additional analysis to determine the most economic deployment of processing technologies should be performed.

Although much of the handling equipment for retrofitting Dunkirk is already purchased, this report compares the economics of cofiring, reburn, and advanced reburn on a turnkey basis and all prior investments in equipment and installation are included.

#### 4.2.2 *Changes in Plant Efficiency*

Plant heat rate increases have been experienced in cofiring operations and they are an inevitable cost associated with new processing and handling systems. Based on past, published experiences with biomass cofiring systems, the boiler is also expected to experience a slight decrease in efficiency due to the high moisture content of biomass.

#### *Parasitic Load Changes*

Based on ANTARES estimates using data supplied by the plant and equipment vendors, a net increase in plant parasitic load of 180-530 kW will be experienced as a result of the cofiring/reburn retrofits relative to coal-only operations. A summary of these changes is presented below in Exhibit 4-1.

**Exhibit 4-1: Increase Plant in Parasitic Load**

Load Source	Load Change (kW)		
	Cofiring	Reburn	Adv. Reburn
Coal Processing	(354)	(354)	(354)
Biomass Processing	<u>537</u>	<u>737</u>	<u>881</u>
<i>Net Parasitic Load Change</i>	<i>183</i>	<i>383</i>	<i>527</i>

### *Changes in Boiler Efficiency*

The plant is also likely to experience a slight decrement in boiler efficiency because biomass has a higher moisture content than coal. This loss, although difficult to measure, is estimated in this analysis to reduce boiler efficiency 1.13% from (88.8% to 87.7%.) This decrement is based on estimates derived from an independent biomass power model developed by EPRI. This decrement assumes that biomass provides 15% of the heat input into the boiler.

### **4.2.3 Operation and Maintenance Costs (excluding fuel)**

The additional operation and maintenance costs associated with the biomass reburn retrofit consist of maintenance on new equipment, additional operating personnel, and for the advanced reburn case, urea injection.

Repairs and maintenance for new equipment is estimated to be 5 percent of the investment cost per year. This figure is for engineering estimates only and may need to be revised based on the system's performance.

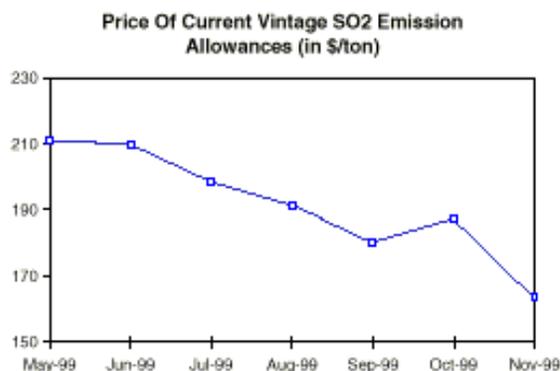
The requirement for additional operating personnel to oversee receipt, processing, and injection of biomass at a coal-fired station is still a subject of debate. It has been suggested that these responsibilities could be delegated to current plant personnel. However, it was the opinion of various biomass handling experts and the ANTARES group that one additional operator would be required to oversee these functions adequately and ensure steady operation.

Urea requirements for the advanced reburn option were estimated based on a study commissioned by the EPA to study NO<sub>x</sub> control technologies for the Northeast and Mid-Atlantic regions of the United States. This data, where possible, was cross referenced with information provided by GE/EER. Based on these sources, urea is estimated to cost \$385/ton. Urea usage is estimated based on a Normalized Stoichiometric Ratio (NSR) of 1.5. This factor describes the amount of urea required relative to the amount of NO<sub>x</sub> reduction experienced<sup>1</sup>.

### **4.2.4 Emissions Reductions and Value**

#### *SO<sub>2</sub> Benefits*

Title IV of the 1990 Clean Air Act Amendments (CAAA) established marketable SO<sub>2</sub> allowances or credits, each equivalent to one ton of SO<sub>2</sub>. Exhibit 4-2 shows recent activity in this market as reported by Fieldston Publications.



**Exhibit 4-2**

Fieldston Publications, *Clean Air Compliance Review*, 12/1/99

<sup>1</sup> Reagent utilization is very difficult to generalize and 1.5 represents a rule of thumb. A more rigorous analysis is required before an SNCR system is installed.

The value of SO<sub>2</sub> allowances has an important impact on the economics of biomass reburn, since most biomass sources contain only small amounts of sulfur even when compared to low-sulfur coals. This means that Btu for Btu, biomass fuels avoid nearly 100% of the SO<sub>2</sub> that would have been emitted by coal combustion. For the purposes of this analysis, SO<sub>2</sub> allowances have been assigned a value of \$150/ton over the life of the project.

#### *NO<sub>x</sub> Benefits*

Based on guidelines provided in the CAAA, Congress established the Ozone Transport Commission (OTC) to address the region-wide transport of ozone and its precursor gases including NO<sub>x</sub>. Early in 1999 the OTC announced the beginning of a new emission trading program for NO<sub>x</sub>. This cap and trade system allows purchasers to buy offsets, and deals on NO<sub>x</sub> reductions have already been negotiated. Exhibit 4-3 lists recent OTC price trends for NO<sub>x</sub> credits.

**Exhibit 4-3:** Estimate of OTC NO<sub>x</sub> allowance prices

Vintage	Price (\$/ton)
1999	\$1,700
2000	\$2,200
2001	\$2,100
2002	\$1,800

*July 1999 Price Index - Air Daily, Fieldston Publications, Vol 6, No. 136*

The value of NO<sub>x</sub> credits is very important to calculating the economic benefits of biomass reburn. For this analysis, a price of \$1,700/ton has been assigned to NO<sub>x</sub> credits over the life of the project. Credits are generated only during the ozone season per CAAA Title I requirements. However, based on provisions in Title IV, it is also possible that in the future NO<sub>x</sub> credits could be generated during the Non-Ozone season. Recent evidence of this can be found in Governor Pataki's (NY) announcement that he intends to order New York power plants to cut their annual of NO<sub>x</sub> emissions levels to the levels slated for summer only in 2003. As part of this plan, SO<sub>2</sub> emission levels would be cut to less than half of the federal requirements.

#### *CO<sub>2</sub> Benefits*

Although examples are few, carbon has been traded internally within large companies and externally among a few innovators. Values range from \$1.20 to \$15.00 per ton of carbon dioxide emitted, indicative of the instability of an infant market. However, because an official policy driver does not exist for CO<sub>2</sub> reductions at this time, this analysis does not assign any value to carbon emission reductions resulting from substituting biomass for coal.

#### **4.2.5 Ash Sales and Disposal costs**

Cofiring biomass and coal may also adversely affect existing revenue streams from coal ash sales. The ASTM standard for flyash sales (ASTM C 618) restricts the use of coal-and-biomass derived ash sales. In this analysis, it was assumed that 70% of the ash generated from baseline coal operations is sold into markets with an average ash value of \$2.00/ton (this figure is typical of current ash markets). By introducing biomass into the fuel mix it was assumed that this entire revenue stream is converted to a liability of \$10.00/ton. This is probably a conservative assumption since many coal-fired generators using mixed fuels have reported finding alternative markets for their ash. This assumption has been used in all of the cases evaluated.

#### **4.2.6 Biomass Production Tax Credit**

Section 45 of the 1986 Internal Revenue Code allows an inflation adjusted tax credit of 1.7 cents per kWh for renewable electricity production for closed-loop biomass (energy crops) facilities.<sup>2</sup> In order to qualify, the facility must be owned by the taxpayer and have been originally placed in service after December 31, 1992 and before July 1, 1999. The 1.7 cent credit received by a qualified closed-loop biomass facility may be reduced if that facility uses grants, tax-exempt bonds, subsidized energy financing, or other tax credits.

To date, no biomass facility has been able to take advantage of this credit because of its narrow definition for biomass. As a result, several new pieces of Federal legislation were introduced to modify the current law and attempt to provide a practical incentive for increasing biomass power capacity in the United States. Although too numerous to explore in depth in this report, many "opened the loop" to include biomass residues and provided a credit for electricity generated through biomass cofiring. Only the portion of the electricity generated via biomass heat input is eligible. For comparative purposes, this report presents cases that include and exclude a 1.7 c/kWh tax credit.

### **4.3 Modeling Results**

#### **4.3.1 Summary of Inputs**

Exhibit 4-4 summarizes the key inputs for this analysis. For all cases, common input assumptions include:

- gross plant electric output of 96 MW
- gross plant efficiency (coal only) of 36%
- plant capacity factor of 72%
- plant operating 24 hours/day, 7 days/week
- cofiring/reburning fuel on 24 hours/day, 7 days/week
- biomass delivery 10 hours/day, 5 days/week
- coal is eastern bituminous, HHV of 12,997 Btu/lb, \$1.37/MMBtu

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<sup>2</sup>The code also provides a tax credit for wind facilities but only the biomass portion is treated in this report.

- biomass is mill waste, HHV of 7,359 Btu/lb, \$0.75/MMBtu
- biomass heat input is 15%
- baseline plant emissions (lb/MMBtu) are 3.66 for SO<sub>2</sub>, 0.42 for NO<sub>x</sub>, 238 for CO<sub>2</sub>
- 70% of ash generated currently sold @ \$2.00/ton
- disposal cost of ash \$10.00/ton
- cofiring/reburn cases assume an additional operator is required to manage biomass system at a fully loaded rate of \$17.00/hour. Time in excess of 2,000 hours/year is charged at \$25.50/hour
- ozone transport season is 5 months long
- emission credit values (\$/ton): NO<sub>x</sub> (\$1,700), SO<sub>2</sub> (\$150), CO<sub>2</sub> (None)
- CO<sub>2</sub> emission reductions assume that biomass is CO<sub>2</sub> neutral.

**Exhibit 4-4: Summary of Input Variables**

<b>Case Input Variable</b>	<b>Cofiring</b>	<b>Reburn</b>	<b>Adv. Reburn</b>
\$/kW-biomass	\$244	\$362	\$404
\$/kW-total plant	\$34	\$51	\$56
Net Plant Heat Rate	10,285	10,308	10,325
NO <sub>x</sub> Reduction (%)	8%	59%	83%
Reagent (tons/year)	0	0	430
Incr. O&M (\$/year)	\$196,079	\$241,584	\$428,869

#### **4.3.2 Discussion of Analytical Methods**

Results of this analysis could be presented on two different bases. These viewpoints reflect differences in the way power providers are evaluating operational cost improvements and emission control technology options.

Cofiring is primarily a fuel cost reduction strategy. The benefits of cofiring are primarily measured based on the incremental benefit the plant experiences by substituting a lower cost fuel for coal. Ancillary benefits like emission credits are usually rolled into the incremental economics by assuming that either new credits will be generated or by assuming the plant will have a reduced requirement to purchase credits. The sum of these benefits less new liabilities (e.g. increased O&M, decreased ash sales) is used to calculate a return on the retrofit investment.

This type of analysis is very useful for considering cofiring opportunities against other operational improvements which use "business as usual" as the baseline. However, since it does not consider the need for plants to meet current or future environmental regulations it is not as useful in comparing technologies targeted toward deep emission controls.

In contrast, reburn technology is usually viewed as an emission control strategy. Therefore, its

benefits are expressed in terms of the investment required to move from a baseline NO<sub>x</sub> emission level to a new, lower NO<sub>x</sub> emission level. Since reburn applications often use natural gas, a premium fuel, there are no fuel cost savings to offset the investment<sup>3</sup>. The result is a net cost/ton of NO<sub>x</sub> removed. This number can readily be compared to other NO<sub>x</sub> control technology choices such as SCR. However, when using a discounted fuel such as biomass, a positive incremental benefit may be experienced and the net cost/ton of NO<sub>x</sub> removed can be a negative number.

Since the goal of this analysis is to compare biomass cofiring and reburn options (admittedly an apples and oranges comparison) a new comparison criterion was developed. Instead of comparing the benefits of cofiring and reburn on an incremental emissions benefit basis, an absolute basis was adopted.

Under this type of comparison, assumptions are made about the regulatory conditions which the plant must meet. These conditions must be obtained either through purchasing emission credits or reducing emissions. The total cost to comply with these regulations are then used as the basis of comparison. This is more representative of how power plant operators will consider their choices in an environment where emission regulations are as much a concern as lowering production costs. An example helps illustrate this point.

A plant operator currently exceeds the Title IV SO<sub>2</sub> emission cap and is purchasing credits from another operator to comply with Federal regulations. He has several options including installing an FGD emissions system which will bring his plant into compliance or biomass cofiring. Although the FGD will cost less, the benefits used to offset the costs of the system are limited to reducing the cost of purchasing SO<sub>2</sub> allowances. On the other hand, a more expensive biomass system will reduce his SO<sub>2</sub> emissions and can reduce fuel costs. However, some allowances will still need to be purchased since cofiring alone will not bring the plant into compliance. Therefore the total cost to comply must be considered. An absolute analysis that considers the regulatory compliance point must be used to determine the most economic option.

An analysis of the retrofit options for Dunkirk was completed using both an incremental and absolute analysis viewpoints. The results of the absolute analysis are presented based on the cost of regulatory compliance (\$/ton of pollutant emitted) and separated among the three air pollutants evaluated. The incremental analysis results are presented using more traditional project finance criteria such as return on investment and payback period.

For reference, both analyses will rely on forecasts regarding current baseline emissions, future compliance points and emission reductions resulting from the application of cofiring and reburn technologies. The cost to achieve reductions or total compliance can then be calculated from the capital and ongoing maintenance requirements for each technology. The results of this analysis are presented below.

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<sup>3</sup> Although NO<sub>x</sub> credits are factored into the equation, the current ozone season does not afford sufficient credits to result in a positive incremental benefit.

4.3.3 Results

Exhibit 4-5 lists the emission reductions benefits estimated in this analysis relative to baseline emission levels. Exhibit 4-6 and 4-7 summarize the results of the absolute economic comparison, while Exhibit 4-8 and 4-9 summarize the incremental economic comparison.

**Exhibit 4-6: Summary of Absolute Analysis without Production Tax Credit**

Case Output Variable	Cofiring	Reburn	Adv. Reburn
<b>Exhibit 4-5: Summary of Emission Reductions (tons)</b>			\$610
	<b>TECHNOLOGY DESCRIPTION</b>		
	<b>Cofiring</b>	<b>Reburn</b>	<b>Adv. Reburn</b>
<b>Baseline Emission Levels - Coal Only</b>			
SO2	10,515	10,515	10,515
NOX	1,200	1,200	1,200
CO2	683,991	683,991	683,991
<b>Maximum Legal Emission Levels</b>			
SO2	3,491	3,491	3,491
NOX	861	861	861
CO2	N/A	N/A	N/A
<b>Required Reductions</b>			
SO2	7,024	7,024	7,024
NOX	340	340	340
CO2	-	-	-
<b>Reductions Achieved</b>			
SO2	1,459	1,459	1,459
NOX	129	708	826
CO2	95,088	95,088	95,088
<b>Reduction Shortfall*</b>			
SO2	5,565	5,565	5,565
NOX	211	(369)	(487)
CO2	(95,088)	(95,088)	(95,088)
<small>*Negative values indicate reductions requirements exceeded N/A - Not applicable for this case</small>			
Cost to control (\$/ton SO <sub>2</sub> ) before tax	\$810	\$654	
Cost to control (\$/ton SO <sub>2</sub> ) after tax	\$501	\$412	\$388
Cost to control (\$/ton NO <sub>x</sub> ) before tax	\$9,171	\$1,347	\$1,078
Cost to control (\$/ton NO <sub>x</sub> ) after tax	\$5,672	\$848	\$684
Cost to control (\$/ton CO <sub>2</sub> ) before tax	\$12	\$10	\$9
Cost to control (\$/ton CO <sub>2</sub> ) after tax	\$8	\$6	\$6

*Cost to control equals the total emissions reduction over the life of the project divided by the total cash flow on a before/after tax basis.*

**Exhibit 4-7: Summary of Absolute Analysis with Production Tax Credit (1.7 c/kWh)**

Case Output Variable	Cofiring	Reburn	Adv. Reburn
Cost to control (\$/ton SO <sub>2</sub> ) before tax	\$810	\$654	\$610

Cost to control (\$/ton SO <sub>2</sub> ) after tax	(\$488)	(\$575)	(\$598)
Cost to control (\$/ton NO <sub>x</sub> ) before tax	\$9,171	\$1,347	\$1,078
Cost to control (\$/ton NO <sub>x</sub> ) after tax	(\$5,518)	(\$1,184)	(\$1,057)
Cost to control (\$/ton CO <sub>2</sub> ) before tax	\$12	\$10	\$9
Cost to control (\$/ton CO <sub>2</sub> ) after tax	(\$7)	(\$9)	(\$9)

*Cost to control equals the total emissions reduction over the life of the project divided by the total cash flow on a before/after tax basis.  
Numbers in "( )" indicate net revenues*

**Exhibit 4-8: Summary of Incremental Analysis without Production Tax Credit**

Case Output Variable	Cofiring	Reburn	Adv. Reburn
Before Tax Annual Revenue Impact	\$631,392	\$964,700	\$1,064,767
Before tax ROR	22%	24%	23%
After tax ROR	17%	17%	17%
Before tax payback period (years)	5.2	5.0	5.1
After tax payback period (years)	5.9	5.7	5.7

**Exhibit 4-9: Summary of Incremental Analysis with Production Tax Credit (1.7 c/kWh)**

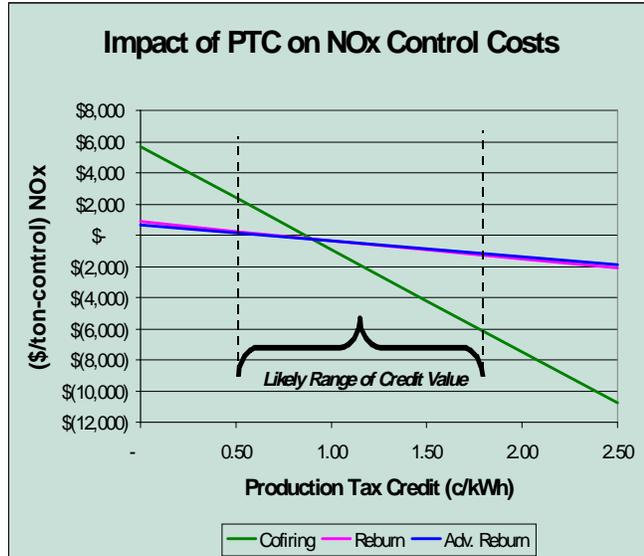
Case Output Variable	Cofiring	Reburn	Adv. Reburn
Before tax ROR	22%	24%	23%
After tax ROR	188%	101%	88%
Before tax payback period (years)	5.2	5.0	5.1
After tax payback period (years)	1.5	1.9	2.1

#### 4.3.4 Discussion of Results

The results of this analysis demonstrate the stark differences between these technologies in their ability to control NO<sub>x</sub> emissions and the corresponding economics. It is apparent from these exhibits that cofiring is not in the same class of NO<sub>x</sub> emission control as reburn. Exhibit 4-5 lists NO<sub>x</sub> reductions for the reburn technologies that are roughly an order of magnitude better than those for the cofiring case. In Exhibit 4-6, the cost to control NO<sub>x</sub> emissions shows a similar result. Although a reburn or advanced reburn technology is more expensive to implement, deeper NO<sub>x</sub> control is obtained. Other emissions benefits remain fairly flat across the cases. Note that the annual reduction of SO<sub>2</sub> and CO<sub>2</sub> emissions is the same for all three cases since biomass was used in the same quantities for all three cases.

Exhibit 4-7 lists the results for the cases that include a renewable production tax credit. Under these circumstances the after-tax value for each scenario was positive which resulted in a negative cost to control. This suggests that the plant can comply with the emission standards used in the analysis and still have a positive cash flow. In the cofiring case, the benefit of this credit is such that it overwhelms any requirement to buy emission allowances to meet regulations. In other words, firing biomass under this tax credit scenario has more value than making the additional investment in reburn technologies to control NO<sub>x</sub> emissions. However, a moderate reduction in the tax credit (PTC) of just a few mills/kWh dramatically changes this result and the reburn cases become the more attractive alternatives for controlling emissions. This is illustrated in Exhibit 4-10. Recently, congress has passed an extension of the existing closed-loop biomass tax credit. The new provision includes poultry litter but would still exclude cofiring and reburn technologies. Although it is very likely that this issues will be addressed again next year, there is significant financial risk in relying on the tax credits for economic justification of a project.

**Exhibit 4-10: PTC v. Control Costs**



Exhibits 4-8 and 4-9 represent an incremental economics analysis. The production cost benefits (lower fuel costs and emission credits) are used to offset the investment in the capital equipment. The results of this analysis are consistent with those shown in the absolute analysis. The scenarios without tax credits favor the reburn technologies, while the tax credit cases favor a combination of cofiring and purchasing emission allowances. However, the real value in presenting these cases is to point out a fundamental difference between biomass and natural gas reburn options. This analysis suggests that biomass reburn can pay for itself while providing deep NO<sub>x</sub> control. Although a detailed analysis of natural gas reburn options was not performed, a sample economic analysis provides a useful baseline.

Price of natural gas -	\$2.76/MMBtu
<u>Price of coal -</u>	<u>\$1.37/MMBtu</u>
Price differential -	\$1.39/MMBtu

NO <sub>x</sub> allowances	\$1,700/ton
SO <sub>x</sub> allowances	\$150/ton

Heat rate -	10,000 Btu/kWh
Natural gas cofire rate -	15%
Capacity factor -	72% <i>during ozone season</i>
NO <sub>x</sub> reductions (tons/ozone season) -	295
SO <sub>2</sub> reductions -	608

Annual increase in fuel cost -	\$0.53M <i>assumes natural gas used only during ozone season</i>
<u>Value of annual emissions offset -</u>	<u>\$0.59M</u>
<b><i>Net Benefit not including capital or O&amp;M - \$0.06M</i></b>	

The natural gas case (which does not include capital or operational costs) results in a slight decrease in annual production costs of \$0.06M per year. When all other things are considered, this benefit would be insufficient to generate a positive return on the investment required for the reburn upgrade. Further, natural gas reburn would not benefit from any of the proposed renewable energy legislation including possible tax credits. In contrast, the comparison case for biomass results in an annual benefit of over \$0.9M and favorable returns in excess of 15% per year. As noted previously, adding in tax credits, green power incentives, or other valued renewable energy benefits only increases the disparity between these cases.

## 5.0 CONCLUSIONS

Natural gas reburn has already emerged as a commercially viable NO<sub>x</sub> control strategy. It has proven effective in obtaining substantial reductions in NO<sub>x</sub> and SO<sub>2</sub> emissions at a number of power plants across the United States. However, natural gas remains a premium fossil fuel.

It appears that for a moderate investment in biomass handling and processing equipment, some power plants will be able to capitalize on low-cost opportunity fuels to lower production costs and obtain NO<sub>x</sub>/SO<sub>2</sub> emissions comparable to those obtained using natural gas. Additionally, since biomass fuels are renewable, CO<sub>2</sub> reductions are also obtained. Although not valued in this analysis, a substantial value may eventually be attributed to this benefit.

It is important to point out an additional item with respect to reburn technologies whether natural gas or biomass is used as the fuel. In these cases, reburn uses a secondary fuel to obtain NO<sub>x</sub> control. The cost of these fuels is dependent on their supply and demand. Therefore, there is a direct relationship between the ability of the plant to meet its NO<sub>x</sub> requirements in a cost effective manner and the availability of fuels at a reasonable price. For biomass, this will mean new fuel supplier relationships and potential new fuel management issues. However, this analysis

suggests that the rewards will be worth the hassle and a competitive edge may be gained by those willing to modify their business practices to take advantage of them.

Power plants in the Northeast are facing more stringent air emission regulations. Since this part of the country is also rich in biomass resources, these plants should consider biomass reburn as an option. The focus of this report, Dunkirk Station, is well positioned to capitalize on this opportunity. The plant is already undergoing retrofits to cofire biomass, and much of the equipment needed to explore reburn is already on-site. This analysis suggests that biomass reburn can be even more economically attractive than biomass cofiring and that a demonstration project should be seriously considered. As part of the demonstration, the effort represented by this report should be revisited with a more in-depth technical and economic analysis of the plant's performance, with more precise data collected from combustion models and vendor/contractor quotes.

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## **Appendix D. CFD Modeling**

**[DOE Task 2]**

The CFD Modeling Report, to be supplied by the NETL R&D group, describes activities under DOE Task 2.

## **Appendix E. Biomass Preparation Economics**

**[DOE Task 4]**

The Biomass Preparation Economics Report, to be supplied by the NETL R&D group, describes activities under DOE Task 4.

## **Appendix F. Evaluation of Slagging and Fouling**

**[DOE Task 5]**

The Biomass Preparation Economics Report, to be supplied by the NETL R&D group, describes activities under DOE Task 5.