Reduction of NO_x via Coal Combustion Catalysts

Final Report

Reporting Period Start Date: 9/19/02

Reporting Period End Date: 11/18/03

Principal Authors: Jeff Hare, George Ford, Stephanie Black, Bing Zhou
and Stan Harding

Report Date: February 13, 2004

DOE Award Number: DE-FG26-02NT41618

Headwaters Incorporated
10653 S River Front Parkway
Suite 300
South Jordan, UT 84095

Grant awarded to:
Headwaters Technology Innovation Group (HTIG)
(Formerly Hydrocarbon Technologies, Inc.)
A Subsidiary of Headwaters Incorporated
1501 New York Avenue
Lawrenceville NJ 08648

Covol Fuels
A Division of Headwaters Incorporated
10653 S River Front Parkway
Suite 300
South Jordan, UT 84601

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ABSTRACT

Air pollution is a growing concern for both the United States government and its citizens. Current legislation is moving in the direction of lower emissions standards for the major pollutants, SO_x and NO_x. The work performed under this DOE grant focused on finding a catalyst that, when added to coal, will effectively reduce the amount of NO_x produced during combustion. The test program was divided into four major tasks: 1) Evaluating the impact of a combustion catalyst on nitrogen release; 2) Optimizing catalyst formulation; 3) Preparing a preliminary economic evaluation; and 4) Outlining future test plans, costs and schedule.

More than 100 bench-scale, proof-of-concept tests were completed with more than 30 different catalysts, using two different coal types, River Hill Pittsburgh 8 (River Hill) and PRB, under oxidizing and reducing conditions. The results showed that catalysts were effective in increasing, by more than 30%, the nitrogen gas (N₂) release in River Hill Pittsburgh 8 coal and more than 20% in the PRB coal. Preliminary economics suggest this technology is comparable with current combustion NO_x control technologies such as overfire air addition, SNCR and reburning. Pilot-scale tests are planned in a system with low-NO_x burners to further evaluate the technology.

TABLE OF CONTENTS

<u>Item</u>	<u>Page No.</u>
Abstract	iii
Table of Contents	iv
List of Illustrations	v
Executive Summary	vi
Introduction	1
Background	1
Objective	1
Approach	1
Experimental Program	3
Theoretical Background	3
Program Approach	5
Nano-Catalysts	6
Industry Involvement	7
Combustion Facility	7
Screening Test Facility	11
Analytical Equipment	12
Test Program	15
Task 1: Impact of Catalysts on Nitrogen Evolution	15
Task 2: Optimize Catalyst Formulation and Application	16
Task 3: Perform Preliminary Economic Analysis	17
Task 4: Estimate Cost of Pilot-scale Testing and Demonstration	17
Results and Discussion	18
Task 1: Impact of Catalysts on Nitrogen Evolution	18
Task 2: Optimize Catalyst Formulation and Application	23
Task 3: Perform Preliminary Economic Analysis	31
Task 4: Estimate Cost of Pilot-scale Testing and Demonstration	32
Conclusions and Recommendations	34
Conclusions	34
Recommendations	35
References	36

LIST OF ILLUSTRATIONS

<u>Tables</u>	<u>Page No.</u>
Table 1: Pyrolysis results at 900°C	4
Table 2: Air/Argon Flow Rates for each Test.....	9
Table 3: Complete Task 1 Testing Chart	16
 <u>Figures</u>	
Figure 1: Combustion Apparatus Schematic	8
Figure 2: Combustion Apparatus	9
Figure 3: Calibration Curve for Coal Feeder	10
Figure 4: LECO TGA-601	12
Figure 5: Analyzers	13
Figure 6: Task 1 Coal Analyses	18
Figure 7: Task 1 Fuel-lean Top Ash Analyses.....	19
Figure 8: Task 1 Fuel-lean Bottom Ash Analyses	20
Figure 9: Task 1 Fuel-rich Top Ash Analyses	20
Figure 10: Task 1 Fuel-rich Bottom Ash Analyses	21
Figure 11: Task 1 Fuel-lean Gas Analyses	22
Figure 12: Task 1 Fuel-rich Gas Analyses.....	22
Figure 13: Original Screening Test River Hill Common Catalysts	24
Figure 14: Original Screening Test River Hill Nano-Catalysts	25
Figure 15: Original Screening Test River Hill Improvement	25
Figure 16: Original Screening Test PRB Common Catalysts.....	26
Figure 17: Original Screening Test PRB Nano-Catalysts.....	27
Figure 18: Original Screening Test PRB Improvement.....	27
Figure 19: Re-test Screening Test Results	28
Figure 20: Re-test Screening Improvement Results	28
Figure 21: Task 2 Baseline coal/catalyst Analyses	29
Figure 22: Task 2 Fuel-rich Top Ash Analyses	30
Figure 23: Task 2 Fuel-rich Bottom Ash Analyses	30
Figure 24: Task 2 Fuel-rich Gas Analyses.....	31

EXECUTIVE SUMMARY

Air pollution is a growing concern for both the United States government and its citizens. Current legislation is moving in the direction of lower emissions standards for the major pollutants, SO_x and NO_x. The current state-of-the-art technology for reducing NO_x emissions focuses on chemically changing the emissions to a less harmful compound. Low-NO_x burners are one of the only current industrial NO_x reduction strategies that focus on *producing* less NO_x emissions. Headwaters Incorporated, through its Covol Fuels Division and Headwaters Technology Innovation Group (HTIG, including the former Hydrocarbon Technologies, Inc.) feel this is an area where advancements can be made to help industrial and utility power generating facilities meet the future regulations to improve air quality.

The work performed under this DOE grant focused on finding a catalyst that, when added to coal, will release harmless nitrogen (N₂) and effectively reduce the amount of NO_x produced during combustion. The test program was divided into four major tasks:

- 1) Evaluating the impact of a combustion catalyst
- 2) Optimizing the catalyst formulation;
- 3) Preparing a preliminary economic evaluation; and
- 4) Outlining future test plans, costs and schedule.

More than 100 bench-scale, proof-of-concept tests were completed with more than 30 different catalysts, using two different coal types, River Hill Pittsburgh 8 and PRB, under oxidizing and reducing conditions to determine if a pre-combustion catalyst could be utilized as a NO_x reduction technology. The concept is to combine an effective catalyst with low-NO_x burner technology and/or combustion technologies such as SNCR, reburning, etc. to reduce NO_x emissions to acceptable regulatory limits. Two sets of catalysts were prepared: nano-catalysts, relying on Headwaters confidential preparation technology, and common catalysts that are readily available in the industry. From these tests and evaluations, the following conclusions are made:

- There is a distinct difference in nitrogen release between River Hill Pittsburgh 8 (River Hill) coal and the PRB coal with the PRB showing the higher release rates, 50% compared to 30%.
- More than 75% of all catalysts evaluated were effective in increasing nitrogen release in the PRB coal.
- Only 5 of the 31 catalysts were effective in increasing nitrogen release in the River Hill coal.
- The nano-catalysts were more effective in increasing nitrogen release on the target coal, River Hill; but the common catalysts were more effective on PRB coal.

- The maximum increase in nitrogen release for the River Hill bituminous coal was over 30%, while the maximum increase for the PRB coal was just over 20%.
- These initial nano-catalysts contained only 2% active ingredient and dosage rates up to 2.5% were utilized. Recent work has demonstrated that the nano-catalysts can be prepared with more than 10% active ingredient and dosage rates lower than 1.5% can be used.
- Preliminary economic estimates suggest that a pre-combustion catalyst will be cost competitive with current combustion NO_x control technologies.
- Pilot-scale testing with a low-NO_x burner is necessary to evaluate the technology in an actual combustion system.

This test program led to the following recommendations:

- Continued efforts should be made to improve the nano-catalysts preparation and active ingredient concentrations.
- Additional screening and bench-scale combustion tests should be conducted to evaluate a wider range of possible catalysts, including improved nano-catalysts.
- Pilot-scale combustion tests should be conducted on only the most promising, in terms of effectiveness and economics, of the catalysts evaluated from the bench-scale tests.
- Discussions should occur with potential catalyst suppliers to evaluate production methodologies.
- An initial investigation should be done to locate a small boiler (50-100 MW) as a potential demonstration site.
- An evaluation of alternative methods of applying the catalyst to the coal should begin.
- The economic estimates should be continually refined.

This program has demonstrated a distinct potential that a combustion catalyst may be a cost effective way to work synergistically with low-NO_x burners to help coal-fired facilities reduce their NO_x emissions.

SECTION 1: INTRODUCTION

Background

Nitrogen oxide (NO_x) emissions generated from the burning of fossil fuels can cause significant adverse effects on human health and the environment when they are released into the atmosphere. NO_x is believed to contribute to ozone formation, acid deposition, particulate pollution, and visibility degradation within the environment. The U.S. government has imposed regulations to limit further damage from these negative effects of fossil fuel combustion.

Control and reduction of these emissions has been a high concern for the U.S. Environmental Protection Agency since the implementation of the Nitrogen Oxides Reduction Program under Title IV of the Clean Air Act Amendments (CAAA) of 1990, which establishes NO_x emissions standards for coal-fired utility boilers. The act attempts to regulate emissions by requiring both new and existing plants to reduce their emissions of SO₂ and NO_x. Unlike earlier legislation, the CAAA does not dictate the use of particular compliance technology or set specific emission rate limits. Instead, the act targets a ten million ton reduction of SO₂ emissions from 1980 levels (a 62% drop from utility coal emissions of 16 million tons in 1980) and a 2 million ton reduction in NO_x emissions from 1980 levels (a 33% drop from utility coal emissions of 6 million tons in 1980). The act assigns an emissions ceiling for each plant based on the total number of Btu's burned by that plant.

The current proposed legislation would even further lower the regulations of NO_x emissions for coal-fired power plants. Reducing the allowable levels of NO_x emissions requires either a reduction in the amount of NO_x produced or an increase in the amount of NO_x that is chemically changed to a less harmful compound. This study examines the feasibility of producing less NO_x by adding a catalyst to the coal before combustion.

Objective

The objective of this study is to verify the technical feasibility and effectiveness of adding a combustion catalyst to reduce NO_x emissions in a pulverized coal-fired power generating station and to determine the economic impact this method would have on NO_x reduction in the energy industry.

Approach

Certain catalysts have shown promise in reducing the amount of char nitrogen (nitrogen present in devolatilized coal) in certain types of coals under pyrolysis conditions. It is proposed that the catalysts drive more of the nitrogen from the coal matrix into the gas phase in heated environments where little or no oxygen is present. This process could aid in reducing the production of NO_x emissions by converting the fuel nitrogen to harmless N₂ gas. While this concept is encouraging, little work has been done to prove that this

idea will succeed in a combustion environment. This study addresses the following fundamental questions to determine whether this is a feasible NO_x reduction technology:

- Is a catalyst effective under combustion conditions?
- Are liquid catalysts more effective than solid catalysts?
- What quantity of the catalyst is needed to promote an increase in nitrogen release?
- What effect does the catalyst have on different types of coal?
- Does more than one catalyst exist that may be effective?
- Would a combustion process resulting in lower NO_x emissions be economically efficient?

In response to these questions, the Headwaters Incorporated, through its Covol Fuels division with assistance from the Headwaters Technology Innovation Group (HTIG) developed a program to investigate the possibility of using different types and quantities of catalysts to treat a run-of-mine Pennsylvania coal under typical combustion conditions.

SECTION 2: EXPERIMENTAL PROGRAM

Theoretical Background

The design of low-NO_x burners allows volatile nitrogen to be released from the coal in an oxygen depleted environment, thus allowing the nitrogen in the gas phase to form nitrogen gas via several different mechanisms. Headwaters is using this concept, along with its experience in the synfuel industry, to develop a combustion catalyst that will increase the volatile nitrogen release in coal during the devolatilization phase of pulverized coal combustion to prevent subsequent the formation of NO_x.

The concept of a combustion catalyst to reduce NO_x production is supported by research conducted by Dr. Yasuo Ohtsuka, a professor at Tohoku University, Japan. Dr. Ohtsuka's research on the pyrolysis of coal indicates that the addition of an iron catalyst may increase the amount of nitrogen released during devolatilization. Dr. Ohtsuka performed pyrolysis tests using two main types of coal, an Australian Loy Yang brown coal and an Australian Blair Athol bituminous coal. A complete nitrogen balance was performed to identify the state (ie. gas, tars, oils and chars) of the nitrogen from the coal after devolatilization. The testing showed that adding a catalyst to the coal increased the amount of nitrogen gas produced and decrease the amount of nitrogen that remained in the char material after pyrolysis.

Dr. Ohtsuka utilized an aqueous solution of acid waste from a steel pickling process as the starting material for the iron catalyst. The addition of the solution to the coal created a slurry, which was then washed and filtered to remove harmful compounds introduced by the acid waste. The coal samples were loaded with varying amounts of the catalyst to target an optimal addition rate in terms of NO_x reduction.

Approximately five grams of a coal or coal/catalyst sample were placed inside a small quartz fluidized bed reactor. The reactor was heated with a transparent electrical furnace, which allowed observation of the coal as it devolatilized. The sample was fluidized by flowing high-purity helium into the reactor at elevated temperatures. A series of condensers and traps were placed on the back of the reactor to capture the tars, oils and gas that were produced by heating the coal to temperatures above 900°C. After reaching the desired temperature, the sample was held at that temperature for approximately ten minutes.

Following the experiment, the tars, oils and char solids were analyzed for nitrogen content, and the gas was analyzed for HCN, NH₃ and N₂. Table 1 presents Ohtsuka's results (Mori 1996 and Ohtsuka 1998). Note that LY stands for Loy Yang brown coal and BA represents Blair Athol bituminous coal.

Table 1:Pyrolysis results at 900°C

coal	Catalyst Loading (wt%)	Conversion of coal-N (%)						
		N ₂	NH ₃	HCN	Oil-N	Tar-N	Char-N	Total
LY	0	3.9	16	5.8	22	7.6	52	107
LY	0.73	49	10	2.1	10	5.4	25	102
LY	2.8	53	13	1.3	14	3.6	17	102
BA	0	7.8	17.2	4.7	12.5	3.1	62.5	108
BA	1.9	28.1	12.5	1.6	10.9	3.4	46.9	103

Table 1 shows that the addition of a catalyst results in a significant increase in the amount of N₂ gas produced from the pyrolysis of both types of coal. While both types of coal showed change, the Loy Yang brown coal with catalyst increased the production of nitrogen gas more than Blair Athol bituminous coal with catalyst did. These data represent a total nitrogen balance after pyrolysis. Therefore, the increase of N₂ gas production relates to a decrease in the amount of nitrogen found in other areas. The brown coal showed a slight decrease in the amount of nitrogen found in NH₃, HCN, oil-N, tar-N and char-N with the largest decrease appearing in the amount of nitrogen remaining in the char. The increase of N₂ gas is almost 50% greater for the catalyst added samples than the baseline, and the decrease in char nitrogen was 35%. The bituminous coal with catalyst showed a 20% increase in N₂ gas produced over the baseline and a decrease in NH₃, HCN, oil-N and char-N products, with the char nitrogen showing a reduction of about 16% from baseline. These results suggest that both types of coal with iron catalyst added showed an increase in the nitrogen release rates, with the brown coal exhibiting a more positive result than the bituminous coal.

Studying the data presented above may lead to a couple of observations. When comparing the baseline brown coal to the baseline bituminous coal, the data indicate that less nitrogen remains in the brown coal char after pyrolysis, which suggests the possibility that the release rates within the two coals differ. Applying this observation to the use of low-NO_x burners suggests that brown coal could produce less NO_x than bituminous coal since less nitrogen remains in the char material that is introduced into an oxygen environment during char oxidation. In addition, it has been documented that some coals (ie. Indonesian and Powder River Basin (PRB)) produce 10-15% less NO_x emissions on an equivalent basis than bituminous coals produce. It has been explained, that the reason for the decrease can be attributed to the fact that Indonesian and PRB have different nitrogen devolatilization kinetics than eastern bituminous coals (Tillman and Harding, 2004).

Dr. Ohtsuka's work indicates that adding an iron catalyst to coal may lead to the removal of more nitrogen from the char material. His work can be seen as a positive step towards finding a method of creating less NO_x emissions in utility coal-fired power plants if applied properly. Headwaters is applying concepts studied in Ohtsuka's research to develop a catalyst that will increase nitrogen release rates when added to coal that cause an eastern bituminous coal to approach the nitrogen release behavior of the Indonesian and PRB coals.

Program Approach

NO_x emission standards will likely continue to decrease in the future. Unfortunately, no viable combustion pre-treatment process currently demonstrates the ability to decrease the production of NO_x. Headwaters' goal is to meet the need to lower the amount of NO_x emissions produced using the theory presented by Dr. Ohtsuka. This section outlines the reason for using a Pittsburgh 8 coal as the baseline coal, shares information about why previous work may show similar results in a low-NO_x burner system, explains the theory used in outlining the test program encompassing devolatilization screening tests under fuel-rich and fuel-lean combustion conditions and defines how success will be measured.

River Hill, a Pittsburgh 8 bituminous coal, was used as the baseline in this study for two major reasons. First, eastern coals produce higher levels of NO_x emissions when compared to some PRB coals on an equivalent firing basis. The second reason was that River Hill coal was previously characterized by Headwaters in a separate program at Penn State University and Advanced Fuel Research. These separate programs have given a wealth of knowledge about the physical and chemical characteristics of the coal that will assist in determining the impact of the catalyst on NO_x emissions. A second coal, a typical PRB, was used as a comparison coal to evaluate the effects of coal type on catalyst performance.

The test matrix for this study was based on the functioning of a low-NO_x burner in a coal-fired power plant. Typically in a commercial boiler, the coal is transported through the pulverizer and to the burner with between 15-18% of the stoichiometric amount of air required for complete combustion; this air is termed primary air. All remaining air is introduced as secondary, or combustion air in the regions surrounding the primary air/coal stream or in the overfire air ports separated from the burners. Low-NO_x burners, which are now the standard burner in the U.S., are designed to create an oxygen-depleted zone in the near-burner region of a full-scale boiler. This fuel-rich zone allows the coal to devolatilize where oxygen is not present. The products from the nitrogen devolatilization form cyano-compounds and amines rather than oxides. These compounds then react with hydrocarbon radicals to form nitrogen gas. The more and faster the nitrogen devolatilizes in the fuel-rich, near-burner region, the opportunity to reduce the final NO_x concentration improves. After some devolatilization occurs, the secondary air surrounds the initial fuel-rich flame and completely mixes into the flame at a significant distance from the burner face, thus completing the combustion of the fuel. This delay in mixing the combustion air allows the majority of the nitrogen in the fuel to devolatilize in

a fuel-rich environment and proceed as explained above. By applying Dr. Ohtsuka's research results to the concept of low-NO_x burners, Headwaters seeks to increase the amount of nitrogen removed from the coal in the near burner region.

The screening, or devolatilization test, identifies which catalyst improves the nitrogen release rate in an oxygen-depleted zone by measuring the amount of nitrogen remaining in the char after pyrolysis. The combustion testing then provides a simulation of both the fuel-rich, near-burner region and fuel-lean, overall combustion in a full-scale boiler. The fuel-rich portion of the testing is conducted at 18% of the required combustion air in order to simulate the near-burner region of a low-NO_x burner. Fuel-lean tests are run with 20% excess air to simulate overall combustion. Testing under these three conditions will help identify whether the combustion catalyst will affect the amount of nitrogen remaining in the char material after any of the three test methods have been performed.

This study applies probable theory found in simulated research environments to solve problems at the forefront of our society. Headwaters outlines the steps taken to use a coal that has already been extensively characterized in another program, apply a catalyst to it and utilize the method of a low-NO_x burner to produce less NO_x emissions. The testing in this study will attempt to simulate the devolatilization, near burner and final combustion environments with a variety of catalysts in an effort to find a catalyst that will help lower NO_x pollution.

Nano-Catalysts

Adding catalysts to established processes has been shown to greatly improve many procedures in various industries. Dr. Bing Zhou, a member of HTIG, is a leader in the area of nano-catalyst technology. This section will outline the major differences between nano-catalysts and common catalysts and briefly describe the procedures Dr. Zhou used to prepare catalysts for this program.

The use of nano-catalysts is expected to decrease the amount of catalyst material needed because of the increased effectiveness of the catalyst. The main advantage of the nano-catalyst over a traditional catalyst is the difference in particle size and spacing of the molecules. A traditional catalyst disperses particles at about 50 nm in size, whereas the nano-catalysts are designed to produce particles less than 10nm. In solution, the nano-catalyst has a particle size of 1 to 2 nm, but application and drying of the catalyst increases the agglomeration and hence the overall cluster size. This size difference is very important because the smaller size provides more available surface area and thus creates a better opportunity for catalyst interaction.

Lattice structure also greatly impacts catalytic reactions. The starting material for the catalyst used in this study forms five possible lattice structures. Two of these lattice structures have a higher activity, which makes them more likely than the other three structures to display catalytic characteristics. One reason these two structures have a higher activity is because the spacing between molecules in these two structures is greater than the spacing in the other three lattice structures. This increase in spacing between

molecules creates greater catalytic efficiency by increasing the available surface area. Headwaters evaluated sixteen different nano-catalysts during this study by using four different starting materials and a variety of different chelating agents. The different chelating agents were evaluated to determine which achieved the most stable suspension of the catalyst in solution in one of the two high activity lattice structures.

Although the production of the nano-catalysts is proprietary, the following generic procedure was used to prepare the nano-scale catalysts used during this program. The desired amount of catalyst powder was dissolved in a nano-dispersion agent solution, using a ratio of the dispersion agent-to-catalyst of at least 1:1, and ideally higher than 3:1. Once the powder and solution were mixed, the pH of the solution was adjusted to less than 5. The solution was agitated overnight or heated to boiling for at least 5 hours under reflux conditions to allow the formation of organometallic complexes between the nano-dispersion agent and the catalyst. The colloidal suspension formed by such preparation techniques has a typical nano-catalyst particle size of less than 2 nm.

The knowledge and ability to create a nano-catalyst will benefit Headwaters in its search for a successful catalyst. The advantages of particle size and ability to create solutions with high activity lattice structures should benefit the search for an effective combustion catalyst.

Industry Involvement

Headwaters has built a strong relationship over the years with two leading chemical companies, DOW Chemical and Dow Reichhold Specialty Latex LLC (DRSL). DOW Chemical is one of the leading science and technology companies in the world and serves customers in more than 170 countries. Dow Reichhold Specialty Latex is the world's largest producer of specialty latexes and has six global offices. Headwaters engineers met with DOW Chemical and DRSL's research and development divisions for the purpose of applying their cutting-edge knowledge and technologies towards finding a combustion catalyst that will have a positive effect on NO_x emissions for coal-fired power generating facilities.

Combustion Facility

After identifying a proposed method of increasing the nitrogen release rates from coal during pyrolysis, a testing apparatus and procedure were developed to apply the method to real world conditions. The engineers at Headwaters designed, constructed and assembled an apparatus with the ability to carry out the desired testing. A summary description of the apparatus and procedure used for the fuel-rich and fuel-lean combustion tests that were performed over the course of the grant period at the Headwaters laboratory located in Provo, Utah will be outlined.

In order to apply Ohtsuka's work to real-world conditions, the design of the combustion apparatus needed to meet five distinct requirements. The essential design requirements included a method of feeding coal continuously, the ability to change combustion

environments (fuel-lean and fuel-rich) and combustion temperatures, a means of collecting real-time analysis of off-gases [NO_x, oxygen gas (O₂) and carbon monoxide gas (CO)] and the ability to collect char and ash products for analysis. One major design problem that existed was how to create an airtight combustion vessel that would accommodate ports for the inlet, outlet and a temperature thermocouple and yet overcome any catalytic effects created by using stainless steel parts. The solution was to design a ceramic vessel that fit inside the protective outer stainless steel chamber to act as a liner and eliminate the catalytic effects of stainless steel.

There are four major parts (coal feeder, combustion chamber, electric furnace and off gas analyzers) of the apparatus that work together to achieve the desired testing conditions as shown schematically in Figure 1. The sweep gas, made up of air and argon, is metered and sweeps past the end of the coal auger from which coal enters the gas mixture. The mixture of coal, air and argon then drops into the ceramic combustion chamber located inside the electric furnace. The ratio of the amount of air to argon in the sweep gas depends on which testing condition is being targeted, fuel-rich or fuel-lean. A thermocouple inserted into the ceramic chamber records the temperature. As the mixture of air, argon and coal enters the heated combustion chamber, the coal ignites. As the coal devolatilizes, the heavier ash particles fall to the bottom of the chamber and are collected after the experiment ends. The off-gases, with any entrained ash particles, pass from the ceramic chamber to a particulate trap to remove this ash material. The clean gases flow through a series of moisture traps designed to remove any water vapors and tars. After removing these substances, the gas flows to three flue gas analyzers to measure NO_x, CO and O₂. The flue exhaust is then vented according to regulations.

Another area of concern in the design of the procedure was in determining how to achieve 18% combustion air and still have enough flow to run the apparatus smoothly. During the preliminary testing it was determined that at least 8 SCFH of air must be flowing to be able to properly run the gas analyzers, therefore, using just 18% of the required air would not provide adequate airflow to properly use the gas analyzers. As a result, a mixture of air and argon was used to sweep past the exit of the coal auger and carry the coal into the furnace.

Using much more than 8 SCFH would cause the airflow to entrain the ash material out of the ceramic vessel and into the particle traps. Therefore, the gas flow rate was set at 8.6 SCFH; this corresponds to 25-g/hr coal feed for the River Hill coal. Table 2 lists the air and argon flow rates needed and the percent O₂ in the feed-gas mixture for both the fuel-rich and fuel-lean tests using River Hill coal. Note that all the fuel-rich tests had 18% of the required stoichiometric air, and the fuel-lean tests all had 20% excess air. Figure 2 is a picture of the combustion apparatus.

Table 2: Air/Argon Flow Rates for each Test

River Hill Coal	Air Flow (SCFH)	Argon Flow (SCFH)	Mixture O₂ (%)
Fuel-Rich Tests	1.3	7.3	3.1
Fuel-Lean Tests	8.6	0.0	20.8

Figure 2: Combustion Apparatus

Air and coal flow rates were calibrated before each experiment to ensure accurate and consistent rates. The airflow was measured using a TSI 4100 series real-time digital air flow meter, while the coal feeder was calibrated by measuring the weight gain in a vacuum bag over a period of time as a function of the feeder potentiometer setting. Figure 3 shows the calibration curve for this Acrison coal feeder. The three gas analyzers were also calibrated with certified standards at the beginning and ending of each test.

Figure 3: Calibration Curve for Coal Feeder

Numerous preliminary tests were completed in the combustion facility in order to determine the most effective and efficient way to evaluate the catalysts. The most important facet of the procedure is consistency between tests for both baseline and all catalyst-treated tests. In order to maintain consistency, the following general procedures were used in all combustion tests:

1. Carefully prepare the catalyst-doped coal per the test condition.
2. Place the coal sample in the coal feeder. Ensure the coal hopper is sealed tightly to create a closed system environment.
3. Place the combustion chamber in the furnace and make all coal and air line connections. Begin air and argon gas flows into the furnace at the required flow rates, and then initiate furnace heat-up.
4. Calibrate the NO_x, CO and O₂ analyzers.
5. When the system is at the desired temperature condition, record the time, start recording data and begin coal feed.

6. Continuously record the NO_x, CO and O₂ measurements.
7. After one hour, shut off the air/Ar flow and coal feed and record the time.
8. Leave the crucible in the furnace at temperature for one additional hour.
9. Collect and weigh all samples and prepare the facility for the next test.

The following data were recorded during each test:

1. All operating conditions including coal and gas flow rates
2. Important times (initial, ending, etc.)
3. Continuous NO_x, CO and O₂ analyses
4. Weight of all collected char and ash samples

A large fraction of time spent on this project consisted of designing, constructing and assembling the experimental apparatus, along with developing the practical testing procedures. After outlining the desired features of the apparatus, design, construction and assembly began. Checkout tests helped solidify the procedure and timing needed to obtain the desired results. The apparatus and procedures have yielded repeatable results, and it is felt that any major combustion difference could be attributed to the affect of the catalyst.

Screening Test Facility

The screening test was not part of the original test plan for this study, however this test became necessary to reduce the amount of time required to evaluate individual catalysts. After completing the Task 1 combustion testing (See Test Program Section), it was decided that a quicker screening test that would mimic the pyrolysis tests performed by Ohtsuka was necessary. The catalyst-screening test was designed to evaluate an approximate efficiency of a large number of different catalysts in a short period of time. This test introduced the coal or coal/catalyst sample to a pyrolysis environment, after which the char material was analyzed for nitrogen content. Samples that showed a decrease in nitrogen remaining in the char compared to the baseline coal would then be re-evaluated in the combustion apparatus.

Tests were performed using a standard LECO TGA-601. This piece of equipment performs a variety of different ASTM tests ranging from moisture to a short proximate analysis. This hardware has the capability and freedom of programming different temperature ramp rates and hold times and it allows one to choose the gas environment. The TGA holds up to nineteen different samples and was designed to record the weight of each sample in sequence. Figure 4 shows the LECO-TGA 601 used during this study.

Figure 4: LECO TGA-601

The procedure for the screening tests began by placing about 2.5 grams of a coal or coal/catalyst sample in a single crucible and weighed by the TGA microbalance. After all nineteen samples were loaded, the machine was programmed to ramp at 6°C per minute from room temperature to 107°C and hold for 30 minutes while Argon gas flowed into the chamber area. This step was designed to remove any surface or inherent moisture in the sample. After this initial step, the instrument opened and lids were placed on each crucible. The furnace was then ramped at 43°C per minute to 950°C and held for sixty minutes. Following the hold time, the furnace was cooled while continuing to weigh each sample and flow Argon gas into the furnace area. Once the furnace temperature reached 400°C the instrument opened and the test was ended. After the instrument cooled to room temperature, each char sample was removed and placed into a marked container in preparation for analysis. The TGA-601 converted the recorded data onto a spreadsheet that displayed the weight of the sample as a function of the temperature and time.

With the freedom of testing up to nineteen different samples in a single screening test, a second type of coal, PRB, was added to the test matrix for comparison. Each of these coals was mixed with two different catalyst application rates using each type of catalyst. Several checkout tests were preformed before this procedure was finalized.

Analytical Equipment

The test protocol for this study utilizes several different solid and gas analyzers. Over the course of this grant, Headwaters purchased all of these analyzers as their cost sharing and to reduce the cost of outsourcing future samples. The major pieces of analytical equipment used in this study were the LECO TGA-601, an elemental carbon, hydrogen and nitrogen (CHN) analyzer and the three gas analyzers: O₂, NO_x and CO. Figure 5 shows pictures of the Perkin Elmer 2400 Series II CHN analyzer (left) and the three gas analyzers (O₂ in center, CO upper right and NO_x bottom right) used during this study. The gas analyzers and the LECO TGA-601 were located at the Headwaters Laboratory.

The CHN analyzer was a recent purchase so the CHN analyses for this study were outsourced to Timpview Analytical Laboratories located in Orem, UT.

Figure 5: Analyzers

The LECO TGA-601 was used to perform the short proximate analysis using ASTM D-5142. This procedure determines the percent moisture, ash, volatile matter and fixed carbon found in a sample. The other solid analysis test, CHN, was instrumental in identifying which catalysts showed an increase in the amount of nitrogen removed from the coal matrix. This test was outsourced to a local accredited laboratory, Timpview Analytical Laboratory which uses a LECO CHN-100 and follows ASTM D-5373 to determine the amount of elemental carbon, hydrogen and nitrogen in a sample on a percentage basis.

The three gas analyzers used during combustion testing measured the concentration of O₂, NO_x, and CO in the off-gas. Each of the analyzers collects real-time analysis and utilizes different methods to determine the concentration of the target gas. The NO_x and CO analyzers were both manufactured by California Analytical Instruments. The NO_x analyzer uses a chemiluminescence method that allows for the use of five different NO_x ranges: 0-30, 0-100, 0-300, 0-1000 and 0-3000 ppm. The NO_x analyzer requires a constant flow of oxygen gas that is converted to ozone, which then converts any NO to NO₂, allowing for a more accurate measurement of the NO_x concentration. The CO analyzer incorporates a non-dispersive infrared technology that detects concentrations of CO in the range of 0-1000 ppm. The O₂ analyzer utilizes a patented weak acid electrolyte system made by Alpha Omega and has a range of 0-25%. The CO and O₂ analyzers are used to determine the combustion characteristic inside the vessel during the testing. The NO_x analyzer helped identify any changes that occurred between tests in both the duplicates of the baseline and the catalyst-treated samples.

Elemental analyses of the sample were also outsourced to Timpview laboratory and were completed using AA methodology following ASTM D-3682 procedures.

These five analytical tests were instrumental in helping to identify any physical or chemical changes that might have occurred during the testing. Each was calibrated with certified standards on a regular basis to ensure the correct calibration of each instrument.

SECTION 3: TEST PROGRAM

To accomplish the objectives listed above, this program had four main tasks. Each of these tasks and their respective sub-tasks are presented along with a description of the work accomplished to complete each task.

Task 1: Impact of Catalysts on Nitrogen Evolution

The goal of task 1 was to evaluate the impact that adding a pre-combustion catalyst would have on nitrogen release from River Hill coal when the mixture was burned in an environment simulating a power generating facility. The first of three sub-tasks was to select the type of catalyst that would be examined and the application rate for each of the catalysts. Second, after the catalyst types were selected, the method for and the actual application of these catalysts to the coal would be determined and performed. Finally, bench-scale combustion testing under fuel-rich and fuel-lean conditions would be performed on each of the prepared samples as well as the baseline coal.

After studying the results presented by Ohtsuka and speaking with Headwaters personal about the possibility of applying nano-catalyst technology, it was decided to test three different catalysts under Task 1. Two of the three catalysts were nano-catalysts prepared by the process described above in the previous section. The third catalyst was basically a duplication of the starting material used by Ohtsuka. The nano-catalyst was applied at about 0.067% wt of the coal sample and the common catalyst was applied at a much higher rate, 1.1% wt. Note that the application rate of nano-catalyst was 28 times less than that used by Ohtsuka on a bituminous coal. It was hoped that the nano-catalyst would be an order of magnitude more effective than the common catalyst; thus, the difference between the two dosage rates.

The second area of concern was the application of the catalyst to the coal to ensure maximum surface area coverage. In order to guarantee the best possible mixing, the baseline coals were pulverized to the typical power generation size such that 70-75% of the material was smaller than 200 mesh (75 microns). Each of the catalysts was dissolved into an aqueous solution that allowed for the best possible dispersion. The catalyst solution was put into a spray bottle and misted onto the coal as the sample was mixed. A 3000-gram sample was prepared; the required quantity to run the coal feeder properly. After the catalyst was mixed on to the coal sample, each sample was allowed to dry at room temperature to remove any moisture added during the application process.

After the design, construction and experimental testing of the apparatus was complete, combustion tests were performed under both fuel-rich and fuel-lean conditions. It was decided that all samples, both baseline and catalyst-added mixtures would be repeated at least 3 times for statistical purposes. A comparison of the off-gas analyses (CO, O₂ and NO_x) and solid material analysis, a full proximate analysis and C, H and N elemental determinations were performed on each sample collected to identify any affects from the additive. The bench-scale testing was performed using the procedures outline in the

combustion apparatus section (See Section 2). Table 3 outlines the conditions of the completed combustion tests. These tests included five fuel-rich and four fuel-lean tests of the baseline coal, three fuel-rich and four fuel-lean tests of catalyst HTI-A, three fuel-rich and fuel-lean tests for catalyst HTI-B and four fuel-rich and two fuel-lean tests of the common catalyst.

Table 3: Complete Task 1 Testing Chart

Test No.	Test Type	Catalyst type	Iron Amount (%)	Gas Flow rates	Coal Feed Rate	Coal Type	No. of Test	Test Finished
1	Fuel-rich	None	Baseline	1.3 Air / 7.3 Ar (3.1% O ₂)	25 gram/hr	River Hill	2	4/2 4/4
11	Fuel-lean	None	Baseline	8.6 Air	25 gram/hr	River Hill	2	4/7 4/8
12	Fuel-lean	HTI-A IG 16.5	1.0	8.6 Air	25 gram/hr	River Hill	4	4/9 4/10 4/11 4/16
2	Fuel-rich	HTI-A IG 16.5	1.0	1.3 Air / 7.3 Ar (3.1% O ₂)	25 gram/hr	River Hill	3	4/17 4/21 4/22
5	Fuel-rich	HTI-B IRG 16.5	1.0	1.3 Air / 7.3 Ar (3.1% O ₂)	25 gram/hr	River Hill	3	4/23 4/24 4/25
15	Fuel-lean	HTI-B IRG 16.5	1.0	8.6 Air	25 gram/hr	River Hill	3	4/28 4/29 4/30
14	Fuel-lean	None	Baseline	8.6 Air	25 gram/hr	River Hill	2	5/1 5/2
4	Fuel-rich	None	Baseline	1.3 Air / 7.3 Ar (3.1% O ₂)	25 gram/hr	River Hill	3	5/5 5/6 5/7
8	Fuel-rich	FeCl ₃	2.2	1.3 Air / 7.3 Ar (3.1% O ₂)	25 gram/hr	River Hill	4	5/12 5/13 5/14 5/15
18	Fuel-lean	FeCl ₃	2.2	8.6 Air	25 gram/hr	River Hill	2	5/16 5/17

The selection, application and initial bench-scale testing of the three different catalysts laid the foundation for this program. This work identified trouble spots with the testing procedures and methods for finding a successful combustion catalyst.

Task 2: Optimize Catalyst Formulation and Application

The objective of Task 2 was to optimize the formulation of the combustion catalyst and improve on application methods if necessary. This objective was broken into two sub-tasks: evaluate the results of Task 1 and conduct additional combustion tests with any modified catalyst.

The evaluation of the work performed under Task 1 allowed the team to review the direction and status of the program. The assessment concluded that no improvements to the catalyst application process were necessary at this time, but that additional catalysts needed to be tested and that a new quicker screening method was necessary to create the ability of evaluating an expanded number of catalysts and application rates within a couple of days compared to forty-five days for three catalyst types at one application rate. Not only did this new testing method need to allow for a large number of samples to be tested in a short time period, but a relationship between the results of the screening test

and how the catalyst might perform under combustion conditions needed to be established.

After the screening method was instituted, additional testing was completed. The new screening test allowed Headwaters to include a second type of baseline coal, PRB, into the program. Including the PRB into the screening test program allowed for the comparison between baseline coals and what difference, if any, the baseline coal had on the catalyst effectiveness. The testing program included thirty-one different catalysts, of which sixteen were nano-catalysts and fifteen were common compounds, nine solids and six liquids. At least two different concentrations (ie. high and low) of each catalyst type were added to the baseline reference coals. The high and low concentrations for the common catalyst were approximately 5.5% and 2.5% by weight of sample, respectively, whereas, the nano-catalyst concentrations were 3.5% and 2.0%, respectively. To ensure a firm analysis of the baseline coal, four separate samples of the River Hill and three separate samples of the PRB coals were tested. Each of the catalysts and coal types were tested once, then those that showed promise were re-tested to show repeatability. A total of 78 different samples were tested via the screening method. As stated earlier, a successful catalyst would remove more nitrogen from the coal matrix when compared to the baseline coal.

After the screening tests, the results were analyzed and the most promising catalysts were then tested in the combustion apparatus. Two catalyst types were identified and tested under the fuel-rich testing conditions only because this condition more closely represented the near-burner region in a utility boiler.

The testing completed for Task 2 provided results on 31 different catalyst types at two different application rates. This work also compared the effect the different catalysts had on the bituminous River Hill coal and on the sub-bituminous PRB coal.

Task 3: Perform Preliminary Economic Analysis

The purpose of Task 3 was to perform a preliminary economic analysis of the pre-combustion treatment processes compared to the standard state-of-the-art post-combustion methods, SCR and SNCR, for NO_x control. This analysis involved comparing the effectiveness of the current technologies with using a combustion catalyst to reduce NO_x. In conjunction with the technical study, an economic model was developed that compared current technology costs to the cost of using a combustion catalyst.

Task 4: Estimate Cost of Pilot-scale Testing and Demonstration

The intention of Task 4 was to estimate the cost of performing a pilot-scale test burn of the most effective catalysts evaluated and to calculate the cost of modifying an existing plant to complete a field-scale demonstration. The scope of the pilot and field tests were defined, and a cost estimate prepared. This analysis projected the cost and time-to-commercialization of implementing the technology.

SECTION 4: RESULTS AND DISCUSSION

Task 1: Impact of Catalysts on Nitrogen Evolution

The objective of Task 1 was to quantify the impact a pre-combustion catalyst would have on nitrogen evolution from coal. Three different catalysts and a baseline sample were tested under both fuel-rich and fuel-lean conditions. A total of 15 fuel-rich and 13 fuel-lean tests were completed. The performance of the fuel-rich and fuel-lean testing can be broken into three separate categories for the analysis of the results: coal, ash material and gas analysis. The results and discussion for the work done on the 28 different combustion tests along with an outline of some of the problem areas and possible corrections identified with the apparatus will be discussed.

Each coal sample was analyzed to determine the amount of moisture, ash, volatile matter, fixed carbon and elemental carbon, hydrogen and nitrogen. The purpose of these analyses was to provide a baseline for comparison with catalyst-dosed samples. The results for these analyses are located in Figure 6. There was no significant difference seen between the coal and coal/catalyst samples. The one area where a slight difference occurred was an increase in the amount of ash product present in the common catalyst mixture when compared to the baseline coal. One explanation can be that the catalyst has a higher amount of ash than the coal; therefore, the mixture results in an increase in ash.

Figure 6: Task 1 Coal Analyses

The analysis of the ash products were categorized into two groups; fuel-rich and fuel-lean and within these two groups each is divided into top and bottom ash. The bottom ash was the material that was collected from the ceramic vessel at the end of the test, while the top

ash was the material that was collected from the particle traps. Each sample of bottom ash was analyzed for moisture, ash, volatile matter, fixed carbon and elemental carbon, hydrogen and nitrogen, whereas each sample of the top ash was only analyzed for moisture, ash, volatile matter and fixed carbon. The top ash material was not analyzed for elemental CHN because this information was deemed unnecessary. Figure 7 compares the top ash materials for the fuel-lean tests; most of the samples were similar, except the common catalyst showed higher ash and volatile matter with a decrease in the amount of fixed carbon. Figure 8 illustrates this same trend when comparing the fuel-lean bottom ash material. When comparing the fuel-lean bottom ash elemental CHN analysis, the differences seen between the samples were thought to be caused by the ash samples being analyzed in three separate groups creating the difference in the data. Comparing the top ash material tested under fuel-rich conditions, Figure 9 displays no significant differences between the baseline and treated samples. Figure 10 shows the comparison for the fuel-rich bottom ash short proximate data and elemental CHN data with no significant differences.

Figure 7: Task 1 Fuel-lean Top Ash Analyses

Figure 8: Task 1 Fuel-lean Bottom Ash Analysis

Figure 9: Task 1 Fuel-rich Top Ash Analyses

Figure 10: Task 1 Fuel-rich Bottom Ash Analyses

The third area of analysis was the real-time gas analyzers that recorded concentrations of NO_x, O₂ and CO. Again these test are broken into fuel-rich and fuel-lean conditions. The data for the fuel-lean off gases, shown in Figure 11, were fairly consistent between the baseline and the three catalyst samples, as were the results for the fuel-rich analysis displayed in Figure 12. The variation displayed in both figures may be attributed to the inability to finely calibrate the air flow and coal feed rates. This problem is discussed below and has been rectified. The data show no solid evidence that the three catalysts had an effect on increasing nitrogen release from the coal matrix.

Figure 11: Task 1 Fuel-lean Gas Analyses

Figure 12: Task 1 Fuel-rich Gas Analyses

After compiling the data from the combustion testing, four changes to the procedure were necessary to increase the effectiveness of the apparatus. The three major changes were identified:

- CHN analysis showed that a furnace temperature of 750°C was not high enough to burn off a high percentage of the carbon present in the coal, so Task 2 testing was done at furnace temperatures of 950°C.
- The coal feed controller and the air flow meter were not allowing the accuracy needed as shown by the variations in O₂ levels between tests, therefore a new more accurate controller and a digital air flow meter were purchased.
- CHN analysis would be performed at a local lab and the samples would be sent as a single set to help reduce any variability between sample sets.

Task 2: Optimize Catalyst Formulation and Application

The objective of Task 2 was to optimize the formulation of the combustion catalyst and perform additional combustion tests if necessary. The work performed for this task was outlined above. The results and observations made from evaluating Task 1 results, performing the screening test and analyzing the data, and results from the second round of combustion testing will be outlined.

After evaluating the data collected from the Task 1 combustion testing, it was decided that the amount of nitrogen in the char showed no significant difference between the baseline and catalyst-added samples and that the slight differences identified in the gas analysis were created by minor differences in the air and coal feed rates. In addition to seeing no significant difference in the results, the common catalyst contained a corrosive compound that could harm the apparatus and equipment. Therefore, it was decided to discontinue using the common catalyst because of the potential negative effect on the equipment. The two nano-catalysts would also not be used again, but different formulations would be tested.

The addition of the screening test allowed the researchers to choose a wider range of possible combustion catalysts. With this freedom, 31 different catalysts at two different application rates were selected along with including a second baseline coal, PRB. As the catalyst was mixed with the coal, two of the catalysts were removed from testing because the oil-based catalyst would not allow the coal sample to dry sufficiently for testing purposes. Therefore, 84 different samples were tested using the screening method.

Following the procedure outlined above for the screening test and receiving back all the analysis on the starting and char materials, a method of analyzing the data was determined. Because some of the catalysts contained nitrogen, comparing the amount of nitrogen remaining in the char to the amount the sample had before undergoing pyrolysis would not represent the true effect the catalyst had on the amount of coal-nitrogen released. In addition, the moisture levels of all samples were not the same. Therefore, care was taken during data reduction to have all samples evaluated on the same dry bases: total nitrogen released and coal nitrogen released.

The screen testing was preformed in two groups; first all 84 samples were evaluated and secondly those catalysts that performed well or were questionable were re-tested for statistical purposes. This re-test group consisted of 13 total samples: four River Hill baseline samples, six common catalysts and three nano-catalysts. The PRB coal was not re-evaluated in this group because River Hill was the target coal and the information on the PRB coal from the original testing was sufficient. The results for the two types of baseline coals are shown in Figures 13-18.

Figures 13 and 14 show the complete analysis for the common catalysts and nano-catalysts, respectively, when applied to the River Hill coal. The red line indicates the performance of the baseline coal; so all samples that performed above that line removed more nitrogen from the coal matrix with the catalyst than without. Two common catalyst and three nano-catalysts performed better than the baseline on River Hill coal. Figure 15 shows the percent increase over the baseline sample for the five catalyst samples; the nano-catalyst Covol-11 had the highest improvement with a 29% increase over the baseline

Figure 13: Original Screening Test River Hill Common Catalysts

Figure 14: Original Screening Test River Hill Nano-Catalysts

Figure 15: Original Screening Test River Hill Improvement

Figures 16 and 17 display the results of the screening test for PRB coal with the common catalysts and the nano-catalyst, respectively. Again the red line represents the amount of nitrogen that was removed from the baseline coal sample. Any result above that mark removed more nitrogen from the coal matrix than the baseline sample. A total of 24 different samples out performed the baseline, 10 different nano-catalyst samples and 14 different common compound samples. Figure 18 presents the percentage improvement of the catalysts compared to the baseline. The leading catalyst, C 27, for PRB coal increased nitrogen removal by 20%.

Figure 17: Original Screening Test PRB Nano-Catalysts

Figure 18: Original Screening Test PRB Improvement

After reviewing the result from the original tests, four catalysts were selected to be re-tested. Figure 19 shows the analysis of the retested samples and Figure 20 compares the results of the two sets of data. The average values clearly showed that nano-catalyst samples Covol-15 and 17 performed the best of the four different catalyst samples, with an average of 30.5% and 27.6% increase of nitrogen release over the baseline, respectively. Covol-11 and RH C22 also performed well with average increases of 16.5 and 8.3%, respectively. This information is promising, but additional tests are needed to confirm these findings.

Figure 19: Re-test Screening Test Results

Figure 20: Re-test Screening Improvement Results

After the screening tests were completed and the data were analyzed, two catalyst samples were chosen and tested in the combustion apparatus. The two samples that were chosen were RH C15 and RH C24, both of these catalysts were available in the laboratory and were thought to have some potential in larger scale testing. These two catalysts were tested under fuel-rich conditions at application rates of 5.5% for RH C15 and 2.35% for RH C24. The ash material and gases were again analyzed and the results are shown in Figure 21. The ash material was grouped into top and bottom ash just as before. The top ash was analyzed for moisture, ash, volatile matter and fixed carbon, while the bottom ash was analyzed for the same plus elemental carbon, hydrogen and nitrogen. The results of the top and bottom ash material are shown in Figures 22 and 23, respectively. The ash material CHN analysis shows the amount of carbon in RH C24 decreased slightly, this difference maybe caused by an increase in the amount of volatile matter present in the sample because of the addition of the catalyst. The results of the gas analysis is displayed in Figure 24, which indicates a slight increase of the amount of NO_x present in the flue gas for both catalyst samples, which may be a result of the catalyst removing more nitrogen from the coal matrix. This is consistent with the finding that less nitrogen was found in the ash material for both catalyst-added samples when compared to the baseline. These results show some differences between the baseline and the catalyst samples, but further testing is required to prove the concept that a catalyst added to the coal before combustion would reduce the amount of NO_x emissions produced.

Figure 21: Task 2 Baseline Coal/Catalyst Analyses

Figure 22: Task 2 Fuel-rich Top Ash Analyses

Figure 23: Task 2 Fuel-rich Bottom Ash Analyses

Figure 24: Task 2 Fuel-rich Gas Analyses

The evaluation of Task 1, performance of screening test and the additional combustion testing was the work that was completed for Task 2. The results have shown some promise, but more work is required before a go/no-go decision can be made.

Task 3: Perform Preliminary Economic Analysis

A preliminary economic analysis was completed that estimates the cost of this pre-combustion NO_x removal technology with the current combustion and post-combustion technologies. As stated earlier, this combustion catalyst technology is not designed to stand-alone; it is designed to work in conjunction with low-NO_x burners and other combustion technologies such as overfire air, reburning and/or selective non-catalytic reduction (SNCR). The goal is to provide a method of enhancing the efficiency of the current combustion-based NO_x reduction technologies at very low capital cost and competitive O&M costs. This technology would target those utility power plants that are close to meeting their regulations and do not want to utilize the expensive selective catalytic reduction (SCR) technology.

There are four main areas that influence the cost of this pre-combustion NO_x control technology:

1. The cost of catalyst production
2. The amount of active ingredient in the catalyst

3. The dosage rate required on the coal
4. The efficiency of the process

As this program was to investigate the potential for a pre-combustion catalyst to effectively reduce NO_x emissions, the majority of the efforts were focused on proving the feasibility of the concept. After successfully completing the tests and demonstrating that the nano-catalysts are more effective than common catalysts in removing nitrogen from the coal matrix during devolatilization, significant progress has been made over the last few months to increase the amount of active ingredients in the catalyst and to investigate methods of producing the catalyst at reduced costs.

The catalysts used in this test program only contained 2% of the active ingredient, and it was estimated that it would cost about \$0.14 to prepare one pound of catalyst. Based on the results of the experiments, the cost to reduce one ton of NO_x was in the tens of thousands of dollars. Currently, we have produced catalysts with ~10% active ingredient and estimate the cost to produce that catalyst at about \$0.05 per pound. This has dropped the estimated cost to remove one ton of NO_x to about \$3000. It is anticipated that during the next year or two the catalyst preparation cost will drop to below \$0.04 per pound and that we will be able to prepare catalysts with more than 15% active ingredient – this will reduce the cost per ton of NO_x removed to less than \$1000. These new formulations will be investigated during the next pilot-scale testing phase.

With continued improvements and cost reductions, this new combustion catalyst technology may be a solution for facilities that cannot afford the expensive capital investment of SCR, but need to reduce emissions in conjunction with low-NO_x burners to meet the new more stringent regulations.

Task 4: Estimate Cost of Pilot-scale Testing and Demonstration

The objective of Task 4 was to estimate the cost of performing a series of pilot-scale (~300lb/hr) test-burns and to estimate the cost of a demonstration in a 50-100 MW boiler. Included in this work is a projected time line and cost to commercialize this technology.

The next step in testing the idea of adding a pre-combustion catalyst to reduce NO_x emissions is to go to a larger scale testing apparatus that has the capability of low-NO_x burner firing. The combustion facilities at the University of Utah in Salt Lake City, UT house a five million BTU/hr experimental furnace that has low-NO_x burners and analysis equipment to measure emissions. The cost of performing this testing is estimated to be about \$15,000 per week of testing. The proximity of the facility will allow little to no travel fees and convenience when transporting coal samples from the preparation laboratory in Provo, UT. The scope of the pilot tests will again be to identify the feasibility of using a pre-combustion catalyst that results in less NO_x emissions. The catalyst effectiveness will be combined with conventional low-NO_x firing methodologies in these pilot-scale tests.

One of the critical components of the pilot-scale tests will be to develop a methodology for adding the catalyst in the most cost-effective and efficient manner. Several options are available; however two seem to be the most practical. The first is to add the catalyst on the crushed coal prior to pulverization – similar to what is done at synfuel plants currently. The second is to add the catalyst to the pulverized coal after the mill and before the burner. This method should provide the best coverage, but may be more difficult to accomplish. These options will be evaluated in the pilot testing.

The field-scale demonstration will be performed at a smaller approximately 50-100 MW boiler, hopefully at one of the industrial sites in the Salt Lake area. This test will build on the results from the bench-scale and pilot-scale tests. Only the most effective and economic catalysts will be tested at this level. Feed stock for this testing will have to include industry application methods including modifications needed at one of the existing synfuel plants to prepare the sample. The cost of this testing is estimated to be about \$750,000 plus labor costs.

After the successful completion of a field test, commercialization will be targeted. This testing would include burning the catalyst-applied coal in a utility boiler of about 250 MW size. The estimated cost of this commercialization tests are estimated to be about \$1.5 million plus labor. A five-year commercialization test plan has been outlined by Headwaters and is outlined below:

- 2003-2004 – Bench-scale testing to prove concept and screen catalysts
- 2004-2005 – Additional bench-scale testing and theoretical work to understand chemistry, thermodynamics and kinetics and begin pilot-scale testing. A go/no go decision will be made following these tests.
- 2005-2006 – Test technology in field-scale combustion test and begin commercialization
- 2006-2007 – Complete commercialization testing and take product to market

The future-testing outline shown in Task 4 implements the idea of finding success at each level before moving on to larger-scale testing, this plan has been agreed upon by Headwaters Management.

SECTION 5:

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

More than 100 bench-scale, proof-of-concept tests were completed with more than 30 different catalysts, using two different coal types, under oxidizing and reducing conditions to determine if a pre-combustion catalyst could be utilized as a NO_x reduction technology. The concept is to combine an effective catalyst with low-NO_x burner technology and/or combustion technologies such as SNCR, reburning, etc. to reduce NO_x emissions to acceptable regulatory limits. The coals used were a Pittsburgh 8 and a Powder River Basin (PRB).

Two sets of catalysts were prepared: nano-catalysts, relying on Headwaters confidential preparation technology, and common catalysts that are readily available in the industry. From these tests and evaluations, the following conclusions are made:

- There is a distinct difference in nitrogen release between Pittsburgh 8 coal and the PRB coal with the PRB showing the higher release rates, 50% compared to 30%.
- More than 75% of all catalysts evaluated were effective in increasing nitrogen release in the PRB coal.
- Only 5 of the 31 catalysts were effective in increasing nitrogen release in the River Hill coal.
- The nano-catalysts were most effective in increasing nitrogen release on the target coal, River Hill; but the common catalysts were more effective on PRB coal.
- The maximum increase in nitrogen release for the River Hill bituminous coal was over 30%, while the maximum increase for the PRB coal was just over 20%.
- These initial nano-catalysts contained only 2% active ingredient and dosage rates up to 2.5% were utilized. Recent work has demonstrated that the nano-catalysts can be prepared with more than 10% active ingredient and dosage rates lower than 1.5% can be used.
- Preliminary economic estimates suggest that a pre-combustion catalyst will be cost competitive with current combustion NO_x control technologies.
- Pilot-scale testing with a low-NO_x burner is necessary to evaluate the technology in an actual combustion system.

In summary, development of a pre-combustion nano-catalyst with a high percentage of active ingredient and low dosage rate is expected to provide three significant advantages in NO_x control at coal-fired power plants:

- increased release of nitrogen gas from coal prior to combustion, thus reducing the amount of NO_x produced,
- lower catalyst cost than conventional catalyst and
- significantly reduced amount of ash production compared to conventional catalyst due to lower overall weight of nano-catalyst added to the coal prior to combustion.

Recommendations

This test program led to the following recommendations:

- Continued efforts should be made to improve the nano-catalysts preparation and active ingredient concentrations.
- Additional screening and bench-scale combustion tests should be conducted to evaluate a wider range of possible catalysts, including improved nano-catalysts.
- Pilot-scale combustion tests should be conducted on only the most promising, in terms of effectiveness and economics, of the catalysts evaluated from the bench-scale tests.
- Discussions should occur with potential catalyst suppliers to evaluate production methodologies.
- An initial investigation should be done to locate a small boiler (50-100 MW) as a potential demonstration site.
- An evaluation of alternative methods of applying the catalyst to the coal should begin.
- The economic estimates should be continually refined.

SECTION 6: REFERENCES

Mori, H., K. Asami and Y. Ohtsuka, "Role of Iron Catalyst in Fate of Fuel Nitrogen during Coal Pyrolysis," *Energy & Fuels*, 10, 1022-1027, 1996.

Ohtsuka, Y., T. Watanabe, K. Asami and H. Mori, "Char-Nitrogen Functionality and Interactions between the Nitrogen and Iron in the Iron-Catalyzed Conversion Process of Coal Nitrogen to N₂," *Energy & Fuels*, 12, No. 6, 1998.

Tillman, D. A. and N. S. Harding, *Fuels of Opportunity: Characteristics and Uses in Combustion Systems*, Chapter 4, El Sevier, 2004.