**Oxygen-enriched Coal Combustion with Carbon Dioxide Recycle and
Recovery: Simulation and Experimental Study**

Semiannual Report

1 September 2000 – 1 March 2001

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April 2001

Project DE-FG26-00NT40828

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Abstract

This report examines coal combustion using oxygen feed with carbon dioxide recycle to control the adiabatic flame temperature. Computer simulations using an existing state-of-the-art 3-dimensional computer code for turbulent reacting flows with reacting particles were employed to study the effects of increased carbon dioxide mole fraction on the char burnout, radiant heat transfer, metal partitioning, and NO_x formation.

TABLE OF CONTENTS

Disclaimer:.....	i
Abstract.....	ii
Introduction.....	1
Task 1(Completed) Summary of literature search on O ₂ -CO ₂ Combustion.....	2
Task 2: Setup of Model Using Best-Available Data.....	3
Experimental.....	3
Results and Discussion	4
Table 1: List of Simulations carried out	4
Task 3: Key Variables to be studied (Metal Vaporization)	9
Task 4: Metal Vaporization Model.....	10
Conclusion	13
Remaining Tasks in Project	13
Task 5: Design of Future Experimental Studies	13
Task 6: Publication of results.....	13
References.....	14

Oxygen Enriched Coal Combustion with Flue Gas Recycle

Introduction

Concerns over the role of greenhouse gases in forcing global warming have led to international agreements like the Kyoto Protocol, that have set targets for controlling carbon dioxide emissions. Achieving these goals will require emissions trading, increasing energy efficiency, fuel substitution, and changes in combustion practice. Coal is an abundant, low cost fuel but with a high ratio of carbon to hydrogen, making CO₂ control a major concern for the future use of coal. In lieu of our growing energy demands, carbon sequestration provides an alternative to sharply reducing coal use. Carbon sequestration can be defined as the capture and secure storage of the carbon that is emitted as a result of human activities as well as the carbon that is already present in the atmosphere. However, it is necessary that the concentration of CO₂ in the gas or liquid stream be more than 90% before it can be injected into the oceans or deep underground geological formations. Concentrated high pressure CO₂ can also be injected into oil wells to dissolve the CO₂ in the oil, this not only causes the oil to expand but also decreases its viscosity and surface tension resulting in enhanced oil recovery.

Ordinarily coal combustion results in only about 15% CO₂ in the flue gas. The capture of CO₂ from the flue gas for sequestration is made difficult due to its relatively low concentration and the presence of other gaseous species like sulfur oxides that interfere with its separation. As an alternative, nitrogen can be separated from the air stream prior to combustion. However, combustion with pure oxygen results in very high flame temperatures that the current materials of construction cannot withstand. A novel method of using enriched oxygen for coal combustion with flue gas recycle to control the adiabatic flame temperature is being investigated so that the new technology can easily be applied as a retrofit to existing boilers. This method results in more than 90% CO₂ in the flue gas.

Experimental and 1-D computer modeling studies [1-4] have shown that dry and wet recycle conditions do exist at which the heat transfer rates are similar to those in conventional boilers. This project will involve carrying out 3-D computer simulations of the coal-fired boiler employed by [4] in their study at the base (combustion with air)

condition, a dry (remove water by condensation) and a wet (not removing water by condensation) recycle conditions. The results obtained from the simulations will be compared with the experimental and modeling results of [4] to find out if the applicability of the CFD software that is being used can be extended to study combustion under these novel conditions. The study will progress by first carrying out similar simulations on natural gas fired boilers for simple geometries and then gradually proceeding towards coal-fired boilers and actual boiler geometries and conditions. The results obtained from the modeling studies will be used to design future experimental studies on two research furnaces located at the University of Utah.

The formation of sub-micron aerosol during coal combustion is known to be due to the phenomena of coal ash vaporization. Sub-micron particles are not easily captured by air-pollution control devices and have long atmospheric residence time thereby raising atmospheric and health concerns. The results from the modeling will be given as input to a metal vaporization model [10,11] in order to study and compare the extent of metal vaporized from coal under the different operating conditions.

Task 1(Completed)

Summary of literature search on O₂-CO₂ Combustion

A 1-D model was developed by Argonne National Laboratory to simulate and compare the heat transfer characteristics of burning coal in a mixture of CO₂ and O₂ rather than air [1]. Their results showed little differences between the predicted theoretical values and experimental values of the exit temperature and the amount of heat transferred and that CO₂/O₂ ratios between 2.23:1 and 2.42:1 imitate heat transfer characteristics of a conventional air burn. In a subsequent paper [2] they made comparisons for the axial distributions of the component mass fractions of coal, axial temperature, O₂, CO, CO₂ concentrations and combustion efficiencies between experimental and modeling studies with a 1-D model (1-DICOG). This study confirmed that the combustion of pulverized coal could be completed in a CO₂/O₂ atmosphere over a range of mole ratios between 2.23 and 3.65. Pilot scale experiments and the use of a boiler performance model were able to demonstrate the feasibility of recovering CO₂ by using flue gas recycle to control the temperature [3]. Studies have also been carried out that employed pressurized combustion and combined cycles to increase the efficiency of

the combustion process in different concentrations of O_2 and CO_2 [5]. However O_2/CO_2 – pulverized coal burners are associated with reduced ignition stability and simulation studies by [6] have shown that the addition of an oxygen injection nozzle to the burner improves the ignition stability. Studies have also shown reduced emissions of NO_x in enriched oxygen combustion with flue gas recycle [7]. Design, economics and life cycle analysis of a power plant operating under these conditions have also been previously done [8-9].

Task 2: **Setup of Model Using Best-Available Data**

Experimental

Simulations of a coal-fired boiler with a capacity of 10 Mbtu/hr are being carried out. Details of the furnace are available elsewhere [4]. The current version of GLACIER, a three-dimensional code for turbulent reacting flows and reacting particles provided by Reaction Engineering International is being used to carry out the simulations. GLACIER solves the continuity and Navier-Stokes equations in an Eulerian framework with particle source terms representing the coupling between the particle phase and the fluid phase. The k- ϵ model is used to model the turbulence and the differential equations are favre-averaged and the resulting Reynolds-stress terms are modeled with an eddy diffusivity. This code assumes that the chemical reaction rates are limit (ed by turbulent mixing and not by kinetics, local equilibrium is assumed for fast reacting gas phase based on the mixture fraction and is used to calculate the local gas concentrations. A metal vaporization model [10-11] is being used as a post processor to study ash vaporization.

A brief description of the furnace is given below [4]:

Boiler Type: Tower Furnace (indirectly fired)

Boiler Capacity: 10 Million Btu/hr

Geometry: 4 ft* 4ft*16.5 ft (internal dimensions)

Burner: Single, variable swirl coal burner. Fired from the top. The burner is being fed by two streams.

- (1) Mixture of oxygen and recycled flue gas.
- (2) Pulverized coal entrained in recycle flue gas.

A swirl number of 0.75 is currently being used.

Boiler Walls: 3" Refractory with 1" Water Jacket (to reproduce typical boiler temperature histories).

Coal: Sub-Bituminous coal from Wyoming (Black Thunder).

Size(μm)	Mass Fraction
400	0.075
250	0.075
200	0.1
125	0.1
100	0.1
65	0.05
50	0.05
30	0.45

Test Conditions: Boiler operating at full capacity with 3.5% O₂ (dry basis) in the exit flue gas.

Results and Discussion

Table 1 lists the different modeling studies that have been carried out so far.

Table 1: List of Simulations carried out

Furnace	Geometry (in meters)	Nodes	Operation	Comments
Hot Box	10*1*1	24,150	5 MBtu/hr, Natural Gas and Air	
Hot Box	10*1*1	24,150	5 MBtu/hr, Natural Gas CO ₂ /O ₂ =2.92	A comparative study carried out.
Hot Box	4.95*1.2*1.2	3168	10 Mbtu/hr, Coal and Air	
Hot Box	4.95*1.2*1.2	3168	10 Mbtu/hr, Coal and (CO ₂ +H ₂ O)/O ₂ =2.94	A comparative study carried out
Argonne Furnace	4.95*1.2*1.2	135,000	10 Mbtu/hr, Coal and Air	
Argonne Furnace	4.95*1.2*1.2	135,000	10 Mbtu/hr, Coal and	

			(CO ₂)/O ₂ =2.66	
Argonne Furnace	4.95*1.2*1.2	135,000	10 Mbtu/hr, Coal and (CO ₂ +H ₂ O)/O ₂ =3.00	A comparative study in progress
Configured Furnace Simulator (CFS)	58*15*11	30,000	Full Scale Boiler	A comparative Study of Base case and CO ₂ recycle case in progress
	43*13*8	506,660	Full Scale Boiler	A comparative Study of Base case and CO ₂ recycle case in progress

Flow conditions

Stream	Air	Dry Recycle = 2.66	Wet Recycle = 3.0
Coal feed rate (Kg/sec)	0.127	0.127	0.127
Primary Stream	Air at 530.2 K, 0.2284 Kg/sec, O ₂ = 21%, N ₂ = 79%	Oxidant at 362.4 K, 0.2328 Kg/sec, O ₂ = 10%, N ₂ = 5%, CO ₂ = 68%, H ₂ O = 16%	Oxidant at 511.3 K, 0.2395 Kg/sec, O ₂ =9%, N ₂ =6%, CO ₂ =53%, H ₂ O=32%
Secondary Stream	Air at 530.2 K, 0.9136 Kg/sec O ₂ = 21%, N ₂ = 79%	Oxidant at 362.4 K, 1.1481 Kg/sec, O ₂ = 17%, N ₂ = 4.7%, CO ₂ = 63.4%, H ₂ O = 14.9%	Oxidant at 511.3 K, 1.204 Kg/sec, O ₂ =16.7%, N ₂ =5.4%, CO ₂ =48.5%, H ₂ O=29.3%

Grid Size: 150*30*30 (135,000 nodes)

Figure 1 shows the results of axial gas emissivities obtained for dry recycle and base case for “Preliminary studies” carried out on a 10m*1m*1m Natural Gas Fired

Furnace. Notice the higher emissivity for the CO₂ Recycle case due to the higher concentration of CO₂ within the furnace (Polar molecules like CO₂, H₂O and CH₄ have distinct absorption bands associated with their vibrational and rotational modes and radiation is able to escape through windows between these strongly absorbed wavelengths. This explains the higher emissivity of the gases for the CO₂ recycle case).

Figure 1: A comparison of axial gas emissivity for dry CO₂ recycle with the air combustion case as calculated by GLACIER for natural gas combustion.

A comparison of the net heat transferred to the wall (Figs 2), in our preliminary study with the natural gas fired furnaces also shows that heat transfer rates are comparable at certain recycle conditions. The recycle condition shown here is CO₂/O₂ molar ratio of 2.92 in the oxidant.

A	-10000.000
B	0.000
C	10000.000
D	20000.000
E	30000.000
F	40000.000
G	50000.000
H	60000.000

A	-10000.000
B	0.000
C	10000.000
D	20000.000
E	30000.000
F	40000.000
G	50000.000
H	60000.000

Figure 2: Net Heat Transferred to the wall of a natural gas fired furnace (flue gas recycle).

Figure 3: Shows a comparison of the axial gas temperature profile for our model (base case) with that of the Argonne Furnace.

We expect the match to get closer as we continue to work on improving our wall boundary conditions by modeling the cooling panels and the refractory more accurately.

In fact when runs were conducted with a wall heat resistance of $0.001 \text{ m}^2\text{-K/W}$ throughout the furnace the outlet temperature (1427.3K) was comparable to the experimentally obtained temperature (1355 K).

At present we are getting about 70% CO₂ (on a dry basis).

SO₂ (expected) = 560 ppm

Obtained = 1965 ppm

Oxygen concentration in the exit is not 3.5%, CO₂ concentration lower than expected and CO concentration higher (0.1%).

Temperature-Time History

Figure 4 shows a comparison of the temperature-time histories and the temperature profiles of the GLACIER simulations with the Argonne furnace. Our models

temperature –time history is that tracked for a single coal particle whereas the experimental and model profile for the furnace is the gas temperature.

Figure 4: A comparison of GLACIER (particle temperature) with the measured gas temperature in the Argonne furnace

Task 3: Key Variables to be studied (Metal Vaporization)

Vaporization of metal oxides from a burning char occur as a result of the reducing conditions occurring within a char particle and are suspected to proceed according to the carbothermal reduction reactions $MO + CO \rightarrow M + CO_2$. The volatile sub-oxide formed vaporize and diffuse to the surface of the char where they re-condense to form the original metal oxide upon contact with oxygen and form the nucleus of the sub-micron vapor.

Sub-micron particles are not easily captured by air-pollution control devices and have long atmospheric residence time thereby raising atmospheric and health concerns. The results from the modeling will be given as input to a metal vaporization model [10,11] in order to study and compare the extent of metal vaporized from coal under the different operating conditions.

Task 4: **Metal Vaporization Model**

The formation of sub-micron aerosol during coal combustion is believed to be due to the phenomena of coal ash vaporization. Coal char contains various metal oxides. Under, combustion conditions these metal oxides form volatile sub-oxides as a result of the reducing conditions found within the char particle. These sub-oxides vaporize easily (as a result of their higher vapor pressure) and diffuse to the surface of the char. On encountering oxygen in the bulk gas phase, the sub-oxide is re-oxidized to form the original oxide that condenses and forms the nuclei of the sub-micron particle. This study will involve making modifications to a metal vaporization model in order to get an accurate measure of the reducing conditions within the burning char and then use the model as a post processor to study and compare the metal vaporization that occurs under flue gas recycle conditions with that under conventional firing. It is suspected that the increased concentration of CO_2 under recycle conditions would suppress ash vaporization.

In order to study this phenomenon it is important to have an accurate prediction of the reducing conditions within a char particle. The mathematical model developed by [12] assumed that CO was the only primary product of the heterogeneous reaction of carbon, however CO_2 is also produced and this affects the metal-metal oxide equilibrium at the surface of the mineral inclusion. Efforts are on to determine the CO/CO_2 ratio within char particles at different temperatures. The temperature of the burning particle will also have to be corrected since the formation of CO_2 releases much more heat than when CO alone is the primary product of combustion. Also, the CO_2 diffusing out will affect the rate of diffusion of oxygen, and hence the burning rate. The following figure

shows that if we account for the formation of CO_2 , the calculated particle temperature is much more than the predicted temperature without accounting for CO_2 formation. As a result of the increased temperature the vaporization rates should also increase. However, the presence of CO_2 tends to suppress the amount of metal vaporized. Hence, it would be interesting to find out how the vaporization phenomena are affected by these two opposing effects. Efforts are on in this direction.

Figure 5: The temperature of a burning char particle with and without accounting for the formation of CO_2 as a product of the heterogeneous reaction. (old = CO is the only product of heterogeneous carbon reaction, new = Both CO and CO_2 are products of the heterogeneous reaction of carbon, rp = radius of the particle)

Figure 6 compares the amount of Aluminum vaporized experimentally (FV(exp)) with the calculated amount of Aluminum vaporized by the old model (FV(calc)) for different types of coals (labeled in the x-axis). It can be seen that for inclusion sizes between 1 and 5 microns the model fits the experimental data. Figure 7 compares the amount of Aluminum vaporized experimentally (FV(exp)) with the calculated amount of

Aluminum vaporized by the new model (FV(calc)) that accounts for the increased temperature rise resulting from CO₂ formation for different types of coals (labeled in the x-axis). It can be seen that for inclusion sizes close to 40 microns the model fits the experimental data.

Figure 6: A comparison of the amount of Aluminum vaporized experimentally (FV(exp)) with the calculated amount of Aluminum vaporized by the old model (FV(calc)) for different types of coals (labeled in the x-axis).

Figure 7: A comparison of the amount of Aluminum vaporized determined experimentally(FV(exp)) with the amount of aluminum vaporized as calculated by the improved model (FV(calc))

Conclusion

Work is proceeding according to the original plan. The work to date shows the feasibility of using existing modeling tools to study oxygen-enriched combustion with CO2 recycle.

Remaining Tasks in Project

Task 5:
Design of Future Experimental Studies

Task 6:
Publication of results

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