

2011 Fall Technical Meeting
 of the Western States Section of the Combustion Institute
 Hosted by the University of California at Riverside, Riverside, CA
 October 16-18, 2011
 Paper # 11F-72

Experimental investigations of pulverized coal char reactions with oxygen, carbon dioxide and steam

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Abstract

Predictive modeling of the performance of a coal-fired boiler under oxy-fuel conditions is dependent on fundamental data of how coal chars burn in these environments. An oxy-fuel boiler will contain much higher concentrations of carbon dioxide and steam than a traditional air-fired boiler. Higher concentrations of oxygen are also required to match the combustion temperature and heat transfer rates of a traditional boiler. In this work, chars are generated from two bituminous and one sub-bituminous coals and combusted in different environments in Sandia's optical entrained flow reactor. Oxygen concentrations range from 24-60 vol-%, steam concentrations range from 10-16 vol-%, and both nitrogen and carbon dioxide are used as a diluent. The coal chars burn hotter when N₂ is the diluent rather than CO₂, at lower steam concentration, and at higher oxygen concentration. Photographs also suggest that faster conversion is achieved at higher oxygen and/or steam concentrations. Implications of these observations are discussed, including differing transport properties and the importance of gasification reactions in an oxy-fuel environment.

1. Introduction

Among the promising means of carbon capture and storage from coal-fired power plants is oxy-combustion. Oxy-combustion involves the separation of oxygen from air before introduction to the boiler, and then combustion of the solid fuel with pure oxygen diluted with recycled flue gas to control the temperature. Recycle could occur before or after moisture removal, but the recycle stream (which is primarily CO₂) is likely to contain some amounts of moisture [1]. After condensing out the moisture, the oxy-combustion effluent is highly-concentrated CO₂, which can be readily condensed, transported, and stored. At the University of Utah, a DQMOM/LES formulation for heterogeneous chemistries has been developed [2] for which validation and verification data is necessary for predictive modeling of the oxy-combustion of coal. A predictive model with quantified uncertainty will allow the rapid development of new build and retrofit oxy-combustion boilers.

For a retrofit application, recirculation of the flue gas could cause CO₂ levels in the furnace to approach 60-70 vol-%., and water vapor levels of up to 25-35 vol-% in post-flame furnace

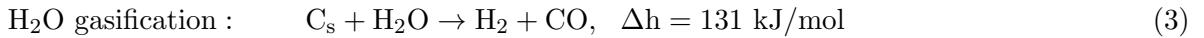
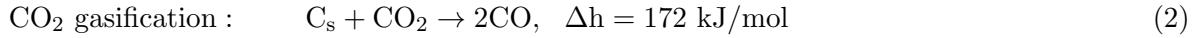
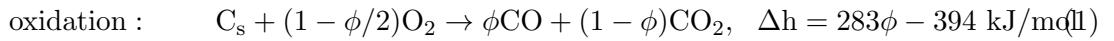
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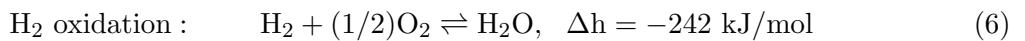
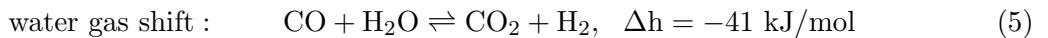
gases. Both CO_2 and H_2O have higher molar heat capacities than N_2 , and are radiantly active gas species while N_2 is not. These gas properties will cause obvious heat transfer differences between air-fired and oxy-combustion environments. In addition, oxygen diffuses more rapidly through N_2 than CO_2 , but more rapidly through H_2O than either N_2 or CO_2 , which will change the mass transfer characteristics during oxy-combustion. Previous research has shown that the substitution of CO_2 for N_2 delays coal ignition and reduces the rate of coal volatile consumption, for a given furnace temperature and oxygen concentration [3–5]. A reduced burning rate in a oxy-combustion environment has been attributed to the reduced rate of oxygen diffusion in the boundary layer [5–7].

In addition to these known effects, with such elevated levels of CO_2 and H_2O , gasification reactions, which are traditionally neglected for air-fired combustion may begin to impact the char combustion rate and temperature. There has been some evidence that gasification reactions enhance the combustion rate under oxy-combustion conditions [8–10], but the high endothermicity of the gasification reactions lowers the combustion temperature, complicating the effects of these reactions. In some recent modeling efforts, we found that when a char particle is reacting at a temperature near the gas temperature (i.e. when there is a low O_2 concentration in the surrounding gas), the CO_2 gasification reaction increases the overall consumption of solid carbon, but only by a small amount. Alternatively, when the particle is reacting at a temperature considerably higher than the ambient gas temperature (i.e. in a high O_2 concentration environment), the CO_2 gasification reaction decreases the overall carbon removal rate, again by a small amount [11]. With a different treatment of the surface area, we found that although both the CO_2 and H_2O gasification reactions reduced the combustion temperatures, the char carbon removal rate slightly increased in a wide range of environments [12].

Even for a single char particle reacting in a quiescent environment and considering only global reactions there are many transport and kinetic phenomena involved. From the bulk gas, there is transport of reactants and inerts, which in the current study consists of N_2 , CO_2 , H_2O , and O_2 . Heterogeneous reactions occur at the char particle surface, including



Gas diffuses into and out of the pores in the char particle where further reactions may take place, and products diffuse through the boundary layer back into the bulk gas. Gas phase chemistry can occur in the boundary layer and in the pores of the particle as well, with reactions including



In this work, fundamental data of single coal char particle combustion in oxy-combustion environments are reported. Combustion in a wide range of gaseous environments were studied to isolate contributions to heterogeneous carbon consumption by oxygen, steam and carbon dioxide. This data will provide insight into important reactions and transport phenomena for validation and verification of a model for the oxy-combustion of coal chars.

2. Method

Three coals were chosen for this work. A representative high volatile bituminous coal from the Illinois #6 seam, a western bituminous coal from the Utah Skyline mine, and Black Thunder sub-bituminous coal from the Powder River Basin (PRB). A proximate and ultimate analysis of

Table 1: Proximate and Ultimate analyses for the three project coals

Coal	Black Thunder	Utah Skyline	Illinois #6	
Moisture	23.69	3.18	9.64	wt-%, as received
Ash	4.94	8.83	7.99	wt-%, as received
Volatile Matter	33.36	38.6	36.78	wt-%, as received
Fixed Carbon	38.01	49.39	45.58	wt-%, as received
C	75.27	80.24	78.51	wt-%, dry, ash free
H	5.03	5.75	5.49	wt-%, dry, ash free
N	1.09	1.61	1.36	wt-%, dry, ash free
S	0.32	0.60	4.83	wt-%, dry, ash free
O (by diff)	18.29	11.80	9.81	wt-%, dry, ash free
HHV	12720	14327	14080	BTU/lb., dry, ash free

these coals is shown in Table 1. The PRB coal has the lowest fixed carbon, the highest moisture content, and the lowest heating value. The two bituminous coals are similar in composition and heating value, although the Illinois #6 coal has a higher sulfur content.

These coals were first devolatilized using a drop tube furnace at the University of Utah. The furnace was operated at 1200 °C while flowing 15 SLPM nitrogen with approximately 1 vol-% oxygen to burn off any tars that might be generated during devolatilization. The furnace has an ID of 5 cm and a heated length (of temperatures between 1000 and 1200 °C) that is about 60 cm long. This led to a residence time of about 0.9 sec. Chars were collected and then sieved into 6 narrow size bins (53-63 μ m, 63-75 μ m, 75-90 μ m, 90-106 μ m, 106-125 μ m, and 125-150 μ m). Interestingly, the majority of PRB char was smaller than the parent coal (likely through fracturing and loss of volatiles), the Utah Skyline char was roughly the same size as the parent coal, while the Illinois #6 chars seemed to swell during devolatilization.

Chars in the narrowly sieved size bins were then fed into the Sandia's optical entrained flow reactor that has been described previously (see, e.g.[13]). A flat-flame Hencken burner is used to generate a high-temperature, well characterized environment into which the char particles are fed. As the particles flow upwards in the reactor, optical diagnostics simultaneously measure size, velocity, and temperature of individual particles. Twelve different environments were used in this study, two at 24 vol-% O₂, with 14 vol-% H₂O, and a balance N₂ or CO₂. Four at 36 vol-% O₂, with 10 and 14 vol-% H₂O, and a balance of N₂ or CO₂, and 6 at 60 vol-% O₂, with 10, 14 and 16 vol-% H₂O, and a balance N₂ or CO₂. Significantly oxygen-enriched conditions were chosen so that oxidation reactions would increase the combustion temperature, and the rate of the gasification reactions to measurable levels. Intuition might suggest that at high temperatures reactions would proceed very fast leading to diffusion limitations, but Murphy and Shaddix found that char particles react under increasing kinetic control at higher oxygen concentrations because of the higher oxygen flux available to the particle at these elevated oxygen concentrations[13]. When nitrogen was used as a diluent, the Hencken burner was operated at an adiabatic flame temperature of 1750 K, and with the CO₂ diluent, at 1850 K. A thermocouple was used to measure the reactor temperatures, and these conditions produced similar temperature profiles that all peaked around 1650 K. Temperature, velocity and size measurements were made at 3-7 heights for around 100 particles in each of the size bins in all of the environments.

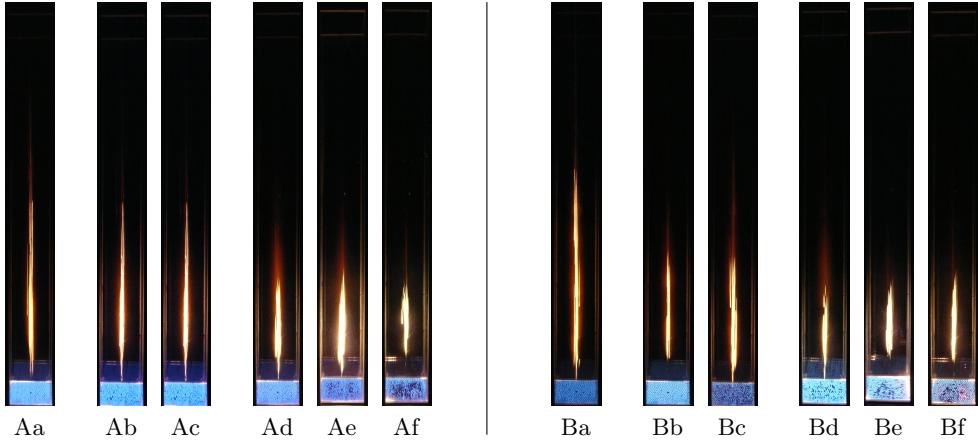


Figure 1: Digital photos of $90\text{-}106\text{ }\mu\text{m}$ Utah Skyline char combustion in different environments. Capital letter A denotes a diluent (balance) gas of CO_2 and capital B denotes a N_2 diluent. Lowercase letters denote: a) 24% O_2 , 14% H_2O b) 36% O_2 , 10% H_2O c) 36% O_2 , 14% H_2O , d) 60% O_2 , 10% H_2O , e) 60% O_2 , 14% H_2O , f) b) 60% O_2 , 16% H_2O . The bright blue at the bottom of the picture is the Hencken burner and the particles are flowing and reacting upwards in the pictures. The top of the picture is about 18 in above the burner, and the limit of the quartz chimney.

3. Results and Discussion

A commercial digital camera was used to take photographs of the reacting char particles. The aperture and exposure time were set manually in an attempt to gather consistent photos, but the char feed rate varied causing inconsistent particle loading during any given photo. Photographs of the reacting $90\text{-}106\text{ }\mu\text{m}$ Utah Skyline particles can be seen in Fig. 1 as a typical series. Trends in this figure are also evident in the other size bin photos, and for the different chars, although there is scatter due to the inconsistent feed rate. While these photos do not contain any quantitative information, qualitative information about burnout can be deduced from the length of the visible emissions, and the pixel brightness is related to temperature.

As one might expect, as the oxygen concentration increases, the lengths of the visible emission traces decrease, and the emission brightnesses increase. With a higher oxygen concentration in the bulk gas, greater diffusion of oxygen through the boundary layer allows the exothermic oxidation reaction to proceed at a higher rate. This lowers the time required for burnout (shorter visible emission) and increases the temperature at which the particles are burning (brighter emission).

The visible traces are noticeably shorter with the N_2 diluent compared to the CO_2 diluent, at a given steam and oxygen concentration. This can be attributed to the greater diffusivity of oxygen through N_2 than CO_2 [5–7]. Although the trend is not completely evident in this series of photographs, in the complete set of photos, there appears to be a trend of faster burnout as the steam concentration increases. This effect is not as pronounced as the variation due to oxygen concentration differences, but the variation in steam concentration (10–16 vol-%) is also much less than the variation in oxygen concentration (24–60 vol-%). This could be due to either (or a combination of) steam gasification reactions consuming the char at a greater rate, or the higher diffusivity of oxygen through steam than either CO_2 or N_2 . At 2000 K and 1 atm, the binary diffusion rate of oxygen through nitrogen is 5.2×10^{-3} , through CO_2 is 4.1×10^{-3} , through H_2O is 6.9×10^{-3} m^2/s .

There is also evidence of more spreading of the chars as they react in higher oxygen concentration environments in Fig 1. The complete set of photographs shows that the PRB and Illinois #6 chars stray from the centerline more than the Utah Skyline char. This lateral movement of the chars as they react is probably due to remaining volatile matter in the char jetting from the pores and propelling the particles away from the centerline. At higher reaction tem-

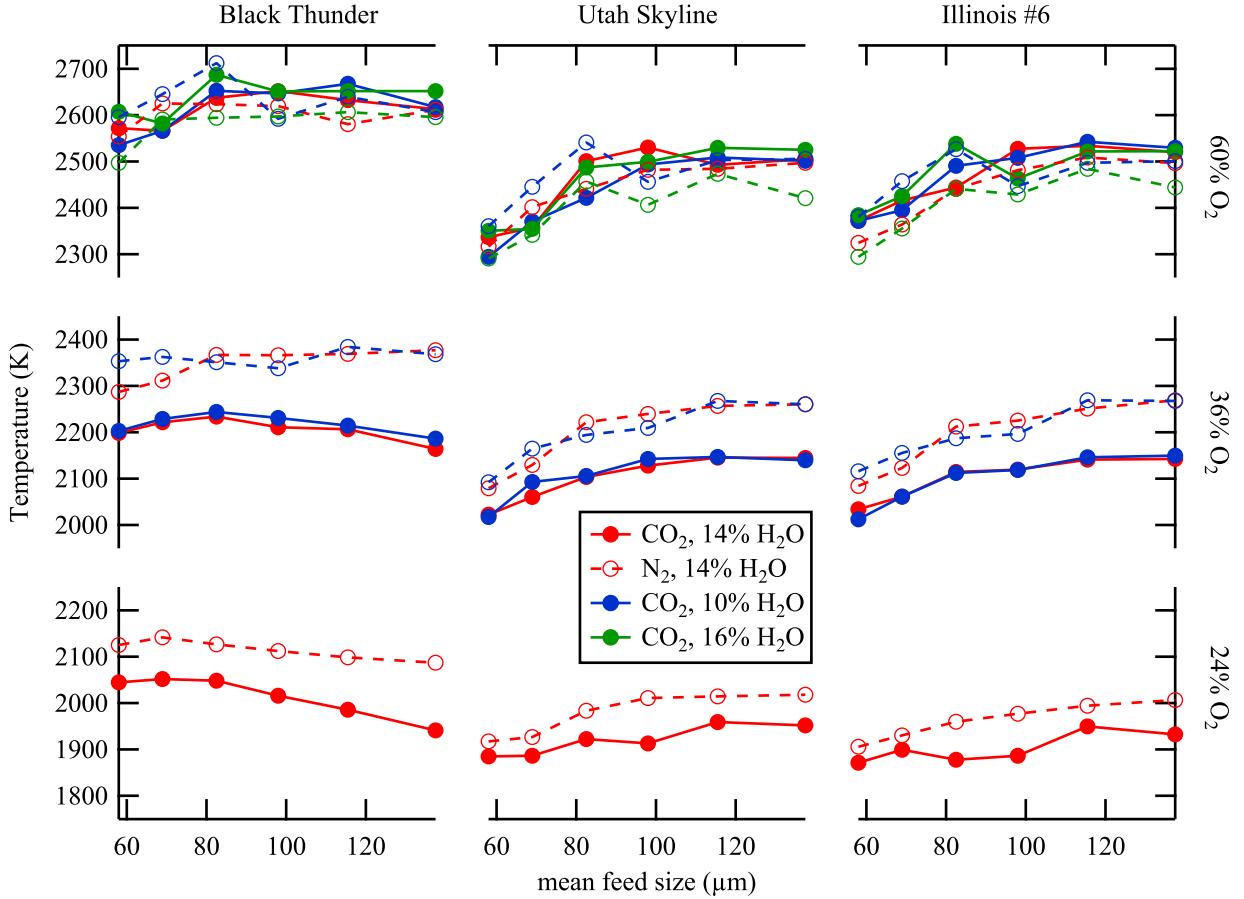


Figure 2: Char temperatures as a function of fed char diameter. Closed circles with solid lines have CO_2 as a diluent while open circles and dashed lines have N_2 as a diluent. Colors are different steam concentrations, and the oxygen concentration varies with the vertical frames, as shown on the right of the graph.

peratures (in the higher oxygen concentration environments), the rapid release of volatiles is more likely.

Quantitative measurements of temperature are shown in Fig. 2. As particles were reacting, temperature measurements were made at 3-7 heights of roughly 100 char particles. These measurements were averaged at each height, and the maximum temperature of these means are the temperatures plotted in Fig. 2. These temperatures are not a direct measurement of reactivity, but in general, higher temperatures for a given particle size correlate with higher combustion reactivity.

The more reactive sub-bituminous PRB char burns at a higher temperature than either of the two bituminous chars, which burn at about the same temperatures in all of the different environments. There is some dependence of temperature on particle size. For the Black Thunder char, the temperature seems to peak around $80 \mu\text{m}$, while the Utah Skyline and Illinois #6 char temperatures increase (although they appear to level off) up to the largest particle size. A trade off exists between heat losses and available reactive surface area, leading to the dependency of temperature on particle size.

At both 24 and 36% O_2 , there is an obvious influence of diluent on particle temperature. Particles combust about 100 K hotter with the N_2 diluent than with the CO_2 diluent. This is consistent with the photographic evidence in Fig. 1, and other experimental observations [5, 6]. However, at 60% O_2 , all of the curves seem to collapse, and there are no obvious trends in temperature either due to diluent or steam concentration. The hypodermic fuel tubes of the

Hencken burner had a tendency to clog at 60% O₂ (as can be seen by variations in flat-flame brightness in Fig. 1), leading to a more scatter in the data, making it more difficult to observe trends. The amount of diluent is significantly less with 60% O₂, with only 24-30% of the gas as a diluent, while there is 58-64% diluent in the 36% O₂ environment. Since the temperature difference between N₂ and CO₂ atmospheres is attributed to diffusion differences through the diluent, it is not too surprising that the difference decreases when there is very little diluent and a greater oxygen concentration. Independence of temperature from diluent may also be evidence of improved kinetic control in highly oxygen-enriched environments, as Murphy and Shaddix observed [13].

In the environments where the steam concentration was varied, there is no obvious trend of combustion temperature with steam concentration. However, as previously mentioned, the trace length in Fig. 1 decreased slightly as the steam concentration increased, suggesting faster burnout. An increase in the diffusivity of oxygen through steam would cause the exothermic oxidation reaction to proceed at a higher rate, and an increased concentration of H₂O would cause the endothermic steam gasification reaction to proceed at a higher rate. These two effects are in competition to limit the temperature change in these environments, but lead to a greater consumption rate of carbon because of the higher concentrations of reactants at the particle surface. A model has predicted little temperature change, but an increase in carbon consumption as the steam concentration increases when the gasification reactions are considered [12].

4. Conclusion

Coals from the Illinois #6 seam, Utah Skyline, and Black Thunder mines were devolatilized to form chars. These chars were sieved into six narrow size bins, and fed into Sandia's optical entrained flow reactor. Twelve gaseous environments were chosen for study, spanning a wide range of conditions, from 24-60 vol-% O₂, 10-14 vol-% H₂O, with CO₂ and N₂ diluents. In all environments, the sub-bituminous PRB char burns at the highest temperature with 80 μm particles burning at the highest temperature. Both bituminous chars increase in combustion temperature up to the largest mean fed char size of 140 μm . The substitution of CO₂ for N₂ lowers the combustion temperature in the 24 and 36 vol-%O₂ environments, due to the lower diffusivity of oxygen through CO₂ as compared to N₂. At 60 vol-%O₂, there was no discernible influence of combustion environment on combustion temperature, which may be a sign of improved kinetic control under highly oxygen-enriched combustion conditions. In all cases, there was no meaningful influence of steam concentration on temperature. Qualitative photos suggest that burnout occurs in less time as the steam concentration is increased, which could indicate that a higher steam concentration and the improved diffusion of oxygen through steam causes both exothermic oxidation reactions and endothermic steam gasification reactions to proceed at faster rates, but have little effect on temperature.

Analysis of this data is ongoing and samples of many of the chars reacting in these environments have been collected. Surface area and burnout measurements are being made on the collected samples which will quantify model parameters. A validated sub-model for combustion of coal chars in an oxy-combustion environment will be used in a DQMOM/LES CFD code for boiler design

5. Acknowledgments

This research was sponsored by the U.S. Department of Energy (DOE) under Award Number DE-NT0005015, managed by David Lang and through the National Energy Technology Laboratory's Power Systems Advanced Research Program, managed by Dr. Robert Romanosky. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for DOE's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

References

- [1] Y. Tan. *Oxy-fuel combustion for power generation and carbon dioxide (CO₂) capture*, chapter Oxy-fuel power plant operation, pages 35 – 53. Woodhead Publishing, 2011.
- [2] A. F. Sarofim, J. S. Lighty, P. J. Smith, K. J. Whitty, E. Eyring, A. Sahir, M. Alvarez, M. Hradisky, C. Clayton, G. Konya, R. Baracki, and K. Kelly. Chemical looping combustion reactions and systems task 5 topical report, utah clean coal program. Technical report, University of Utah, 2011.
- [3] A. Molina and C. R. Shaddix. Ignition and devolatilization of pulverized bituminous coal particles during oxygen/carbon dioxide coal combustion. *Proc. Combust. Inst.*, 31(2):1905 – 1912, 2007.
- [4] C. R. Shaddix and A. Molina. Particle imaging of ignition and devolatilization of pulverized coal during oxy-fuel combustion. *Proc. Combust. Inst.*, 32(2):2091 – 2098, 2009.
- [5] C. R. Shaddix and A. Molina. Ignition, flame stability, and char combustion in oxy-fuel combustion. pages 101 – 124, 2011.
- [6] C. R. Shaddix and A. Molina. Effect of O₂ and high CO₂ concentrations on PC char burning rates during oxy-fuel combustion. Proceedings of the 34th International Technical Conference on Coal Utilization and Fuel Systems, June 1-5, 2008.
- [7] M. B. Toftegaard, J. Brix, P. A. Jensen, P. Glarborg, and A. D. Jensen. Oxy-fuel combustion of solid fuels. *Prog. Energy Combust. Sci.*, 36:581–625, 2010.
- [8] P. Heil, D. Toporov, H. Stadler, S. Tschunko, M. Frster, and R. Kneer. Development of an oxycoal swirl burner operating at low O₂ concentrations. *Fuel*, 88(7):1269 – 1274, 2009.
- [9] R. K. Rathnam, L. K. Elliott, T. F. Wall, Y. Liu, and B. Moghtaderi. Differences in reactivity of pulverised coal in air (O₂/N₂) and oxy-fuel (O₂/CO₂) conditions. *Fuel Process. Technol.*, 90(6):797 – 802, 2009.
- [10] D. Toporov, P. Bocian, P. Heil, A. Kellermann, H. Stadler, S. Tschunko, M. Frster, and R. Kneer. Detailed investigation of a pulverized fuel swirl flame in CO₂/O₂ atmosphere. *Combust. Flame*, 155(4):605 – 618, 2008.
- [11] E. S. Hecht, C.R. Shaddix, A. Molina, and B. S. Haynes. Effect of CO₂ gasification reaction on oxy-combustion of pulverized coal char. *Proc. Combust. Inst.*, 33(2):1699 – 1706, 2011.
- [12] E. S. Hecht, C. R. Shaddix, M. Geier, A. Molina, and B. S. Haynes. Effect of CO₂ and steam gasification reactions on the oxy-combustion of pulverized coal char. *to be submitted 2011*.
- [13] J. J. Murphy and C. R. Shaddix. Combustion kinetics of coal chars in oxygen-enriched environments. *Combustion and Flame*, 144(4):710 – 729, 2006.