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Effects of Catalytic Mineral Matter on CO/CO₂ Ratio, Temperature and Burning Time for Char Combustion

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Quarterly Progress Report No. 2

January - March 1990

Prepared for

U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania
Technical Project Officer - S. Akhtar
Grant No. DE-FG22-89PC89774

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DOE/PC/89774--T7

DE93 008536

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Introduction

The high temperature oxidation of char is of interest in a number of applications in which coal must be burned in confined spaces. These include: the conversion of oil-fired boilers to coal using coal-water slurries, the development of a new generation of pulverized-coal-fired cyclone burners, the injection of coal into the tuyeres of blast furnaces, the use of coal as a fuel in direct-fired gas turbines and in large-bore low-speed diesels, and entrained flow gasifiers. In addition there is a need to better understand the temperature history of char particles in conventional pulverized-coal-fired boilers in order to better understand the processes governing the formation of pollutants and the transformation of mineral matter.

The temperature of a char particle burning in an oxygen containing atmosphere is the product of a strongly coupled balance between particle size and physical properties, heat transfer from the particle, surface reactivity, CO_2/CO ratio and gas phase diffusion in the surrounding boundary layer and within the particle. In addition to its effects on burning rate, particle temperature has major effects on ash properties and mineral matter vaporization. Measurements of the temperature of individual burning char particles have become available in recent years and have clearly demonstrated large particle to particle temperature variations which depend strongly on particle size and on particle composition. These studies, done with pulverized coal, do not allow direct determination of the CO_2/CO ratio produced at the char surface or the catalytic effects of mineral matter in the individual char particles and it has generally been assumed that CO is the only product of the carbon-oxygen reaction and that CO_2 is formed by subsequent gas phase reaction. More recent work, however, has pointed out the need to take CO_2 production into consideration in order

to account for observed particle temperatures.

The importance of the CO₂/CO ratio of carbon oxidation products is illustrated by examination of the heats of reaction for formation of these two products

The heat released by formation of CO₂ is a factor of 3.5 higher than for CO so the temperature of a particle will depend strongly on the CO₂/CO ratio produced. If gas diffusion through the boundary layer is fast, increased direct production of CO₂ produces a higher temperature and a higher burning rate. If the supply of oxygen to the surface is limited by diffusion through the boundary layer, production of CO₂ consumes half as much carbon as production of CO so carbon consumption rate is reduced even though temperature may be somewhat higher. Models of these complex interactions have been developed; however, the CO₂/CO ratio produced by the carbon-oxygen reaction must, at present be assumed or inferred from measurement of particle temperature.

CO₂/CO ratios can be strongly influenced by catalytic material in the carbon and by the char temperature. In this program we are measuring the CO₂/CO ratio for both catalyzed and uncatalyzed chars over a wide range of temperature. These results will then be used to develop predictive models for char temperature and burning rates.

Measurements of CO₂/CO ratio for an uncatalyzed char (spherocarb) were reported in the Oct-Dec 1989 progress report. This ratio varied from a maximum of 1.5 at 700 K and 100% oxygen to 0.06 at 1430 K and 5% oxygen.

In this report, the development of our kinetic model for both catalyzed and uncatalyzed char is discussed and predictions for the CO_2/CO ratio from calcium a catalyzed char are presented.

The electrodynamic TGA is being modified to allow operation at greater than atmospheric pressure and to provide improved temperature and position control. Progress on this modification is also discussed.

RESULTS

A. Kinetic modeling of CO_2/CO ratio

A model for oxidation of char has been under development in our laboratory for several years. (1, 2) The individual reactions in this model are:

where subscript f denotes the free carbon sites available for adsorption and the subscript E denotes those carbon sites with site energy between E and $E + \Delta E$. For CO formation, oxygen is adsorbed on the carbon sites to quickly form two C-O sites which decompose to form carbon monoxide and to regenerate a new carbon site. The number of sites is assumed to remain proportional to the surface area of the carbon. The energy distribution of these sites was experimentally found to be Gaussian.

For CO_2 formation, experimental evidence indicates that a separate set of sites is involved and that the action of calcium catalysis is to increase the number of these sites with no effect on the CO producing sites.

The CO_2 production reaction is first order in O_2 partial pressure, while the order for CO production at 820 K is .69. The fractional order for CO results from the distribution of site activation energies and will increase with increasing temperature to approach 1.0.

The effect of temperature on reaction rate with air is shown in Fig. 1 for pure soot and the same soot with 2 wt. % calcium added by ion exchange. At 800 K the rate for the catalyzed char is 50 times faster than for the uncatalyzed char. This reactivity ratio is predicted to decrease to approximately 2 at 1600 K. Experimental measurements at high temperature using catalyzed char are needed to establish the validity of this prediction.

Figure 2 presents the ratio of CO_2/CO for catalyzed and uncatalyzed chars.

For the uncatalyzed carbons the results for soot and for Spherocharb agree quite well with relatively little CO (10%) being produced at the highest temperatures. (These results were presented in greater detail in the preceeding progress report). The model agrees well with the data and predicts little change of CO_2/CO ratio with temperature for the highest temperatures.

For catalyzed soot a single low temperature data point is available. The model predicts a CO_2/CO ratio of approximately 10 at the highest temperature thus predicted an extreme sensitivity of this ratio to catalyses. Since all coals contain mineral matter widely varying, CO_2/CO ratios can be anticipated for coal chars in which mineral composition and amount can differ. Measurement of CO_2/CO ratio is expected to offer a method of evaluating the

Fig 1
Effect of Temperature on the
Relative Reaction Rates of Catalyzed
and Uncatalyzed Chars

Fig 2

Effect of Temperature on the CO_2/CO Ratio
for Catalyzed and Uncatalyzed Chars

key: $\square$ Catalyzed soot data
 $\circ$ Uncatalyzed soot data
 Δ Spherocharb
 --- Model calculation for catalyzed soot.
 — Model calculation for STI uncatalyzed soot.

degree to which a coal sample is catalyzed and, therefore, offers a method of evaluating reactivity.

B. Construction of Upgraded Electrodynamic Balance

A new electrodynamic balance capable of operating up to 25 atm pressure, was constructed and installed. The old chamber was limited to atmospheric pressure chamber operation and was not designed to prevent gas leakage. Advantages of this new system are:

1. Better control of gas composition
2. Extension of CO_2/CO ratio and oxidation rate measurements into the pressure regime relevant to gasification and gas turbine combustion.
3. More extensive testing of oxidation models.
4. More accurate determination of surface area by room temperature CO_2 adsorption measurement.

An improved position control system was also installed. The system is similar to the system development of E. Bar-Ziv, at Ben-Gurion University, Israel. The system comprises a He-Ne laser that illuminates the suspended particle, a 128 linear photo-diode array (PDA), and a computer. The particles shadow is measured by the PDA which is then transferred to the computer for tracing the position. A controller uses the position to calculate a value related to the error position (with respect to the center of the chamber). The system is capable of sampling at a frequency of 500 Hz and the response time of the controller is about 200 ms.

Future Program

During the next quarter it is anticipated that construction of the upgraded

electrodynamic TGA will be sufficiently advanced to allow initiation of oxidation experiments.

These will include:

- o Oxidation of uncatalyzed spherocarb to establish correspondence with the results of the first quarter work.
- o Oxidation of spherocarb catalyzed with calcium or iron. Critical temperature for charge loss will be determined followed by measurements of CO_2/CO ratio and oxidation rate.

References

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2. Du, Z., Sarofim, A.F., Longwell, J.P. "Activation Energy Distribution in TPD-Modeling and Application to the Soot-Oxygen System" Accepted for Publication, Energy and Fuels 1990.

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