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PULVERIZED-FUEL COMBUSTION:
MODELING AND SCALEUP METHODOLOGIES,
SECOND QUARTERLY REPORT,
FOR THE PERIOD
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PAUL F. LEWIS, THOMAS L. WOLF, ALAN GELB, and EVAN PUGH

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1. INTRODUCTION AND SUMMARY

Most of the effort during this quarter was devoted to the model element improvement task. The effort in this task has been in four areas:

- 1) chemical reactions of OH and O radicals with carbon surfaces
- 2) effect of particle size distribution on optical absorption properties of the coal feed
- 3) dynamics of a distribution of particle sizes
- 4) development of scaling laws for the location and shape of recirculation zone boundaries

The conclusions of the effort in these four areas are:

- 1) The chemical reactions of OH and O radicals with carbon surfaces are very rapid at combustion temperature. The reactions are first order in total pressure and yield CO as the primary product.
- 2) Optical absorption coefficients of Rosin-Rammler distributions of typical pulverized fuel are about three times the value for mass mean particle size. The model will include the optical absorption coefficient appropriate for the size distribution within the combustor.
- 3) The particle size distribution has a significant effect on the particle velocity distribution and thus on residence times of the larger particles. Calculations of particle dynamics are underway.
- 4) An exhaustive search was conducted for literature related to flow patterns in axisymmetric, confined, combusting flows, both with and without swirl. Correlation of various experimental results was attempted.

2. MODEL ELEMENT IMPROVEMENTS

2.1 Heterogeneous Reactions

During this reporting period we have considered the effects of gas phase radical/carbon-surface reactions on the combustion of coal. The goal of this effort is to review the pertinent literature base in order to determine rates and products of carbon/radical-species reactions. Thus far we have considered O atom and OH radical reactions with carbon.

Both O and OH are expected to be highly reactive species at carbon surfaces. All carbon gasification schemes postulate some oxygen containing surface radical as the reactive species. Reaction is often assumed limited by production of this radical. In combustion it is usual to assume the rate limiting step is the production of adsorbed oxygen atoms on the surface by dissociation of O_2 . O atom reactions are obviously not limited by this constraint. In steam gasification the Ergun mechanism postulates an equilibrium between gaseous H_2O and a dissociated surface species. Direct OH/surface interaction eliminates one of the dissociation steps.

Water gasification of carbon has been described by the Ergun mechanism in which $C(O)$ represents an oxygen atom bound to the surface:

All rate coefficients are for unit surface area of carbon. This mechanism leads to the following law for gasification of carbon,

$$\text{Rate} = \frac{k_3 k_1 p_{H_2O}}{k_3 + k_2 p_{H_2} + k_1 p_{H_2O}} \quad (3)$$

A more detailed mechanism divides (1) into the following steps

This mechanism is equivalent to (1) and (2) if OH and H are short lived intermediates on the surface. The success of Eq. (3) would indicate that this is indeed the case. For the purposes of analyzing possible effects of OH on reaction rates we shall assume reactions (4-6).

The effect of direct OH addition is to accelerate the backward reaction of Eq. (4) and the forward reaction of Eq. (5). The backward reaction of Eq. (4) is the water recombination and does not lead to carbon gasification whereas the forward reaction of (5) leads to carbon gasification via (2).

Mulcahy and Young¹ have measured OH reactions on carbon at 298 K. They found OH interaction leads both to H₂O formation and carbon gasification (as CO and CO₂). The rate of the H₂O recombination was several times that of the carbon gasification reactions. The reaction probability for carbon gasification was measured to be $> 5 \times 10^{-3}$. Rosner and Allendorf² measured OH reaction rates of gasification of isotropic graphite between 1880 and 2000 K. They found reaction probabilities of $2-4 \times 10^{-3}$. No attempt to measure H₂O recombination was made in their work. The results of Mulcahy and Young and those of Rosner and Allendorf differ in several important points, especially with regard to the relative reactivities of O and OH. Mulcahy and Young found OH gasification at least an order of magnitude faster than that of O. On the contrary, Rosner and Allendorf

find O reaction probabilities two orders of magnitude greater than OH rates. It is difficult to understand these results. It is possible that this discrepancy is due to the temperature differences between the two experiments. Most experimenters however, have inferred the rapid gasification of carbon by OH. Fenimore and Jones³ measured soot oxidation rates by OH and concluded that OH gasification reaction probabilities were about 0.1 and that OH was significantly more efficient in soot oxidation than O₂. Note Rosner and Allendorf found the O₂ gasification rate an order of magnitude higher than OH. In a less direct study, Millikan⁴ also concluded that soot oxidation is determined by reaction with OH. Recently Neoh et al.⁵ measured soot oxidation rates in flames of varying compositions. They analyzed the relative reactivities of flame constituents by computing reaction probabilities necessary to account for the measured soot oxidation rates and concluded that OH radical was the principal oxidant of soot under the conditions of their experiments. The average value of the collisional efficiency was determined to be between .28 and .13.

In light of the work of Neoh et al., Fenimore, Mulcahy et al. and Millikan, we conclude that OH is a highly reactive species for carbon oxidation. It would appear that the Rosner and Allendorf results for OH gasification rates of carbon are too low.

In order to incorporate OH reactions in the coal combustion kinetics scheme we postulate that all OH impinging upon a carbon surface reacts to form CO or H₂O. At temperatures of interest in coal combustion it is expected that CO rather than CO₂ production will be favored as a gasification product. Therefore we write the OH consumption rate, $\frac{dp_{OH}}{dt}$, as

$$-\frac{dp_{OH}}{dt} = k p_{OH} \quad (7)$$

where k is the coefficient for OH reaction with coal. The rate of carbon gasification, $R_g(OH)$, is the probability of the gasification reaction α , times the rate of consumption of OH,

$$R_g(\text{OH}) = \alpha k p_{\text{OH}} \quad (8)$$

The reaction of O-atoms chemisorbed on a carbon surface is a common step found in most oxidation and gasification reaction mechanisms. Desorption of chemisorbed O as CO is usually taken as the rate limiting carbon gasification rate.

The literature base for O-carbon reactions is larger than that for OH reactions. However, several authors have reached quite varying conclusions with regard to reaction products and order. We consider primarily the work of Rosner and Allendorf² and Wright.⁶

Rosner and Allendorf measured O-carbon reaction rates and products between 650 and 2000 K. They concluded that the reaction is first order in O-atoms and the primary product CO. The reaction probability achieved its maximum value at 1600 K and was equal to 0.5 at that temperature. Arrhenius plots of reaction probability show strong non-linear behavior above 1300 K. Below that temperature reasonable linear fits could be made. They also determined the activation energy for O-carbon reaction to be about 6-7 kcal/mole below 1300 K. Note that these experiments were carried out at total gas pressures of 1 torr and O pressures varied between 4×10^{-3} and 6×10^{-2} torr.

Wright measured soot oxidation rates at 5 torr total pressure by O-atoms at temperatures between 300 and 850 K. He found the carbon removal reaction to be second order in O-atom pressure and that the principal product was CO₂ with virtually no CO detected. However, he did note that at a lower total pressure measure (.05 torr) some CO was detected. O-atom pressures were varied between 1.1×10^{-2} and 3.1×10^{-2} torr. It is clear that there are seeming discrepancies between the results of Wright and Rosner and Allendorf.

Most experimenters have concluded that CO is the primary oxidation product of carbon by O. In another paper Allendorf and Rosner⁷ noted that the product ratio of CO/CO₂ decreases with increasing temperature between 2000 and 1100 K. At 2000 K the ratio is about 10 whereas at 1100 K the ratio

is about unity. It is not unreasonable that the ratio CO/CO_2 continues to decrease at lower temperatures so that in the temperature range of Wright's work CO_2 formation is favored. A reaction mechanism to account for both products is

In the first step O gas phase atoms are adsorbed. The adsorbed oxygen, C(O) , may desorb (step (9b)) to form gaseous CO or react by a Hinshelwood mechanism (step (9c)) or Rideal mechanism (step (9d)) with an oxygen atom to form gaseous CO_2 . The results of Rosner and Allendorf⁷ indicate that at low pressures and high temperature, step (9b) is fast relative to steps (9c) and (9d). Wright's results imply step (9c) or (9d) is the dominant mode of gasification at low temperatures. At high temperatures one therefore expects from this mechanism the gasification rate has the following pressure dependence

$$R_{\text{gasification}} \approx p_{\text{O}} \quad (10)$$

while at low temperatures

$$R_{\text{gasification}} \approx p_{\text{O}}^2 \quad (11)$$

(assuming relatively low O-atom surface coverage).

This analysis is supported by the results of Mentser and Ergun⁸ on oxygen exchange rates. They measured the rate of the oxygen exchange reaction between CO_2 and CO on carbon and concluded that it was rapid compared to gasification rates at temperatures between 750 and 850°C. Therefore, at low temperatures oxygen atom recombination with adsorbed CO competes effectively with desorption of CO and substantial CO_2 may be formed. At higher temperatures, however, the surface residency time of CO is too short for CO_2 to be formed.

To incorporate O-atom reactions into the coal combustion kinetics scheme we assume that all O-atoms that impinge upon a coal surface are consumed. Further we assume that at combustion temperatures the gasification reaction is first order in p_{O} and produces only CO. Therefore we write for the gasification rate by O-atoms, $R_g(\text{O})$

$$R_g(\text{O}) = k_{\text{O}} p_{\text{O}} \quad (12)$$

In writing this expression we neglect interference between this and other reactions occurring on the carbon surface.

We summarize our main conclusions as the following. Both O-atoms and OH radicals are very effective in coal gasification. At high temperatures the primary gasification product is CO and the reactions are first order in radical (or atom) pressure.

We are now incorporating the gas phase radical contributions to the gasification rate into the O_2 , H_2O and CO_2 kinetic schemes.

2.2 Optical Absorption Coefficient-Particles

The optical absorption coefficient is greater by a factor of three for pulverized coal than for particles of a single size at the mean mass size. In this subsection we show that this is true.

The distribution of particle sizes for standard grind pulverized coal is given by the Rosin-Rammler distribution,

$$u(r) = 1 - \exp\{-r/\bar{r}\}^{1.08} \quad (13)$$

where $\bar{r}$ is the particle radius under which 63% of the mass lies. This distribution is shown in Fig. 1 for $\bar{r} = 50 \mu\text{m}$, a value corresponding approximately to 80% through 100 mesh. If this distribution of particle sizes is suspended in a gas, the optical absorption coefficient can be calculated from

$$k = \int_0^{\infty} n(r) \sigma(r) dr \quad (14)$$

$n(r)$ is the number of particles per unit volume in the interval dr about r and can be found from $u(r)$ as

$$n(r) = \frac{m_T}{m(\bar{r}) \bar{r}} \left(\frac{r}{\bar{r}} \right)^{-2.92} \exp\left(-\left(\frac{r}{\bar{r}}\right)^{1.08}\right) \quad (15)$$

where $m(\bar{r})$ is the mass of a particle of size $\bar{r}$ and m_T is the mass density of particles suspended (g/cm^3). $\sigma(r)$ is the optical absorption cross-section and is approximated by interpolation between the limits for large and small particles. The value for large particles is approximated as the emissivity of carbon times the cross-sectional area,

$$\sigma_{\text{sur}} = \epsilon \pi r^2 \quad (16)$$

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Fig. 1 Rosin-Rammler distribution for $\bar{r} = 50 \mu\text{m}$.

At small particle sizes, including soot sizes, carbon becomes a volume absorber and we have approximated coal as carbon for those purposes,

$$\sigma_{vol} = \frac{4}{3} \pi r^3 \alpha \quad (17)$$

The value of α and ϵ used are $8 \times 10^3 \text{ cm}^{-1}$ and 0.8, respectively. The two cross-sections are equal at a radius of $0.75 \text{ } \mu\text{m}$. We choose to interpolate between the two limits by reciprocal addition for simplicity. We can then write,

$$k = \frac{m_T}{\rho_p} 8640 \int_0^\infty \frac{x^{0.08} e^{-x^{1.08}} dx}{1 + \frac{4}{3} \bar{r} x} \quad (18)$$

where ρ_p is the density of a particle, $\bar{r}$ is in μm and k is in cm^{-1} . The effect of the particle size distribution can most easily be seen from the running integral as a function of particle size. This is shown in Fig. 2 for $\bar{r} = 50 \text{ } \mu\text{m}$ and $25 \text{ } \mu\text{m}$. The absorption coefficients at $\bar{r}$ are shown as x 's. The values integrated over all r are 3.3 and 2.8 times the values of a mono-size at $\bar{r} = 50 \text{ } \mu\text{m}$ and $25 \text{ } \mu\text{m}$, respectively.

In the computer code, the optical absorption coefficient is evaluated from the sum over the particle size distribution that exists in the flow. This can be significantly different from the Rosin-Rammler because of particle chemical reactions and because different size particles can travel at different speeds due to drag and collisional forces. This latter effect is discussed in the next subsection.

Fig. 2 Optical absorption coefficient for Rosin Rammler distribution.

2.3 Particle Dynamics in a Quasi-One-Dimensional Turbulent Jet

The dynamics of the motions of particles in a turbulent jet are extremely complex and beyond the scope of this program. However, we can formulate simple models for the flow in order to establish the regimes of importance of various effects. We have begun this process by describing the flow of a distribution of particle sizes in a quasi-one-dimensional turbulent jet ("top hat" profile) expanding into a stagnant atmosphere. We then apply this description to combustor conditions. Results of these calculations will be presented in our next quarterly report.

2.4 Recirculation Zones

Effort continues to be directed toward identification of scaling laws for flow patterns in axisymmetric, confined, combustng flows, both with and without swirl. Our ultimate objectives in this study are to predict the size and shape of recirculation zones, gas composition and temperature in the recirculation zones, and mass and energy fluxes across the recirculation zones, and mass and energy fluxes across the recirculation zone boundaries. These predictions are to be obtained as functions of inlet flow conditions for each of the geometries of interest. Work to date has included an exhaustive search of the literature and attempts to correlate various experimental results.

The bulk of the experimental literature in this area is empirical in character, frequently employing curve fits to data expressed in terms of appropriate similarity parameters. Theoretical analyses found in the literature can be roughly grouped according to the following classifications: (1) detailed theoretical modeling, e.g., analytical solution of the equations of motion, (2) simple theoretical modeling, usually based on similarity considerations, and (3) detailed computational fluid dynamic simulations. The literature is extensive, and for purposes of the present report only a limited bibliography is included.

For the case of swirling flows, crude theories based on free jet similarity behavior have been used extensively. In the absence of swirl all of the recirculation is external to the primary jet, unless central recirculation is induced by means of a bluff body flame stabilizer or annular inlet nozzle geometry. The simple theories give satisfactory agreement with experiment as to the size of the external recirculation zone and the magnitude of the reverse mass flow rate. The simplest case to have been treated is that of an isothermal constant density flow at large confinement ratio. Corrections to this simple theory are available to account for nonisothermal and confinement effects.

For weakly swirling flows, i.e., no central recirculation is present, simple corrections to the nonswirling theory yield successful predictions of the size of the recirculation zone and reverse mass flow rate as a function of swirl number. Detailed analytical models are also available, but for our purposes the elementary treatments should be adequate.

For strongly swirling flows, i.e., central recirculation is present, no theoretical models are available that successfully predict the flow pattern. (The only simple treatment that has appeared in the literature claims good experimental agreement using an integral approach, but results were found to be inconsistent with much of the experimental data of other researchers.) Sophisticated analytical modeling of the vortex breakdown process that initiates central recirculation has been accomplished, but these theories are unable to predict the fully established vortex structure. Thus far only computational fluid dynamic simulations have achieved any measure of success in predicting flow patterns in strongly swirling flows. These treatments employ sophisticated numerical techniques that are beyond the scope of the present program.

Unfortunately, prediction of the flow pattern in strongly swirling flows has not been thoroughly addressed even on an empirical level. Although the experimental literature is extensive, comparatively little effort has been devoted to measurement of flow patterns at varying degrees of swirl. Using the limited data available, however, it should be possible to assemble satisfactory empirical correlations for the parameters of interest.

It will be advantageous, of course, to supplement this empirical approach with theoretical modeling. Although it is unlikely that a fully theoretical predictive capability will be achieved, enhanced physical understanding is bound to assist interpretation of experimental data. Work in this area is scheduled to receive immediate attention.

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