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PREDICTING THE FORMATION OF CONDENSATION ASH FROM COAL COMBUSTION

SHU-MU HSIEH

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PREDICTING THE FORMATION OF CONDENSATION ASH FROM COAL COMBUSTION

BY

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A DISSERTATION

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in
Engineering

December 1982
This thesis has been examined and approved.

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ABSTRACT

PREDICTING THE FORMATION OF CONDENSATION ASH FROM COAL COMBUSTION

by

SHU-MU HSIEH

University of New Hampshire, December, 1982

This study predicts the nature of condensation ash formed from direct combustion of coal. Three coal-fire combustors, a cyclone-fired (CF) boiler, a pulverized-fuel (PF) and a drop tube (DT) furnace were considered.

Predictions were based on the hypothesis that condensation ash is formed through two consecutive steps: vaporization and recondensation. Metal-containing species in coal are believed to vaporize during high temperature combustion. These vapors then diffuse and condense at the bulk gas phase.

The amount of metal-related vapor transport to the bulk gas phase is dictated by char surface composition which is, in turn, determined by the temperature history of a burning
coal particle. This temperature-burnout relationship was obtained through an energy balance around the burning particle.

The char combustion rate (involved in energy balance) was calculated using a combustion model developed by Simons et al. Condensation and growth were predicted employing Ulrich's coagulation model with modifications to accommodate the formation of condensation ash.

According to the predictions, condensation ash is aggregated in both the CF and PF boilers. Their average primary diameters are 50 and 180 nm for CF and PF boiler, respectively. For the drop tube furnace, particles were predicted to be single particles with average size of 34 nm in diameter. Laboratory data agree quite well with size predictions except that particles also appear to be aggregates in the drop tube furnace (29).

Predicted condensation ash compositions are in poor agreement with published data. Poor activity coefficient data, the heterogeneous distribution of mineral ash, and heterogeneous condensation are believed to be major factors for these discrepancies. Further studies are recommended.
CHAPTER I
INTRODUCTION

Coal has been one of the major fuels in power generation. Nearly a half of this nation's electricity is produced by burning coal. This requires at least 500 million tons of coal per year (1). It has been predicted that by the year 1995, double this amount of coal (about 900 million tons annually) will be burned for electricity (1). Compared to other energy sources such as oil, solar heat, etc., coal is considerably cheaper (1,2). Direct coal burning, however, creates unwanted products, which have been found to threaten the environment. One of these is a large amount of flyash since coal normally contains 2 to 30% noncombustible mineral matter. This ash, when emitted to the atmosphere, degrades air quality and decreases visibility.

To minimize flyash emissions, particle-collecting devices, primarily electrostatic precipitators, have been employed to remove flyash particles from the effluent gases of coal-fired boilers. Unfortunately, these precipitators, although having collecting efficiencies as high as 99% on a mass basis, are less efficient for submicron particles than
for larger ones (3). The submicron fraction, though small in terms of mass, is inordinately large on a number basis. The 1% of total mass which might escape from an electrostatic precipitator might represent as much as 99% of the original ash on a number basis (4). This fraction, in general, has an average diameter of about 0.1 micron as observed by many investigators (1,5,6). According to earlier work in our laboratory, these submicron particles are aggregated into groups or clusters with primary particles of 0.05 to 0.06 micron in diameter (7,8).

Submicron particles, according to various studies, pose a much greater danger to the public health than their mass fraction might suggest (9,10,11). Because of fineness, they penetrate deeply into the lungs. Their larger surface area per unit mass accommodates larger quantities of deposited vapors, some of which may be toxic. In fact, the more volatile metals such as cadmium, manganese, zinc and lead are found to be enriched in the finer ash fractions (9,10,12,13,14,15). These are generally considered to be more hazardous than less volatile metal compounds. Atmospheric visibility and even the greenhouse effect are influenced disproportionately by submicron particles which are similar in size to radiation wavelengths.
Aside from environmental effects, submicron particles, because of their higher mobility in a temperature gradient, are believed to be a key factor in boiler fouling.

Flyash from coal combustion is quite heterogeneous in its size distribution. Some particles are often as large as 50 micron, although the majority of mass falls between 1 and 30 micron. A small mass fraction, as indicated above, is submicron. On either a number or a mass basis, it is usually possible to classify coal ash into two modes, residual ash and condensation ash, because of its bimodal distribution (1,5,6,16). The residual ash, clearly visible in optical micrographs from cyclone-fired boilers, appears as spherical particles of size usually greater than 1 micron (17) (irregular particles such as cenospheres and plerospheres are, however, often observed in flyash from pulverized-fuel boilers (12)). Condensation ash, according to work in our laboratory (7,8), appears to be composed of submicron aggregates. The chemical compositions of these two modes are found to be somewhat different also. Residual ash has the composition of the original coal ash. Condensation ash, on the contrary, is enriched in certain species (1,7,8,13,18). This strongly suggests different formation paths for these two types of ash. Residual ash is apparently formed from direct fusion of mineral inclusions as coal is burned at high temperatures. Flagan et
al. suggest some fragmenting of coal during combustion to yield about 4 residual ash particles per initial coal particle (19). Sarofim et al., from laboratory observations, have verified this break-up mechanism (20). Condensation ash, on the other hand, is much more populous than one would predict from a break-up model (19).

Vaporization and condensation of metallic vapors has been suggested by Ulrich and others as the source of condensation ash (17,19,20,32). Intensive studies have been carried out in several laboratories to clarify the true mechanism (19,20,21). Based on laboratory studies of silica-containing flames, Ulrich et al. have developed a theory for submicron particle growth (21,22,23). This has been applied to predict the size and chemical composition of condensation ash in operating cyclone-fired boilers. Results agree with field data to a certain extent, but several major discrepancies were observed (24). Prediction of condensation ash depends on the composition and rate of diffusion of volatile compounds at the surface of the burning coal char. The former is strongly affected by char temperature which is determined in turn by the kinetics of char combustion. Thus, the choice of a proper combustion model is crucial to these predictions. Desrosiers et al. (24), in predicting condensation ash characteristics in a cyclone-fired boiler, employed Field's char burning model.
His rate expressions, combining both external and internal combustion, may be representative of some experimental conditions, but simulation of actual commercial combustors requires a more general expression which separates the external and internal mechanisms. Another weakness in Desrosiers' model is the means by which vapor compositions at the char surface were predicted.

This study was designed to overcome these limitations. A porous char combustion model developed by Simons et al. (25,26,27,28) has been adopted in this work. Coal data and char properties such as ultimate analysis, porosity and internal surface area are required parameters. Equilibrium surface vapor fractions were computed for conditions that resemble true char burnout conditions. Three combustors, a cyclone-fired (CF) boiler, a pulverized-fuel fired (PF) boiler and a drop tube (DT) furnace have been simulated to represent most systems for which data are available.
CHAPTER II
LITERATURE SURVEY

The formation of condensation ash from direct coal combustion is believed to occur in a series of consecutive steps \((18,20,21,24)\). Metal-containing species form at the surface of burning particles under reducing (deficient oxygen) conditions. These then diffuse to the oxygen-rich bulk phase. During transport, the reduced metal compounds oxidize to more stable states. Nucleation may initiate as the stable metal oxides become supersaturated. Growth of these nucleus continues through interparticle collision and fusion and terminates when the gas phase temperature drops below the ash melting point. This formation mechanism has been tested in several laboratories with reasonable confirmation \((18,29,32)\). Data from operating boilers also support this formation hypothesis \((1,5,6,7,8,17,18)\). In the following paragraphs, studies of submicron flyash formation conducted by various research groups are reviewed.

Markowski et al. at the Electric Power Research Institute (EPRI) conducted a series of investigations concerning flyash size distributions in coal-fired utility boilers \((1,5,6)\). Bimodal distributions have been observed
both before and after ash precipitators. Inlet results revealed that 1 to 1/2 % of the total mass was submicron while the outlet contained about 20% submicron particles. Chemical analysis of the collected submicron fractions showed the enrichment of Zn, As, V, Cr and Co. McElroy et al. concentrated on fine particles ranging between 0.05 and 2 micron (1). Size discrimination was accomplished by employing an electrical aerosol analyzer. The submicron mode was found to contain 0.2 to 2.2% of the total flyash mass. A sharp peak at a diameter of about 0.1 micron was found for all of the boilers investigated. Enrichment of volatile elements such as Hg, Se, As, Zn, and Ni as well as the refractory elements Fe, Al, and Mg was detected.

Laboratory studies on ash evolution during coal combustion were conducted at the Massachusetts Institute of Technology under Sarofim (20,29). These verified two different mechanisms responsible for flyash formation. Fusion and coalescence of the mineral matter during coal combustion accounted for the larger particle fractions. Vaporization and recondensation of volatile mineral species evidently produced the submicron fractions. Up to 4 weight percent of the silica present in ash was found to vaporize in their study. The percentages of submicron particles were also found to increase as combustion temperature increased. Their recent work on vaporization and condensation of
mineral matter from firing lignite coal provides further evidence regarding the submicron flyash formation process (29). According to these findings, the fraction of submicron particles increased from 0.1% by weight of total ash at particle temperatures around 1800 K to 20% by weight at 2800 K. MgO and CaO were found to be the major compounds in these particles. Vaporization of these refractory oxides is believed to occur via more volatile reduced-state species caused by the presence of carbon. These reduced-state vapors are apparently oxidized and then nucleate. A growth model based on Flagan's work (19) was employed by the MIT group to predict final particle sizes. Good agreement was reported between their calculations and experimental findings.

Flagan et al. at the California Institute of Technology have also conducted extensive studies on submicron flyash formation (18,19,30). A vaporization-recondensation model was used to predict submicron particle mass fraction and size distribution from laboratory and commercial combustors. Predictions were found to be in closer agreement with laboratory data than field measurements. This discrepancy was blamed on the limitations in combustion model since full-scale boilers are considerably more complicated than the more simple laboratory combustors. Their data also reveal a bimodal mass distribution with a well-defined peak
in the submicron range at about 0.05 micron. For particles less than 0.3 micron, Si and S were found to be enriched while the residual ash (supermicron mode) contained Al, Si, Ca, Mg, and Na in proportions similar to those in the original coal ash. In general, their investigations also confirm vaporization-condensation as a mechanism of submicron flyash formation in coal combustion.

Ulrich et al. at the University of New Hampshire have long recognized the similarity between formation of condensation ash from burning coal and the growth of silica fumes in flames (21,22,23,31). Besides characterizing condensation ash morphologically and chemically, they have investigated flyash formation in operating boilers (7,8,17,22,24,31,32,33). In his earlier work, based on Brownian collision theory (assuming instantaneous coalescence), Ulrich derived theoretical expressions describing particle concentration and sizes as a function of residence time and other parameters in a silica synthesis flame (21). To test this theoretical model, a laboratory combustion system burning silicon tetrachloride was studied (22,23,31). Milnes (31) reported observed growth rates which agreed closely with theoretical predictions only after the application of a surprisingly small sticking coefficient to the predictions, i.e., 0.004. To reconcile this, Ulrich and Subramanian modified Ulrich's original model to include
finite coalescence (22). Particle morphology studies
revealed particles as being aggregates throughout the growth
process. This is in contrast to the assumption that
particles were spheres that had been made earlier. Based on
the modified model, the number of primary particles per
aggregate was expressed as a function of sticking
coefficient, the initial particle radius and the ratio of
surface tension to viscosity. The final expression is
quoted as follows:

\[
d\frac{N_p}{dt} = 4.84c \left( \frac{3k}{\rho} \right)^{1/2} \left( \frac{3M}{4\pi \rho A} \right)^{1/2} C_0 \cdot \frac{37R_0}{N_p} - 2.5 - (N_p/R_0)^{0.22} \frac{\sigma}{\mu}
\]

where
- \( N_p \) = number of primary particles per aggregate.
- \( c \) = sticking coefficient.
- \( k \) = Boltzmann's constant.
- \( \rho \) = density.
- \( M \) = molecular weight.
- \( A \) = Avogadro's number.
- \( R_0 \) = primary particle radius.
- \( T \) = flame temperature (a function of residence
time).
- \( \mu \) = viscosity.
- \( \sigma \) = surface tension.
- \( C_0 \) = Total concentration of condensable species.
$N_p$ was calculated by numerical integration of the above equation. Quantitative agreement between theoretical predictions and Subramanian's measured results is not that satisfactory. The disagreement was attributed to the limited accuracy of their counting technique. In a four year project, Ulrich and coworkers conducted a systematic investigation of flyash formation in coal-fired utility boilers. Work was carried out in two directions. First, they continued to study the growth of silica fumes in the laboratory. Secondly, they investigated the growth of flyash in full-scale utility boilers. In the laboratory study, Riehl and Ulrich (34), employing light-scattering techniques, determined aggregate sizes in situ. These data were in good agreement with theoretical predictions. Coal combustion is undoubtedly more complicated than are silica flames. However, the formation of condensation ash is expected to be a collision-coalescence process similar to that observed in the formation of silica fume (4). To elucidate this, French (17) investigated flyash formation in a commercial coal-fired boiler. He measured the surface area of ash taken from various locations of the boiler (corresponding to different residence times). Growth occurs between the combustion zone and the fifth floor (judging from the decrease in surface area (increase in primary particle size), 7.0 m$^2$/g in the combustion zone and 0.5
m²/g at the fifth floor). No growth occurred from the fifth floor to ash precipitator hoppers according to surface area data. French also used electron microscopy to study these samples. Under high magnification, a large number of submicron ash particles were observed. To characterize these submicron particles, Chiu (7), employing impaction techniques, separating ash collected from electrostatic precipitator hoppers into 9 size fractions. Six to ten percent by weight of total flyash was found in the submicron fraction. Chemical compositions of these samples were found to be a function of particle size. Si and S are enriched as particle size decreased while Al and Fe are depleted. Particle morphological studies revealed that submicron particles were usually aggregates composed of primary particles which had a relatively uniform diameter of about 0.06 micron. Supermicron particles appeared as distinct spheres. Separation by nucleopore filtration was also attempted. A cleaner size cut was obtained, but the quantity of submicron fractions collectable on nucleopore filters were too small to be analyzed chemically. Parallel to Chiu's study, Hsieh (8) separated hopper ash from a pulverized-fuel fired boiler. No evidence of submicron fractions was observed from impaction separation. Using nucleopore filtration on both CF and PF ash, about 6.4 weight % of submicron ash was found in the CF ash while less
than 0.1% was submicron in the PF ash. A limited amount of submicron ash was prepared for both energy dispersive analysis of x-rays (EDAX) and neutron activation analysis. An abrupt change in chemical composition was observed as particles reach submicron range. These findings supported the hypothesis that submicron flyash is formed through vaporization and condensation. Concurrently, Desrosiers et al. (24), based on Ulrich's growth model, developed a mathematical model for predicting formation of condensation ash in a cyclone-fired boiler. A 5.1 weight % of condensation ash was predicted. Based on this quantity, final particle size was computed to be 40 nm (0.04 micron) in diameter (for coagulation with a residence time of 3.2 seconds). Predicted sizes were smaller than was found in previous experimental studies on hopper ash, where 6 to 10 weight % of submicron ash of sizes about 0.06 micron in diameter was observed (7,8). Aly (33), employing Desrosiers' model, predicted formation of condensation ash in a commercial PF boiler. According to her calculations, no significant quantities of condensation ash would be formed due to much less metallic oxide vaporization at the lower combustion temperatures. This conclusion has been modified herein because of an error that was discovered in her calculations (see Appendix K).
CHAPTER III
MODEL DEVELOPMENT

The nature and quantity of condensation ash is dictated by the transport of ash-related species from burning coal particles to the bulk gas phase. At combustion temperatures, reactions leading to the production of metallic vapors (or metal oxides if volatile enough) are rapid enough to be almost instantaneous. The diffusion of these vapor to gas phase is usually found to be the rate-controlling step. Mass transfer through the boundary layer occurs by ordinary diffusion. The rate is well described by Fick's first law. The familiar expression for species at low concentrations, using a mass transfer coefficient, is

\[ n_i'' = k_i(C_{is} - C_{ib}) \]  

(III-1)

where \( n_i'' \) = molar flux of species i.
\( k_i \) = mass transfer coefficient.
\( C_{is} \) = molar concentration of species i at particle surface.
\( C_{ib} \) = molar concentration of species i at bulk phase.
To obtain the total quantity of ash vapors transported to the bulk phase, Equation (III-1) is to be integrated over the time period from the initiation of char burning to burnout. Details will be discussed later. It is, however, quite obvious that concentration of migrating species in the bulk phase ($C_{ib}$ of Equation (III-1)) may be set equal to zero since their concentrations at the particle surface are much higher. Thus the total mass of metallic vapors transported is in proportion to surface concentrations. These results are generally known to be a strong function of temperature. Thus, the char burnout time-temperature history dictates the amount of ash vaporized and transported to the bulk gas phase.

Both burnout time and temperature history were obtained by simulating the burning of a char particle. A pore char combustion model was employed for this purpose. Theoretical details and parameter evaluation are discussed in section III-a, III-b and III-c. In section III-d, condensation ash size predictions are outlined.
Coal combustion is generally divided into two stages, devolatilization and char combustion. Devolatilization begins as the coal particle heats up. In an oxidizing environment, these volatiles burn vigorously at the particle boundary layer. This creates a distinct bright flame. The resultant heat contributes to an increase in char temperature. As the char ignition temperature is reached, the particle itself begins to burn with an incandescence light which lasts till char burnout (37,38).

With an interest in flyash formation, several studies concerning the transformation of coal minerals at high temperatures have been made(19,20). These reveal that coal minerals remain essentially intact during devolatilization. Significant transformations occur only when the carbonaceous matrix is oxidized, i.e., char combustion. Before this, particle temperatures are too low to vaporize mineral elements (37,39). Thus devolatilization does not affect the important ash-formation processes (19,39). In this study, it is taken for granted that vaporization of metallic vapors starts with char combustion.

Coal itself is a porous matrix having a void fraction as high as 0.3 (37,40). Devolatilization greatly increases voids in the so-called coal char to porosities ranging
between 0.3 and 0.85 (41,42). The combustion of char particles, therefore, must be visualized as the reaction between a porous particle and a gas. Kinetic behavior of this is somewhat more complicated than that of a nonporous particle. Various diffusion and chemical reaction steps are likely to influence the global reaction rate. In general, this usual kinetic sequence involves the following steps:

1. Transport of oxidant from the gas phase to the outer surface of the porous particle;
2. Diffusion of oxidant within the pores of the particle;
3. Chemical reaction at the particle surface including adsorption of reactants and desorption of products;
4. Diffusion of gaseous products through the porous particle;
5. Transport of gaseous products into the bulk gas phase.

One or more of these steps are more important than the others. Different regimes of control are illustrated in the Arrhenius diagram which is shown in Figure (III-1) (39).
Here reactant concentration is plotted as a function of distance from the particle core in three different cases:

**Case I**: rate control by chemical reaction.
**Case II**: rate control by pore diffusion and chemical reaction.
**Case III**: rate control by diffusion to outer surface.

Walker and others (43,44), have discussed these in great detail. A short review follows. Regime I is typical for reactions at low temperatures, where chemical reaction is comparatively slow and the oxidant diffuses deeply into the particle before it reacts with the pore surface. The
overall rate is controlled by the oxidant concentration effectively equal to that of the bulk phase. This is unlikely to be the case in char combustion, which will not occur at such low temperatures. Regime II occurs at moderate temperatures, where the chemical reaction rate is greater and the probability of oxidant penetrating deeply into the particle becomes smaller. Diffusion within the pores as well as chemical reaction limits the overall reaction. Regime III represents reactions at relatively high temperatures where the reaction rate is so high that the oxidant is depleted at the particle surface before it can enter the pores. The overall reaction rate, in this case, depends on external mass transfer.

Regimes II and III are most likely those which apply to char combustion. The actual regime, however, depends on particle size, pore size and the combustion environment.

The kinetics of char combustion, although studied extensively in the past, are still not well-established. Uncertainties stem primarily from complexity of the char structure and the influence of noncombustible constituents such as ash minerals. The combustion model, in this study, is based on the following assumptions:

1. Char particles are static relative to their gaseous surroundings.
2. Char particles are treated as spheres having the same dimension as the original coal particles.

3. Combustion occurs both externally and internally.

4. Char particles are viewed as a homogeneous mixture of carbon and ash.

5. No catalytic effects of mineral matter are considered.

6. Char reaction gives carbon monoxide only.

7. The carbon monoxide formed is further oxidized at a sufficient distance from the surface so as not to affect surface temperature.

The rate of mass transfer of oxidant to the particle surface, or that of heat transfer by convection-conduction is influenced by the relative velocity between particle and gas (37). This effect is, however, insignificant for the burning of PF particles or rather particles smaller than 100 micron (39). Hence, assumption (1) is justified. Assumption (2) is made mainly for mathematical expediency in modeling. In reality, char particles were found larger than their original coal particles due to swelling caused by devolatilization in a high heating rate (37,38,39).

Internal combustion, as pointed out in assumption (3), is to be treated in parallel with external combustion. Conventionally, internal combustion is lumped with the combustion at the surface of the particle (37,39,42,45,46) to avoid unnecessary complications. Recent developments in coal combustion theory, fortunately, have enabled the
simulation of internal burning with good reported results (25,26,27,28,47). Mineral inclusions are nonuniformly distributed in coal char. Theoretical difficulties arise in describing this nonuniform distribution. In the present work, mineral inclusions were considered to be uniformly distributed in char matrix.

It has also been found that mineral matter appears to have a catalytic effect on the oxidation rate (39). Apparently, however, catalysis is significant only at low temperatures, and does not affect the char burning phase. The fifth assumption exempts catalytic effects caused by mineral ash. The sixth and seventh assumptions are found to be more realistic for the combustion of small particles (less than 100 micron) at elevated temperatures (above 1273 K) by many investigators (37,48).

According to what is described above, char combustion may be modelled as the burning of a porous particle immersed in a stagnant gas phase. Oxidation of carbon is controlled by diffusion of oxidant through a stationary film to the surface of the particle where it reacts to form carbon monoxide which then diffuses outward from the particle surface and oxidizes in the bulk gas phase. In the boundary layer, oxidant is conserved. The rate at any imaginary surface is equal to that transported to particle surface.
At steady state, this rate is also the same as the oxidant consumption rate. These are described in sequence as follows:

**III-a-1 Oxidant Diffusion Rate**

The flux of oxidant is determined by a diffusional transport equation. Convective transport or so-called Stefan flow as caused by surface reaction stoichiometry \((C + 1/2 O_2 \rightarrow CO)\) is included in this study (39). From Appendix A, the flux \(n_j^"\) is obtained as

\[
n_j^" = -(D_j P/RT_f) (1/(a^2(1/(a+\delta)))-1/a)) \\ ln((y_j+1)/(y_{jb}+1)) \quad (III-2)
\]

where

- \(D_j\) = diffusion coefficient of oxidant \(j\) in bulk, \(cm^2/s\).
- \(P\) = total pressure of the system.
- \(R\) = universal gas constant.
- \(T_f\) = film temperature.
- \(a\) = particle radius.
- \(\delta\) = boundary layer thickness.
- \(y_j\) = mole fraction of oxidant \(j\) at any radius \(a\).
- \(y_{jb}\) = mole fraction of oxidant \(j\) at bulk phase.
III-a-2 Oxidant Consumption Rate

Oxidant consumption rate is the actual amount of oxidant reacted with carbon both internally and externally per unit time. Reaction of oxygen with carbon is generally described by a sequence of adsorption and desorption process. These are expressed as

\[
C + O_2 \xrightleftharpoons[k_1'k_2]{k_1} C\!(O_2), \text{ and}
\]

\[
C + C\!(O_2) \rightarrow 2\text{ CO}
\]

Reaction constants \(k_1\), \(k_1'\) and \(k_2\) are quoted from Simons' study (28);

\[
k_1 = 900 \exp(-19000/T_s) \text{ g/cm}^2 \text{ sec atm } O_2 \quad (\text{III-3})
\]

\[
k_2 = 90 \exp(-19000/T_s) \text{ g/cm}^2 \text{ sec } \quad (\text{III-4})
\]

\[
k_1' = 200 k_1 k_2 \exp(-3500/T_s) \text{ g/cm}^2 \text{ sec} \quad (\text{III-5})
\]

The carbon consumption rate is thus obtained as,

\[
-(dc/dt) = \frac{k_1k_2P_2}{(k_2 + k_1' + k_1P_2)}
\]

\[\text{g/cm}^2 \text{ sec} \quad (\text{III-6})
\]

where \(P_2\) = partial pressure of \(O_2\).

At high oxidant concentrations, reaction is controlled by the second reaction, i.e., desorption limited, thus

\[
-(dc/dt) = k_2 = k_d \quad (\text{III-7})
\]
where \( k_d \) is the desorption rate constant.

For low oxidant concentrations, the first reaction dominates. \( k_1 P_0^2 \) is relatively smaller than \((k_2+k_1)\). Equation (III-6) may be rewritten as

\[
-(dc/dt) = \left( k_1 k_2 / (k_2 + k_1') \right) P_0^2 \\
= k_a P_0^2 \quad (III-8)
\]

where \( k_a \) (adsorption rate constant) = \( k_1 k_2 / (k_2 + k_1') \)

(a) Internal Combustion

Pore structure is essential in predicting the combustion rate of a porous particle and a gas. In the past, investigators have used a uniform noninteracting cylindrical pore structure, a macro-micro pore model and a grain model. None of these have been totally successful in quantitative predictions. A more successful model must consider a range of pore size as well as interconnections between pores. Pore sizes also apparently change continuously during the course of char combustion (49). The model which includes these improvements, developed by Simons et al. (25, 26), was employed in this study. Their model suggests that the pore structure of coal char resembles that of ordinary tree or river systems. A single pore was
assumed to be a cylindrical tube of length $l_p$ with a radius $r_p$. The number of pores with radius between $r_p$ and $r_p + (dr_p)$ is denoted as a pore distribution function. Through dimensional and statistical reasoning, they expressed the pore distribution function $g(r_p)$ as a function of porosity and pore sizes as follows:

$$g(r_p) = \frac{\theta}{2\pi} \beta r_p^3$$

where $g(r_p)$ = pore distribution function.

$\theta$ = porosity.

$\beta = \ln(r_{max}/r_{min})$, and $r_{max}$ and $r_{min}$ are the maximum and minimum radii, respectively.

The values ($r_{max}$ and $r_{min}$), according to their derivation (25), were given as

$$r_{max} = (2\theta^{1/3}/3K_0)a$$

$$r_{min} = r_{min0}(\theta^{1/3}/\theta_0^{1/3})$$

where $a$ = particle radius.

$K_0$ = an empirical value, inferred from known $r_{max}$; representing ratio of pore length to pore diameter, a value approximately equal to 5 was suggested according to Simons' study.

$r_{min0}$ = initial minimum pore radius.

$\theta_0$ = initial porosity.
Furthermore, the specific surface area has been derived as

$$S_p = 2m \theta_{0}^{1/3} \theta^{2/3} / \beta \rho_s r_{\text{min}0}$$  \hspace{1cm} (III-12)

where $\rho_s = \text{true char density}$.

$$m = 3 \beta / (\beta - 2) = 1.8 \text{ to } 2.0$$

These expressions, $g(r_p)$, $r_{\text{max}}$, $r_{\text{min}}$ and $S_p$, are employed in deriving the expression for internal combustion rate. According to pore sizes, and reaction temperatures, internal reaction was classified into three regimes, i.e., kinetically limited, continuum diffusion limited and Knudsen diffusion limited. Mass depletion rate of oxidant in each regime was derived as shown in Appendix B. Final expressions are

$$M_{pjs} = 4 \pi a^2 (k_{dj}/(1+\epsilon_j)) (K_0 (1-\theta) \theta^{2/3}/r_{\text{min}})$$

$$(r_{ckj} - r_{\text{min}})$$  \hspace{1cm} (III-13)

$$M_{pjk} = 4 \pi a^2 ((2 \rho_{p} V_j C_{o,j} k_{dj})^{1/2}/(1+(2 \epsilon_j)^{1/2})$$

$$((\theta / \beta) \ln (r_{dj}/r_{ckj}))$$  \hspace{1cm} (III-14)

$$M_{pjc} = 4 \pi a^2 ((\rho_{p} C_{o,j} k_{dj})^{1/2}/(1+(2 \epsilon_j)^{1/2}))$$

$$(-2 \theta / \beta) (r_{\text{max}}^{-1/2} - r_{dj}^{-1/2})$$  \hspace{1cm} (III-15)

where $M_{pjs}$ = kinetically limited depletion rate of
oxidant j.

\( M_{pjk} \) = Knudsen diffusion limited depletion rate of oxidant j.

\( M_{pjc} \) = continuum diffusion limited depletion rate of oxidant j.

\( k_{dj} \) = desorption rate constant \((k_a/z)\).

\( \epsilon_j = k_{dj}/(k_{aj}C_0j) \); \( k_{aj} \) being adsorption rate constant \((k_a \rho gM/zM_j)\).

\( p_g \) = total gas pressure.

\( \rho_g \) = gas density.

\( R_{ckj} \) = critical radius separating kinetically and Knudsen diffusion limited regimes.

\( R_{dj} \) = critical radius separating Knudsen diffusion and continuum limited regimes.

\( V_j \) = mean thermal speed of oxidant j.

\( D_j \) = diffusion coefficient of oxidant j.

\( M \) = mean molecular weight.

\( M_j \) = molecular weight of oxidant j.

\( z \) = gram of solid released per gram oxidant consumed (0.75 for \( \text{C}+\text{O}_2\rightarrow\text{2CO} \)).

(b) External Combustion
External surface reaction of char particle is kinetically controlled. Therefore, the mass depletion rate ($M_{sj}$) may be expressed as

$$M_{sj} = 4\pi a^2 (1 - \theta) k_{dj} / (1 + \epsilon_j)$$  \hspace{1cm} (III-16)

where $4\pi a^2 (1 - \theta)$ stands for the surface available for the reaction.

Summing up Equations (III-13), (III-14), (III-15) and (III-16), one obtains the expression for total oxidant consumption rate ($M_t$) as

$$M_t = M_{sj} + M_{pj^+} + M_{pk^+} + M_{jc^+}$$  \hspace{1cm} (III-17)

At steady state, the oxidant consumption rate by reaction is equal to the oxidant diffusion rate. Equation (III-17) may thus be equated to Equation (III-2).

$$M_t = 4\pi a^2 (D_j P_{RTf}) / (1/(a^2 (1/(a+\delta)-1/a)))$$

$$\ln((y_j+1)/(y_{ib}+1))$$  \hspace{1cm} (III-18)

Equation (III-18) is the mass conservation expression for modelling char combustion. This combined with a mathematical expression of energy conservation (to be discussed next) permits burnout time and particle temperature history to be calculated.
III-a-3 Energy Balance

Char temperatures were determined by a heat balance around the burning particle. The balance contains three terms, i.e., heat released by oxidation of carbon to carbon monoxide, heat conducted to the bulk gas phase and heat lost by radiation to the surroundings. Two additional assumptions are required. These are

(1) uniform particle temperature, and
(2) constant gas phase temperature ($T_g$).

The temperature gradient within the char particle can be neglected since the Biot modulus ($hr_0/k_s = 8*10^{-3}$) is smaller than 0.2. This means that the heat transfer resistance for internal conduction is negligible compared with that for surface convection. The gas temperature, however, does vary through char burnout as observed by Seeker et al. (50). In this study, combustion of char was simulated as in an equilibrium state. The gas temperature will thus be taken as the adiabatic flame temperature and treated as a constant.

Based on these conditions, the rate of temperature change ($dT_s/dt$) of a char particle was derived (see Appendix C):
\[
\frac{dT_s}{dt} = \left(3g/a \rho C_s\right)\left((T_b-T_s)/a\right)(1+Re^{1/2}/2)
\]
\[
-\left(3z/(4 \pi a^3 \rho C_s M_o) (M_r) (\Delta H_r)- (3/a \rho C_s)q_r\right)
\]

Equations (III-18) and (III-19) were derived for any values of radius (a) and porosity (\(\theta\)). They are invariant to coordinates a and \(\theta\).

As combustion proceeds, the removal of carbon will either cause a decrease in radius or an increase in porosity according to various regimes of reaction. These continuous change in a and (or) \(\theta\) are related to the depletion rate of carbon. Details of this derivation were done in Appendix D. Final expressions are

\[
\frac{d\theta}{dt} = \frac{3z(M_{pjx} s)}{(4 \pi a^3 \rho S)} \quad (III-20)
\]
\[
\frac{da}{dt} = (-z)(M_{pjx} s^2 + M_{pjx} + M_{pjx} + M_{pjx} s)/(4\pi a^2 \rho) \quad (III-21)
\]
where \( M_{pjs1} + M_{pjs2} = M_{pjs} \'.

\( M_{pjs1} \) = fraction of \( M_{pjs} \) contributing to the change in porosity.

\( M_{pjs2} \) = fraction of \( M_{pjs} \) contributing to the change in radius.

Equations (III-2) to (III-21) describe the burning of a char particle. Table (III-1) lists these equations including equations for describing physical properties or other parameters as defined. This forms a system of 34 equations which were solved numerically. Procedures are shown in the flow diagram (Appendix F).
Table III-1
Equations Simulating Char Combustion

1. \[ \frac{dT_s}{dt} = \frac{3 k_g}{a \rho C_s} \frac{(T_b - T_s)}{a} (1 + Re^{1/2}/2) \]
   \[ - \frac{3 z}{(4 \pi a^3 \rho C_s M_C)} (M_c) (\Delta H_r) - \]
   \[ \frac{3}{a \rho C_s} q_r \] (III-19)

2. \[ \frac{d\theta}{dt} = \frac{3 z (M_{pjs1})}{(4 \pi a^3 \rho_s)} \] (III-20)

3. \[ \frac{da}{dt} = -z (M_{pjs2} + M_{pjk} + M_{pjc} + M_{sj})/(4\pi a^2 \rho) \] (III-21)

4. \[ C_{oj} = \frac{M_{o2} y}{(M_{o2} y + M_{n2}) (1 - y)} \]
   (A-15)

5. \[ M_{sj} = 4 \pi a^2 (1 - \theta) k_{dj} / (1 + \epsilon_j) \] (III-16)

6. \[ M_{pjs1} = 4\pi a^2 (k_{dj} / (1 + \epsilon_j)) (K_0 (1 - \theta) \theta^{2/3} / \beta r_{min}) \]
   \[ (r_{pjs} - r_{min}) \]
   (D-8)

7. \[ M_{pjs2} = 4 a^2 (k_{dj} / (1 + \epsilon_j)) (K_0 (1 - \theta) \theta^{2/3} / \beta r_{min}) \]
   \[ (r_{ckj} - r_{pjs}) \]
   (D-9)

8. \[ M_{pjk} = 4 \pi a^2 \left( \frac{(2 \rho g V_j C_{oj} k_{dj})}{(1 + (2 \epsilon_j)^{1/2})} \right) \]
   \[ \left( \frac{\theta}{\beta} \right) \ln \left( \frac{r_{dj}}{r_{ckj}} \right) \]
   (III-14)

9. \[ M_{pjc} = 4 \pi a^2 \left( \frac{(\rho g D_j C_{oj} k_{dj})}{(1 + (2 \epsilon_j)^{1/2})} \right) \]
   \[ (-2 \theta / \beta) (r_{max}^{-1/2} - r_{dj}^{-1/2}) \] (III-15)
10. \[ M_t = M_{sj} + M_{pj} + M_{pj} + M_{pj} \] (III-17)

11. \[ Y_j = (Y_{jb} + 1) \exp((M_t(1/(a+\delta) - 1/a)RT_{avg}/(4\pi D_j P(M_j)))) - 1 \] (III-18)

12. \[ k_1 = 900 \exp(-19000/T_s) \text{ g/cm}^2 \text{ sec atm O}_2 \] (III-3)

13. \[ k_2 = 90 \exp(-19000/T_s) \text{ g/cm}^2 \text{ sec} \] (III-4)

14. \[ r_{\text{max}} = (2\theta^{1/3}/3K_0)a \] (III-10)

15. \[ r_{\text{min}} = r_{\text{min0}}(\theta^{1/3}/\theta_0^{1/3}) \] (III-11)

16. \[ r_{\text{min0}} = 2m\theta_0/\beta\rho_sS_p \] (III-12)

17. \[ r_{dj} = 3D_j/2V_j \] (B-5)

18. \[ r_{cj} = (\theta^{1/3}r_{\text{min}}(1+\epsilon_j)/(K_0(1-\theta)))^{1/3} \]
\[ (\rho_{D_j}C_{Oj}/k_{dj})^{1/3}/(1+(2\epsilon_j)^{1/2})^{2/3} \] (B-3)

19. \[ r_{ckj} = (\theta^{1/3}r_{\text{min}}(1+\epsilon_j)/K_0(1-\theta))^{1/3} \]
\[ (2\rho_{\psi_j}C_{Oj}/(3k_{dj}))^{1/2}/(1+(2\epsilon_j)^{1/2})^{1/2} \] (B-4)

20. \[ r_{pjs} = 4k_{dj}\lambda_{j}^{2}M_{air}/(.21\rho_{D_j}M_{j} + (k_{dj}/(.21k_{aj}))) \] (D-7)

21. \[ k_1'' = 200k_1k_2 \exp(-3500/T_s) \] (III-5)

22. \[ k_{dj} = k_2/z \text{ ; desorption rate} \]

23. \[ k_{aj} = k_1/z \text{ ; if T\leq 2000 K} \]
\[ = k_1 k_2/(k_1^z); \] otherwise.

24. \[ \epsilon_j = k_{dj}/(k_{aj}^z_j); \] defined value

25. \[ \beta = \ln(r_{\text{max}}/r_{\text{min}}); \] defined value

26. \[ D_j = \lambda_j v_j/3; \] Knudsen diffusivity

27. \[ v_j = (8kT/(\pi M_j))^{1/2}; \] thermal speed

28. \[ \lambda_j = 1/(2^{1/2} \pi N d_m^2); \] mean free path

29. \[ d_m = 3b_m/(2\pi L); \] molecular diameter

30. \[ \rho = \rho_s(1-\theta); \] apparent density

31. \[ \rho_g = P_{\text{air}}/(RT_s); \] density of gas within pores

32. \[ T_{\text{avg}} = (T_s+T_b)/2; \] average temperature

33. \[ N = LP/(RT_s); \] molecular concentration in no./cc

34. \[ \delta = a/(1+Re^{-1/2}/2); \] boundary layer thickness.

where \[ L = \text{Avogadro's number} \]
\[ R = \text{universal gas constant}. \]
\[ T_b = \text{bulk temperature}. \]
\[ M_j = \text{wt. of a molecule (j)}. \]
\[ S_{p0} = \text{initial specific surface of char}. \]
\[ m = \text{calculated value, as used in Simons' model}. \]
\[ K_0 = \text{empirically value, equal to 5 according to Simons' study}. \]
\( b_m \) = molecular volume.

\( \text{Re} \) = Reynolds number.

\( P \) = pressure.

\( C_{jb} \) = concentration of \( j \) at bulk phase.

\( \theta_0 \) = initial porosity.

\( M_{n2} \) = molecular wt. of \( N_2 \).

\( M_{air} \) = molecular wt. of air

\( k_g \) = thermal conductivity of air.

\( \Delta H_r \) = heat of reaction \((C + 1/2 \, O_2 \rightarrow CO)\)

\( k \) = Boltzmann's constant.
Equation (III-1) describes the mass transfer of species i from a particle surface to the bulk phase. As pointed out earlier, the concentration of transported species in the bulk phase is essentially zero. The remaining variables, mass transfer coefficient \( k_i \) and surface concentration \( C_{is} \), can be replaced either by measurable values or calculated ones as shown in the following:

**III-b-1 Mass Transfer Coefficient**

As stated in Assumption (1), the char particle is considered to be stagnant with respect to its gas surrounding. Under such conditions, the Sherwood no. \( N_{sh} \) has a value of 2, i.e.,

\[
N_{sh} = \frac{k_i d}{D_i} = 2 \tag{III-22}
\]

where \( k_i \) = mass transfer coefficient.
\( d \) = particle diameter.
\( D_i \) = gas diffusivity.

Thus, the mass transfer coefficient \( k_i \) may be replaced by the expression \( k_i = \frac{2D_i}{d} \), which leads to

\[
n_i = \frac{2D_i}{d} (C_{is} - C_{ib}) \tag{III-23}
\]
In terms of partial pressure, Equation (III-23) may be rewritten as

\[ n_i" = \frac{2D_i}{(dRT_f)} \left( \frac{P_{is}-P_{ib}}{RT_f} \right) \]  

(III-24)

To obtain the expression of total molar transport rate per particle \( \frac{dN_i}{dt} \), \( n_i" \) must be multiplied by particle surface area, \( \pi d^2 \). Therefore,

\[ \frac{dN_i}{dt} = \pi d^2 \left( \frac{2D_i}{(dRT_f)} \right) \left( \frac{P_{is}-P_{ib}}{RT_f} \right) \]

= \left( \frac{2D_i}{(RT_f)} \right) d \left( \frac{P_{is}-P_{ib}}{RT_f} \right)  

(III-25)

Equation (III-25) is the working equation for predicting metallic vapor transport from a particle surface to the bulk phase.

**III-b-2 Surface Concentration**, \( C_{is} = \frac{P_{is}}{RT_f} = \frac{P_{y_{is}}}{RT_f} \)

Major metallic vapors and their concentrations were estimated through chemical equilibrium calculations. Vapor fractions \( y_{is} \) at different surface temperature were obtained from a modified computer program for treating complex chemical equilibrium (see Appendix G). At any temperature, surface vapor fractions were computed by adjusting the oxidant content until solid carbon appears as an equilibrium species. The logarithmics of these vapor fractions is tabulated for 15 temperatures ranging from 1500
to 2400 K (see Tables H-1, H-2, and H-3 of Appendix H).

III-c Estimating Physical And Transport Properties

Parameters such as thermodynamic and transport properties appearing in equations of Table III-1 are mostly well-known values. Some, nonetheless, are functions of temperature (e.g., heat capacities, c_s) or of coal compositions (e.g., true density of char (\( \rho_s \)), initial porosity (\( \theta_0 \)), specific surface area (Sp_0)).

Both \( \rho_s \) and \( c_s \) were taken from the Coal Conversion System Technical Data Book (51). The true density was evaluated as

\[
\rho_s = \frac{300 \rho_s^0/((%\text{ash}\times \rho_s^0)+3(100-%\text{ash}))}{(111-26)}
\]

where \( \rho_s^0 \) is an empirical function of %H in coal (daf), and was expressed as

\[
\rho_s^0 = \frac{1}{(0.4397+0.1223\times%\text{H}-0.01715\times%\text{H}^2+0.001077\times%\text{H}^3)}
\]

Since char is considered as a homogeneous mixture of ash and carbon, the
heat capacity \( (C_s) \) may be calculated as

\[
C_s = C_{pash} (1 - F_{fixc}) + C_{pfixc} F_{fixc}
\]

(III-28)

where \( F_{fixc} \) = fraction of fixed carbon in char.

\( C_{pash} \) = heat capacity of coal ash.

\( C_{pfixc} \) = heat capacity of carbon.

Both \( C_{pash} \) and \( C_{pfixc} \) were empirically correlated to particle temperatures \( (T_s) \) in degree Fahrenheit (51) with

\[
C_{pash} = 0.180 + 7.78 \times 10^{-5} T_s
\]

(III-29)

\[
C_{pfixc} = 0.145 + 4.7 \times 10^{-7} T_s - 2.63 \times 10^{-7} T_s^2
+ 5.25 \times 10^{-11} T_s^3
\]

(III-30)

Char porosity and specific surface area vary not only with coal type but also with firing rate. Experimental data on these were limited. Walker et al. (41) measured specific surface area of coal char with different origins. Their data were plotted against % fixed carbon in char as shown in Figure III-2. Data were somewhat scattered. They were, however, the most complete set of data available. In this study, for a given percentage of fixed carbon in char, specific surface areas were obtained through this correlation. The specific surface area, once determined, was used to read char porosity from a correlation of specific surface area versus porosity prepared by Simons et al. (26). Table III-2 contains results from these
Figure III-2. Char Specific Surface Area Versus % Fixed C in Coal Char.
Table III-2

Estimated Porosity

<table>
<thead>
<tr>
<th>Boiler Type</th>
<th>Coal Type</th>
<th>% Fixed Carbon in Char</th>
<th>Internal Specific Surface area cm²/g(daf)</th>
<th>Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CF) Bituminous</td>
<td>88.6</td>
<td>4.32x10⁶</td>
<td>0.60</td>
<td></td>
</tr>
<tr>
<td>(PF) Lignite</td>
<td>74.2</td>
<td>5.00x10⁶</td>
<td>0.73</td>
<td></td>
</tr>
<tr>
<td>(DT) Lignite</td>
<td>84.4</td>
<td>4.54x10⁶</td>
<td>0.68</td>
<td></td>
</tr>
</tbody>
</table>
estimations. They are, however, quite primitive.

Transport properties involved in this study include thermal conductivities of product gases and diffusivities of all the metallic vapors. The former are well-documented in the heat transfer literature. Diffusion coefficients \( D_i \) of the metallic vapors in question are not readily available. Since empirical values hardly exist at combustion temperatures, theoretical predictions are required. At high temperatures, Chapman's model is highly recommended \((52,53)\). This model uses scale factors \( \epsilon \) and \( \sigma \) which are parameters as discussed in Lennard-Jones potential \( \phi (r) = 4 \epsilon ((\sigma/r)^{12}-(\sigma/r)^6) \). Such data were also less known for metallic vapors than for organic compounds \((52)\). For those where \( \epsilon \) and \( \sigma \) were available, their diffusivities were calculated as shown in column II of Table III-3. Otherwise, a correlation of diffusivities versus molecular weight has been established over 70 species with known \( \epsilon \) and \( \sigma \) (see Appendix I). Diffusivities of all the metallic vapors involved, obtained through this correlation, were tabulated in column III of Table III-3. Column IV shows the absolute difference between these two approaches. The agreement is acceptable. The diffusivity-molecular weight correlation was used in the present work.
Table III-3

Estimated Diffusivities*

<table>
<thead>
<tr>
<th>Species</th>
<th>Directly Predicted from Known</th>
<th>Indirectly Estimated from Diffusivity- Absolute</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\sigma$ and $\epsilon$</td>
<td>Molecular Wt Difference Correlation $\left(\text{cm}^2/\text{s}\right)$</td>
</tr>
<tr>
<td></td>
<td>$\left(\text{cm}^2/\text{s}\right)$</td>
<td>$\left(\text{cm}^2/\text{s}\right)$</td>
</tr>
<tr>
<td>Al</td>
<td>3.04</td>
<td>2.97</td>
</tr>
<tr>
<td>AlH</td>
<td>---</td>
<td>2.91</td>
</tr>
<tr>
<td>AlO</td>
<td>2.75</td>
<td>2.38</td>
</tr>
<tr>
<td>AlS</td>
<td>2.03</td>
<td>2.12</td>
</tr>
<tr>
<td>AlOH</td>
<td>---</td>
<td>2.37</td>
</tr>
<tr>
<td>Al$_2$O</td>
<td>---</td>
<td>1.95</td>
</tr>
<tr>
<td>Ca</td>
<td>---</td>
<td>2.45</td>
</tr>
<tr>
<td>CaO</td>
<td>---</td>
<td>2.18</td>
</tr>
<tr>
<td>Fe</td>
<td>---</td>
<td>2.19</td>
</tr>
<tr>
<td>FeO</td>
<td>---</td>
<td>1.93</td>
</tr>
<tr>
<td>K</td>
<td>---</td>
<td>2.47</td>
</tr>
<tr>
<td>KOH</td>
<td>---</td>
<td>2.18</td>
</tr>
<tr>
<td>Mg</td>
<td>3.06</td>
<td>3.11</td>
</tr>
<tr>
<td>MgO</td>
<td>---</td>
<td>2.44</td>
</tr>
<tr>
<td>MgS</td>
<td>---</td>
<td>2.18</td>
</tr>
<tr>
<td>Na</td>
<td>2.63</td>
<td>3.24</td>
</tr>
<tr>
<td>NaOH</td>
<td>2.81</td>
<td>2.48</td>
</tr>
<tr>
<td>Si</td>
<td>2.75</td>
<td>2.90</td>
</tr>
<tr>
<td>SiH</td>
<td>---</td>
<td>2.85</td>
</tr>
<tr>
<td>SiO</td>
<td>---</td>
<td>2.36</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>1.89</td>
<td>2.10</td>
</tr>
<tr>
<td>SiS$^2$</td>
<td>1.95</td>
<td>2.10</td>
</tr>
</tbody>
</table>

* Temperature at 1500 K, Pressure at 1 atm, gas phase considered to be pure N$_2$. 
III-d Formation of Condensation Ash

The formation of a condensed phase in a supersaturated vapor mixture is caused either by homogeneous nucleation, where condensation nuclei are generated by vapor itself, or by heterogeneous nucleation in the presence of foreign impurities. In this study, metallic vapors predominate at the particle surface (because of the reducing atmosphere). These, once in the bulk phase, are presumably oxidized to stable oxides. This results in supersaturation even at temperatures higher than adiabatic flame temperatures. Since the number population of residual ash evolved during coal combustion is usually low (17,20), nucleation of these metallic oxides is taken as a homogeneous process. Further growth is controlled by condensation or by coagulation and coalescence of these particles(18,24,29,32,54).

Homogeneous nucleation is caused by the growth of molecular clusters, which in turn are formed due to collisions and cohesions of monomers in a vapor phase, to a critical size. This critical radius of a nucleus can be formulated thermodynamically (21, 55) as

\[ r^* = \frac{2 \sigma}{\rho \Delta F_v} \]  

(III-31)

where \( \sigma \) = surface tension. 
\( \rho \) = density.
$\Delta F_v = \text{free energy change (vapor to condensed phase)}.$

For condensation from a vapor, the free energy change $\Delta F_v$ can be expressed as

$$\Delta F_v = RT_g \ln(P/P_e) \quad (\text{III-32})$$

where $P$ = actual vapor pressure.

$P_e$ = vapor pressure in equilibrium with bulk liquid

$R$ = universal gas constant.

$T_g$ = gas temperature.

Applying Equation (III-31) in silica flames, Ulrich (21) found the impossible result that the calculated radius ($r^*$) was less than a single molecule. He concluded that in that system, the supersaturation ratio is so large that any multimolecular species would be a stable particle. He then used a Brownian collision-coalescence model to describe the growth of these particles. In his subsequent work, Ulrich et al. (22, 23, 34) refined the growth model. According to that work, growth in the short residence-time region is controlled by free-molecule collisions and then followed, as particles become larger, by continuum Brownian collision rates. Equations describing this growth model as derived by Ulrich et al. (34) are outlined as follows:

$$L_{ij} = (8\pi kT_g (m_i + m_j)/(m_i m_j))^{1/2} (R_i + R_j)^2 N_i N_j \quad (\text{III-33})$$
where $L_{ij}$ = collision rate between particles i & j.

$m_i$ = molecular weight of particle i.

$m_j$ = molecular weight of particle j.

$R_i$ = radius of particle i.

$R_j$ = radius of particle j.

$N_i$ = particle concentration of size i.

$N_j$ = particle concentration of size j.

$k$ = Boltzmann’s constant.

$T_g$ = absolute gas temperature.

Equation (III-33) is the expression for free-molecule collision rates where the Knudsen number ($Kn$, ratio of mean-free-path to particle radius) is greater than ten. For the continuum regime, $Kn < 1$, $L_{ij}$ is expressed as

$$L_{ij} = 4\pi(D_i + D_j)(R_i + R_j)N_i N_j$$  (III-34)

where $R_i$, $R_j$, $N_i$ and $N_j$ are as designated in Equation (III-33).

$D_i$ and $D_j$ are the particle diffusivities which can be represented by

$$D_i = \frac{kT_g}{(6\pi\mu R_i)}(1 + A_i \lambda/R_i)$$  (III-35)

where $\mu$ is the viscosity of gas medium.

$\lambda$ is the gas mean-free-path and $A_i$ is the Stokes-Cunningham correction factor;
\[ A_i = 1.257 + 0.4 \exp(-1.10R_i/\lambda) \]  

(III-36)

From Equation (III-33), Ulrich derived an expression for the particle inventory in free molecule particle population.

\[ (-dn_i/dt)_j = 273CP(6kR_0(i+j)/(ij \rho T_g))^{1/2} \]
\[ (1^{1/3} + j^{1/3})^{2n_in_j} \]  

(III-37)

Equation (III-37) was derived originally for spherical particles. Subsequent work revealed that particles in many systems are aggregates or clusters of single particles. This equation was consequently modified to describe collisions between aggregated flocs. This gave the following result

\[ (-dn_i/dt)_j = 273CP(6k(i+j)/(ij \rho T_g))^{1/2} \]
\[ (i^{.435} + j^{.435})^{2BR_0^{1.11}} \]
\[ R_p^{.61} n_i n_j \]  

(III-38)

where

\[ C = \text{sticking coefficient}. \]
\[ P = \text{pressure in atm.} \]
\[ k = \text{Boltzmann's constant}. \]
\[ R_0 = \text{molecular radius}. \]
\[ \rho = \text{density}. \]
\[ B = \text{bulkiness factor, approximately equal to 1.2} \]
\[ R_p = \text{primary particle radius}. \]
\[ n_i = \text{particle concentration of size i at STP}. \]
\( n_j \) = particle concentration of size \( j \) at STP.

The use of either Equation (III-37) or equation (III-38) is determined by primary particle size \( (R_p) \). This is the radius of an elemental particle within a cluster. These particles grow by fusion or coalescence at a rate given by

\[
\frac{\Delta R_p}{\Delta t} = (1 + \alpha)^{1/3} - 1) \sigma / \mu
\]  

(III-39)

where \( \alpha \) is the number of surrounding particles that fused with a central particle in a cell.

\( \sigma \) = surface tension.

\( \mu \) = viscosity of liquid phase.

If \( R_p \) as calculated by Equation (III-39) is larger than or equal to that of a single spherical particle having the same mass of the aggregate, then single spherical particles prevail and Equation (III-37) is employed. Otherwise, clusters prevail and Equation (III-38) applies.

For particles in the continuum regime, Equation (III-34) is used instead of Equation (III-33) to characterize the particle size history. The resulting collision expression is

\[
(-\frac{dn_i}{dt})_j = (0.667(273)CPk/(1.36*10^{-5}T_g^{1/2}))
\]

\[
(1+(1.257+0.4\exp(-1.1/\text{Kn})))\text{Kn})
\]
\[
\frac{1}{R_i+1/R_j}(R_i+R_j)n_in_j
\]  
(III-40)

where \( C \) = sticking coefficient.

\( P \) = pressure.

\( k \) = Boltzmann's constant.

\( K_n \) = Knudsen number \((\lambda/R)\).

\( R_i \) and \( R_j \) are particle radius.

\( n_i \) and \( n_j \) are number of particles of masses \( i \) and \( j \).

Equations (III-33) through (III-40) predict the growth of particles from a single condensable vapor. A computer code characterizing such a system of growing particles was written by Ulrich. He controlled the transition from the free molecule to the continuum regimes by testing the Knudsen number \((Kn)\). If it was greater than 10, the free molecule behavior was assumed and either Equation (III-37) or Equation (III-38), as appropriate, was used. If \( Kn \) was less than 10, the collision rate was taken as the lower value obtained from the continuum and free-molecule expressions. These proved to be a successful means of interpolating through the transition regime of Brownian behavior (34).

The growth model outlined above was proposed and applied by Ulrich et al. to describe the formation of silica-fume in flames. Good agreement was observed between theoretical predictions and experimental data (34). This
same approach is applied herein to the prediction of condensation ash in coal-burning combustors. Although this system contains multicomponent vapors instead of pure condensable species as in silica flames, the adoption seems justifiable since the same assumptions engaging nucleation can be applied. Detailed computations are presented in chapter IV.
CHAPTER IV
COMPUTATIONS AND RESULTS

Three coal-fired combustors were simulated in this study. One is a drop tube (DT) furnace designed by Sarofim et al. (20,26) at the Massachusetts Institute of Technology. The other two are commercial boilers. One of them is a cyclone-fired (CF) boiler operated by the Public Service of New Hampshire. The other is a pulverized-fuel fired (PF) boiler owned by the Republic of South Africa.

Both PF and CF boilers are widely used in coal combustion (56). Their firing conditions, however, are quite different. In PF boilers, pulverized coal particles of sizes mostly less than 100 micron in diameter are mingled with combustion air and burned in suspension. With CF boilers, crushed coals are introduced tangentially with combustion air to a brick-lined cyclone where large size fractions of coal are burned in a molten slag that forms inside the cyclone. Only a small fraction, approximately 15% of the total crushed coal, remains suspended and burns in air stream (24,56). The drop tube furnace was essentially a bench-scale PF combustor. It was operated with burning conditions similar to an operating PF boiler.
(at heating rates of $10^5$ to $10^6$ K/sec).

Table IV-1 is a list of coal properties and operating conditions for each combustor. Based on this information, predictions were executed according to the following sequence:

**IV-a Evaluation of Gas Temperature and Composition**

Since the gas temperature was assumed to be the adiabatic flame temperature during char burnout, these temperatures and compositions were obtained from the modified equilibrium program (see Appendix J). Input data such as weight ratio of each ingredient and heat of formation were calculated from the coal composition and ash analysis data. Activity coefficients were introduced to account for non-ideal behavior in the liquid ash phases. Although data on such are generally limited, activities for mixtures of several species such as SiO$_2$, Al$_2$O$_3$, CaO, and FeO are available from the ceramic and metal smelting literature (57,58). Data employed in this project are listed in Table IV-2. For minor species like Na$_2$O, K$_2$O and others, the activity coefficients were assigned to be 0.1 (59). Tables J-1, J-2 and J-3 of Appendix J are equilibrium gas compositions calculated for coal in the
three combustors. Gas temperatures and total gas moles were summarized in Table IV-3.
Table IV-1
Properties of Coal Studied

(A) CF Boiler

Type of Coal: Bituminous
Gross Calorific Value: 31.5 Mj/kg
Net Calorific Value: 30.3 Mj/kg

Proximate Analysis (As Received)

<table>
<thead>
<tr>
<th>Percentage</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile Matter</td>
<td>33.19</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>56.32</td>
</tr>
<tr>
<td>Total Moisture</td>
<td>3.28</td>
</tr>
<tr>
<td>Ash</td>
<td>7.21</td>
</tr>
</tbody>
</table>

100.00

Ultimate Analysis (As Received)

<table>
<thead>
<tr>
<th>Percentage</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>3.28</td>
</tr>
<tr>
<td>Ash</td>
<td>6.85</td>
</tr>
<tr>
<td>Carbon</td>
<td>75.48</td>
</tr>
<tr>
<td>Sulphur</td>
<td>2.67</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.08</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.35</td>
</tr>
<tr>
<td>Oxygen</td>
<td>5.20</td>
</tr>
</tbody>
</table>

100.00

Combustion Air: 117% Excess

Coal Ash Analysis:

<table>
<thead>
<tr>
<th>Percentage</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>20.52</td>
</tr>
<tr>
<td>CaO</td>
<td>6.77</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>19.62</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.16</td>
</tr>
<tr>
<td>MgO</td>
<td>1.26</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.12</td>
</tr>
<tr>
<td>SiO₂</td>
<td>37.02</td>
</tr>
<tr>
<td>SO₂</td>
<td>9.33</td>
</tr>
<tr>
<td>Balance</td>
<td>3.20</td>
</tr>
</tbody>
</table>

100.00
Table IV-1 (Continued)

(B) PF Boiler

Type of Coal: Lignite
Gross Calorific Value: 21.6 Mj/kg
Net Calorific Value: 20.6 Mj/kg

Specifications of Particle Size
- Before Pulverizing: 100% Passing Through 76.2MM
- After Pulverizing: 70% Passing Through 75 Micron
- 99% Passing Through 0.3 MM

Proximate Analysis (As Received)

<table>
<thead>
<tr>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile Matter</td>
</tr>
<tr>
<td>Fixed Carbon</td>
</tr>
<tr>
<td>Total Moisture</td>
</tr>
<tr>
<td>Ash</td>
</tr>
<tr>
<td>---------------------</td>
</tr>
<tr>
<td>100.00</td>
</tr>
</tbody>
</table>

Ultimate Analysis (As Received)

<table>
<thead>
<tr>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Moisture</td>
</tr>
<tr>
<td>Inherent Moisture</td>
</tr>
<tr>
<td>Ash</td>
</tr>
<tr>
<td>Carbon</td>
</tr>
<tr>
<td>Sulphur</td>
</tr>
<tr>
<td>Hydrogen</td>
</tr>
<tr>
<td>Nitrogen</td>
</tr>
<tr>
<td>Oxygen</td>
</tr>
<tr>
<td>Chlorine</td>
</tr>
<tr>
<td>---------------------</td>
</tr>
<tr>
<td>100.00</td>
</tr>
</tbody>
</table>

Combustion Air: 114% Excess

Coal Ash Analysis:

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<thead>
<tr>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>CaO</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>K&lt;sub&gt;2&lt;/sub&gt;O</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;O</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>SO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>Balance</td>
</tr>
<tr>
<td>---------------------</td>
</tr>
<tr>
<td>100.00</td>
</tr>
</tbody>
</table>
Table IV-1 (Continued)

(C) DT Furnace

Type of Coal: Lignite
Gross Calorific Value: 22.8 Mj/kg
Net Calorific Value: 21.4 Mj/kg

Specifications of Particle Size:
\[ R = 100 \exp \left(-\frac{(X/X')}{n}\right) \]
\[ X' = 77.4 \text{ micron} \]
\[ n = 5.2 \]
Where \( R \): Wt. Percent of Material of Particle Size Greater Than \( X \)
\( X \): Particle Diameter (in

Proximate Analysis (As Received)

<table>
<thead>
<tr>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile Matter</td>
</tr>
<tr>
<td>Fixed Carbon</td>
</tr>
<tr>
<td>Total Moisture</td>
</tr>
<tr>
<td>Ash</td>
</tr>
</tbody>
</table>

100.00

Ultimate Analysis (As Received)

<table>
<thead>
<tr>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
</tr>
<tr>
<td>Ash</td>
</tr>
<tr>
<td>Carbon</td>
</tr>
<tr>
<td>Sulphur</td>
</tr>
<tr>
<td>Hydrogen</td>
</tr>
<tr>
<td>Nitrogen</td>
</tr>
<tr>
<td>Oxygen</td>
</tr>
<tr>
<td>Chlorine</td>
</tr>
</tbody>
</table>

100.00

Combustion Air: 1731% Excess
(0.03 g/min. Coal in 61 Air/min @ 500 K)

Coal Ash Analysis:

<table>
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<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
</tr>
<tr>
<td>( \text{CaO} )</td>
</tr>
<tr>
<td>( \text{Fe}_2\text{O}_3 )</td>
</tr>
<tr>
<td>( \text{MgO} )</td>
</tr>
<tr>
<td>( \text{SiO}_2 )</td>
</tr>
<tr>
<td>( \text{SO}_3 )</td>
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<tr>
<td>Balance</td>
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</table>

100.00
Table IV-2  
Estimated Activity Coefficient

<table>
<thead>
<tr>
<th>Boiler Type</th>
<th>$\gamma_{\text{SiO}_2}$</th>
<th>$\gamma_{\text{Al}_2\text{O}_3}$</th>
<th>$\gamma_{\text{CaO}}$</th>
<th>$\gamma_{\text{FeO}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF</td>
<td>1.070</td>
<td>0.625</td>
<td>0.003</td>
<td>1.2</td>
</tr>
<tr>
<td>PF</td>
<td>1.070</td>
<td>1.480</td>
<td>0.004</td>
<td>(3.0)*</td>
</tr>
<tr>
<td>DT</td>
<td>0.054</td>
<td>0.610</td>
<td>0.100</td>
<td>2.4</td>
</tr>
</tbody>
</table>

*Composition falls out of figure available, 3.0 being obtained by extrapolation.
Table IV-3

Summary of Bulk Phase Properties

<table>
<thead>
<tr>
<th>Boiler Type</th>
<th>Total Moles</th>
<th>Tg (k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF</td>
<td>241.29</td>
<td>1991</td>
</tr>
<tr>
<td>PF</td>
<td>192.67</td>
<td>1565</td>
</tr>
<tr>
<td>DT</td>
<td>185.51 + 2269.1**</td>
<td>1719</td>
</tr>
</tbody>
</table>

* Refer to Appendix J.
** From Excess Air in Flue Gases.
IV-b Calculating Metallic Vapor Concentration at Char Surface

Coal ash usually contains Al, Ca, Fe, K, Mg, Na and Si as major elements. In a reducing atmosphere, the most significant high temperature molecular vapors appear to be Al, AlH, AlO, AlS, Al\(_2\)O, Ca, CaO, Fe, FeO, K, KOH, Mg, MgO, MgS, Na, NaOH, Si, SiH, SiO, SiO\(_2\), and SiS. Their compositions at char surface were calculated, as noted earlier, by using an equilibrium program and reducing the oxidant level until solid carbon appears as a stable component in the system. This apparently is the true situation at the char surface. Tables G-1, and G-2 of Appendix G are input and output of a typical run.

Calculations were made for 15 different temperatures ranging from 1500 to 2400 K for each combustor studied. Results are presented in Figures IV-1 to IV-22. They are plots of vapor mole fractions (based on total metallic vapors) versus temperature. Among them, Figures IV-1 to IV-7 are results for the CF boiler, Figures IV-8 to IV-14 for the PF boiler and Figures IV-15 to IV-19 for the drop tube furnace. To indicate the degree of vaporization among Al, Ca, Fe, K, Mg, Na and Si, oxides including their reduced compounds were summed up. Results were plotted against temperature as shown in Figures IV-20 to IV-22.
Figure IV-1. Surface Vapor Fraction as a Function of Temperature (Aluminum Compounds, Cyclone-Fired Boiler)
Figure IV-2. Surface Vapor Fraction as a Function of Temperature (Calcium Compounds, Cyclone-Fired Boiler)
Figure IV-3. Surface Vapor Fraction as a Function of Temperature (Iron Compounds, Cyclone-Fired Boiler)
Figure IV-4. Surface Vapor Fraction as a Function of Temperature (Potassium Compounds, Cyclone-Fired Boiler)
Figure IV-5. Surface Vapor Fraction as a Function of Temperature (Magnesium Compounds, Cyclone-Fired Boiler)
Figure IV-6. Surface Vapor Fraction as a Function of Temperature (Sodium Compounds, Cyclone-Fired Boiler)
Figure IV-7. Surface Vapor Fraction as a Function of Temperature (Silicon Compounds, Cyclone-Fired Boiler)
Figure IV-8. Surface Vapor Fraction as a Function of Temperature (Aluminum Compounds, Pulverized-Fuel Boiler)
Figure IV-9. Surface Vapor Fraction as a Function of Temperature (Calcium Compounds, Pulverized-Fuel Boiler)
Figure IV-10. Surface Vapor Fraction as a Function of Temperature (Iron Compounds, Pulverized-Fuel Boiler)
Figure IV-11. Surface Vapor Fraction as a Function of Temperature (Potassium Compounds, Pulverized-Fuel Boiler)
Figure IV-12. Surface Vapor Fraction as a Function of Temperature (Magnesium Compounds, Pulverized-Fuel Boiler)
Figure IV-13. Surface Vapor Fraction as a Function of Temperature (Sodium Compounds,
Figure IV-14. Surface Vapor Fraction as a Function of Temperature (Silicon Compounds, Pulverized-Fuel Boiler)
Figure IV-15. Surface Vapor Fraction as a Function of Temperature (Aluminum compounds, Drop Tube Furnace)
Figure IV-16. Surface Vapor Fraction as a Function of Temperature (Calcium compounds, Drop Tube Furnace)
Figure IV-17. Surface Vapor Fraction as a Function of Temperature (Iron compounds, Drop Tube Furnace)
Figure IV-18. Surface Vapor Fraction as a Function of Temperature (Magnesium compounds, Drop Tube Furnace)
Figure IV-19. Surface Vapor Fraction as a Function of Temperature (Silicon compounds, Drop Tube Furnace)
Figure IV-20. Surface Vapor Fraction as a Function of Temperature (Metal-Containing Species Al, Ca, Fe, K, Mg, Na, Si (Cyclone-Fired Boiler))
Figure IV-21. Surface Vapor Fraction as a Function of Temperature (Metal-Containing Species Al, Ca, Fe, K, Mg, Na, Si (Pulverized-Fuel Boiler))
Figure IV-22. Surface Vapor Fraction as a Function of Temperature (Metal-Containing Species-Al, Ca, Fe, Mg, Si (Drop Tube Furnace))
IV-c Prediction of Char Temperature Profiles and Total Amount of Metallic Vapors Transported

The char temperature history is dictated by the energy balance as described in Equation (III-19). Equations listed in Table III-1 describe the burning of a char particle. Equation (III-25) was integrated from initiation of char burning to burnout to obtain the total amount of vapor transported. In actual programming, these equations were solved simultaneously. Appendix H lists the computer codes for these purpose. The particle temperature histories through burnout for all three cases are presented in Figure IV-23. Total amounts of vapors transported to bulk phase are shown in Table IV-4. These results were obtained assuming a uniform particle size (a weight-mean size for both the drop tube furnace and the PF boiler, and particle size of 100 micron in diameter for the CF boiler). The use of uniform particles is justified because of the close agreement between results obtained for both monodispersed and polydispersed coal particle distributions in some initial calculations (see Appendix L).
Figure IV-23. Charparticle Temperature as a Function of Burning Time (for Three Combustors)
**TABLE IV-4**

**METALLIC COMPOSITION IN THE BULK GAS PHASE**

*(CF BOILER)*

-----**CONC. OF ASH VAPORIZED (NG/STD. CC)**-----

<table>
<thead>
<tr>
<th>Element</th>
<th>AL</th>
<th>ALH</th>
<th>ALO</th>
<th>ALS</th>
<th>ALOH</th>
<th>AL2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>AL</td>
<td>52.43</td>
<td>1.98</td>
<td>0.00</td>
<td>0.60</td>
<td>0.00</td>
<td>0.36</td>
</tr>
<tr>
<td>CA</td>
<td>18.57</td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FE</td>
<td>46.40</td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>4.02</td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MG</td>
<td>3.87</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NA</td>
<td>3.47</td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SI</td>
<td>0.10</td>
<td>0.00</td>
<td>2.40</td>
<td>0.00</td>
<td>118.42</td>
<td></td>
</tr>
</tbody>
</table>
**TABLE IV-4 (CONTINUED)**

(DT FURNACE)

-----CONC. OF ASH VAPORIZED (NG/STD. CC)-----

<table>
<thead>
<tr>
<th>Element</th>
<th>AL</th>
<th>ALH</th>
<th>ALO</th>
<th>ALS</th>
<th>ALOH</th>
<th>AL2O</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>23.47</td>
<td>1.53</td>
<td>0.00</td>
<td>0.15</td>
<td>0.00</td>
<td>2.37</td>
</tr>
<tr>
<td>CA</td>
<td>41.11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FE</td>
<td>1.81</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MG</td>
<td>23.82</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SI</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

CAO: 0.00
FEO: 0.00
MGO: 0.00
MGS: 0.01
SIO2: 72.15
SIS: 5.12
### TABLE IV-4 (CONTINUED)

(PF BOILER)

<table>
<thead>
<tr>
<th>Conc. of Ash Vaporized (ng/std. cc)</th>
<th>AL</th>
<th>ALH</th>
<th>ALO</th>
<th>ALS</th>
<th>ALOH</th>
<th>AL2O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>46.65</td>
<td>3.44</td>
<td>0.00</td>
<td>0.03</td>
<td>0.00</td>
<td>12.68</td>
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<tr>
<td>CA</td>
<td>0.77</td>
<td></td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAO</td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FE</td>
<td>2.13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FEO</td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>22.27</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KOH</td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>MG</td>
<td>235.76</td>
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<tr>
<td>MGO</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MGS</td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NA</td>
<td>55.78</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NAOH</td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SI</td>
<td>0.82</td>
<td></td>
<td>2403.05</td>
<td>0.00</td>
<td>1567.24</td>
<td></td>
</tr>
</tbody>
</table>
IV-d Calculating Ultimate Particle Sizes

As shown in Table IV-4, condensation ash may consist of many components. It is, however, believed that metallic vapors or metal oxides vaporized in a reduced state are oxidized to a more stable form once in the oxidant-rich phase. These stable metal oxides are Al$_2$O$_3$, CaO, FeO (or Fe$_2$O$_3$), K$_2$O, MgO, Na$_2$O, and SiO$_2$.

Calculations (Table IV-5) of the critical nucleus radii ($r^*$) yield results that are smaller than the size of their molecules as with silica cited earlier. Mixtures of these oxides may not adhere to the nucleation theory as applied. Note, however, that $r^*$ is determined by the ratio of surface tension to free energy change ($\sigma/\Delta F_v$). Since surface tension is not a strong function of composition, the values $r^*$ is simply controlled by the condensation free energy change. Since $\Delta F_v$ tends to increase for components present in mixtures, the critical radius for a mixed oxide could be even less than that calculated. Thus, nucleation is assumed to be virtually instantaneous and to adhere. Based on these observations, Ulrich's silica growth model can be adopted with some modifications (see Appendix M).
Table IV-6 summarizes the properties of condensable vapors for all three combustion cases. Viscosity data were obtained both from Watt and Tereday (60), which are good for the range of 1.4 to 2.4 in terms of SiO$_2$/Al$_2$O$_3$, and from correlation by Rasin, Bersen and Urbain (61). Surface tension was obtained from the equation developed by Lyon (62). Densities were calculated according to the mixing rule.

The residence time for the CF boiler has been estimated as 3.2 seconds from the radiation section to the entrance of precipitator (32). In the pf boiler, a residence time of 4.6 seconds was estimated from the radiation zone to the entrance of economizer. For the drop tube furnace, a residence time of 0.5 second was taken to simulate the actual operations done by Neville et al. (29).

Temperature profiles in the CF and PF boilers were calculated from energy balance at each section. Results are shown in Figures IV-24 and IV-25 for the CF boiler and PF boiler, respectively. In the drop tube furnace, temperature was treated as a constant which is reasonable for a short residence time (0.5 seconds).
Table IV-5

Calculated Critical Nucleus Radius

Critical Radius $r^*(\AA)$

<table>
<thead>
<tr>
<th></th>
<th>CF</th>
<th>PF</th>
<th>DT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>----**</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>CaO</td>
<td>9.81x10$^{-3}$</td>
<td>1.27x10$^{-2}$</td>
<td>1.22x10$^{-2}$</td>
</tr>
<tr>
<td>FeO</td>
<td>9.59x10$^{-3}$</td>
<td>1.23x10$^{-2}$</td>
<td>1.19x10$^{-3}$</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>MgO</td>
<td>8.79x10$^{-3}$</td>
<td>1.14x10$^{-2}$</td>
<td>1.10x10$^{-2}$</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>8.09x10$^{-3}$</td>
<td>1.05x10$^{-2}$</td>
<td>1.02x10$^{-2}$</td>
</tr>
</tbody>
</table>

* Average molecule diameter : 4.4 Å

** $F_v$ Not available.
Table IV-6
Input Data for Growth Program

<table>
<thead>
<tr>
<th>Boiler type</th>
<th>Mole Fraction of Ash Vapor</th>
<th>Initial Gas Temp.(K)</th>
<th>Initial Particle radius(A)</th>
<th>Initial Density (g/cc)</th>
<th>Surface Tension (dyne/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF</td>
<td>$1.30 \times 10^{-4}$</td>
<td>1991</td>
<td>2.2</td>
<td>3.20</td>
<td>441</td>
</tr>
<tr>
<td>DT</td>
<td>$9.66 \times 10^{-5}$</td>
<td>1719</td>
<td>2.2</td>
<td>3.05</td>
<td>464</td>
</tr>
<tr>
<td>PF</td>
<td>$2.14 \times 10^{-3}$</td>
<td>1565</td>
<td>2.2</td>
<td>2.37</td>
<td>341</td>
</tr>
</tbody>
</table>

Estimated Viscosity as a Function of Temperature

\[
\begin{align*}
\text{CF} & = 10^{(3.97^6/(T-423))-1.05} \; ; \; T \text{ in } ^0\text{K} \\
\text{DT} & = 10^{(3.12\times10^6/(T-423))-1.91} \; ; \; T \text{ in } ^0\text{K} \\
\text{PF} & = 1.33\times10^{-6}\exp(7.8\times10^4/(RT)) \; ; \; T \text{ in } ^0\text{K}
\end{align*}
\]
Figure IV-24. Boiler Temperature Profile as a Function of Residence Time (Cyclone-Fired Boiler)
Figure IV-25. Boiler Temperature Profile as a Function of Residence Time (Pulverized-Fuel Boiler)
From the ash vaporization data and temperature profiles, the final particle size of condensation ash was predicted based on the coagulation model of Ulrich. Both primary particle diameter (geometric mean) for three combustors and average aggregate mass for the CF and PF boilers were plotted against growth time as shown in Figures IV-26 to IV-30.

Compositions of these submicron particles were also calculated and presented in Table IV-7. Complete condensation of all the vapors transported was assumed. Results were normalized to 100%. For comparison, experimental compositions of the CF boiler determined previously in our laboratory (7) and that of the drop tube furnace obtained by Neville et al. (63) are included.
Figure IV-26. Primary Particle Diameter of Condensation Ash as a Function of Growth Time (Cyclone-Fired Boiler)

Data from Hopper Ash Studies (7,8)

CF Boiler
Figure IV-27. Primary Particle Diameter of Condensation Ash as a Function of Growth Time (Pulverized Fuel Boiler)
Figure IV-28. Primary Particle Diameter of Condensation Ash as a Function of Growth Time (Drop Tube Furnace)
Figure IV-29. Average Aggregate Mass as a Function of Growth Time (Cyclone-Fired Boiler)
Growth Time (Pulverized-Fuel Boiler)

Figure IV-30. Average Aggregate Mass as a Function of Growth Time (CSCE)
Table IV-7
Composition of Condensation Ash

<table>
<thead>
<tr>
<th>Component</th>
<th>CF Boiler Predicted</th>
<th>CF Boiler Experimental*</th>
<th>PF Boiler Predicted</th>
<th>PF Boiler Predicted</th>
<th>DT Furnace Predicted</th>
<th>DT Furnace Experimental**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>31.26</td>
<td>10.0</td>
<td>2.08</td>
<td>22.14</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>7.82</td>
<td>10.0</td>
<td>0.04</td>
<td>25.09</td>
<td>8.21</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>20.00</td>
<td>8.0</td>
<td>0.07</td>
<td>1.12</td>
<td>5.86</td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>0.86</td>
<td>1.7</td>
<td>0.30</td>
<td>-----</td>
<td>2.50</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>1.98</td>
<td>1.7</td>
<td>7.18</td>
<td>17.22</td>
<td>66.23</td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.43</td>
<td>2.4</td>
<td>1.41</td>
<td>-----</td>
<td>2.26</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>36.70</td>
<td>48.0</td>
<td>88.91</td>
<td>34.43</td>
<td>5.11</td>
<td></td>
</tr>
<tr>
<td>Others</td>
<td>-----</td>
<td>18.2</td>
<td>---</td>
<td>-----</td>
<td>8.86</td>
<td></td>
</tr>
</tbody>
</table>

* Based on EDAX analysis on Impactor Sample (7).
** Work Done by MIT Group (63).
CHAPTER V
DISCUSSION

The formation of condensation ash is a common phenomenon in coal-fired combustors (1,5,6,17,19,32,64). Its formation mechanism has been postulated as a vaporization and recondensation process. Observations made by many investigators (7,8,17,20,29,32,63) strongly support this hypothesis. This study, based on this postulation, has predicted the condensation ash composition and its size distribution. These are discussed below:

V-a Composition

The composition of condensation ash is dictated by the surface concentration which in turn is a strong function of particle temperature. For the three cases studied, particle temperature history was calculated and is shown in Figure IV-23. As can be seen, three temperature profiles have a similar trend, i.e., a sudden rise to a maximum and then a decrease to the gas temperature. The maximum temperature is caused due to the balance among the three terms in the energy conservation equation, i.e., the heat of reaction,
heat losses by convection and heat losses by radiation (Equation (III-19)). In general, the heat of reaction term increases the particle temperature, while heat losses by both convection and radiation decrease it. As combustion initiates, heat losses are relatively small as compared to the heat generated. This causes char particle to burn at higher temperatures than those of their surrounding gases. Differences between these, as calculated in the three combustors, were as high as 400 K. This may increase the degree of vaporization by one hundred fold as shown in Tables H-1, H-2, and H-3 and Figures IV-1 to IV-19. Obviously, surface composition-temperature history is the important factor which determines the composition of condensation ash in our model. Predicted compositions were listed in Table IV-7. These are discussed as follows:

In the CF boiler, predictions were high in $\text{Al}_2\text{O}_3$, $\text{CaO}$, $\text{Fe}_2\text{O}_3$, and $\text{SiO}_2$ due to higher combustion temperatures. In the DT furnace, $\text{MgO}$ and $\text{CaO}$ were higher than those of the other two cases. That is believed to be caused by high Ca and Mg contents in the original coal ash as shown in Table IV-1. In the PF boiler, $\text{SiO}_2$ compositions as high as 88.91% by weight were predicted. This is a consequence of the low temperature combustion (see Figure IV-23) where only Si-related species vaporize significantly (Figure IV-21). Experimental results were
also included in Table IV-7 for the CF boiler and the DT furnace. $\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3$ are overestimated for the CF boiler. In the DT furnace, predicted compositions are high in $\text{Al}_2\text{O}_3$, $\text{CaO}$ and $\text{SiO}_2$. $\text{MgO}$, on the other hand, was underpredicted. Discrepancies between the predicted and experimental results are worse for the DT furnace. In addition to possible errors in the model, uncertainties in porosity data and activity coefficients may have contributed to this lack of agreement. The former causes a change in the particle temperature profile and the latter controls surface composition. In a sensitivity check, a 30% decrease in the interested Al compound composition was found with a 50% decrease in the assumed activity coefficient at temperatures below 2000 K (see Appendix N).

Other errors could stem from the heterogeneous distribution of mineral inclusions. Ash minerals such as pyrites ($\text{FeS}$) are found to be essentially pure compounds rather than dispersed in the total mineral matter (20). Under such conditions, $\text{FeS}$ would behave like a single phase in the vaporization process. Heterogeneous condensation on supermicron particles may also alter the composition of condensation ash (19,29). Further work in these areas are required.
V-b Particle Size Distribution

Theoretically and experimentally, Ulrich et al. have shown that silica fume formed in flames is composed of aggregates (or clusters) of numerous primary particles. Such is exaggerated in silica fume owing to the unusually high viscosity of silica (about $10^6$ poise at 2000 K). This, however, is evidently not what occurs in the formation of condensation ash because of much lower viscosities (less than 10 poises at their adiabatic flame temperatures for three cases in question). At these low viscosities, instantaneous coalescence is a good assumption. Thus, single particles rather than aggregates are likely. As gases cool, however, the growth process changes because of the rapid increase in liquid viscosity. Coalescence begins to control growth. Therefore, the model must represent the transition from instantaneous to finite coalescence.

Figure IV-26 shows the average predicted primary particle diameter versus growth time for the CF boiler. The transition from instantaneous to finite coalescence occurs at a residence time of approximately 0.79 seconds (in the superheater section). Before this, particles are spherical. After 0.79 seconds, aggregates are formed. The average ultimate primary particle size is predicted to be around 50
nm in diameter. This is in good agreement with our previous studies (7,8) where condensation ash particles appeared to be aggregates of several primary particles, each about 50 to 60 nm (0.05 to 0.06 micron) in diameter (see Figure IV-26). The growth of aggregates is depicted in Figure IV-29 where average aggregate mass is plotted against growth time.

Predictions for the PF boiler are presented in Figures IV-27 and IV-30. Transition here occurs at approximately 1.52 seconds residence time. Average predicted primary particle size is 180 nm (see Figure IV-27). The average aggregate mass was shown in Figure IV-30. No field measurements on this boiler were available for comparison. Investigators have, however, conducted particles size studies in other PF power plants. Primary particle sizes of 100 to 200 nm in diameter are found to be typical in most studies (1,5,6).

In the DT furnace, predictions were prepared for the first 0.5 seconds residence time. During this period, growth is within the complete coalescence range according to calculations. Thus, single particles are predicted. The average particle size was found to be 34 nm in diameter at 0.46 seconds growth time as shown in Figure IV-28. Laboratory results agree quite well with predictions (note that experimental data were for combustion at 30% O$_2$ in
while this prediction simulated combustion in air (25% \( \text{O}_2 \) in \( \text{N}_2 \)) except that particles are predicted to be single spheres instead of aggregates as found in Neville's study (29). Aggregation, however, might have occurred during sampling.
CHAPTER VI
CONCLUSIONS AND RECOMMENDATIONS

The ultimate objective of this study was to predict the nature, i.e., composition and characteristics of condensation ash formed in coal-fired combustors.

Predictions herein are based on a porous char combustion model developed by Simons et al. (25,26,27,28) Growth of condensation ash was calculated employing Ulrich's coagulation model with modifications to accommodate transition from instantaneous to finite coalescence.

Good agreement was observed between the predicted particle size and laboratory findings. In DT furnace, single particle were predicted instead of aggregates found from microscopy study by Neville et al. (29)

Study, however, reveals poor agreement between predicted and actual compositions. Possible sources of error are believed to be caused by the following.

1. Poor activity coefficient data.
2. The heterogeneous nature of mineral matter.

3. Deposition to the wall or heterogeneous condensation on existing particles.

Both activity coefficient and heterogeneity of mineral matter affect the equilibrium surface composition which controls the total quantities of vaporization ash.

Heterogeneous condensation was pointed out by Flagan and others (19,29) as a possible mechanism in ash formation. To describe the competition between homogeneous condensation and heterogeneous one requires a much involved model.

More work is necessary to clarify these discrepancies. A refined model including the size distribution of mineral matter and heterogeneous condensation is recommended. An experimental study of simulated ash is needed to provide reliable activity coefficient data.
Bibliography


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42. Elliott, M. A., Chemistry of Coal Utilization, Second Supplementary Volume, John Wiley & Sons, 1981


Appendix A:
Steady State Mass Transport
with Stefan Flow

For the combustion of a solid particle immersed in a stagnant gas phase (see Figure below), oxidant diffuses from bulk phase and is consumed at particle surface. The diffusional molar flux of oxidant consists of two terms, one from convective flow (or so-called Stefan flow), the other from molecular diffusion. Mathematically,

\[ n_j = vC_j - D_j \frac{dC_j}{dr} \]  \hspace{1cm} (A-1)

where  
\( v \) = net velocity  
\( C_j \) = concentration of \( j \).  
\( D_j \) = diffusivity of \( j \).

In general, Stefan flow may be neglected if diffusivities of all the species are close enough and reaction does not change the total number of moles (39). Such, obviously, is not true in this study where surface reaction is considered to be

\[ 2 \text{C} + \text{O}_2 + 3.76 \text{N}_2 \rightarrow 2 \text{CO} + 3.76 \text{N}_2 \]

Based on this reaction, although the diffusivities of all the components are nearly the same, it is obvious that the stoichiometry of the reaction does not sum up to zero. It is thus necessary to include the Stefan flow. Further
derivations are discussed below:

\[ a = \text{particle radius.} \]

\[ \delta = \text{boundary layer thickness.} \]

In terms of partial pressure \( P_j \), Equation (A-1) can be rewritten as

\[ n_j'' = \frac{v(P_j/(RT)) - (D_j/(RT))(dP_j/dr)}{dP_j/dr} (A-2) \]

Rearranging Equation (A-2), one has

\[ dP_j/dr = \frac{(v/D_j)P_j - (RTn_j''/D_j)}{dP_j/dr} (A-3) \]

Noting that the total pressure \( P = \sum P_j \) is invariant with respect to \( r \), \( dP/dr \) is thus equal to zero, i.e.,

\[ dP/dr = \sum (dP_j/dr) = 0 (A-4) \]

Applying this to equation (A-3), one gets

\[ \frac{(v/D_j)}{RT} = \sum \left( \frac{n_j''}{D_j} \right) \]

\[ (n_j'') = \frac{(v/(RT)) \sum (P_j/D_j)}{A-5} \]
Since \( n_j^{\nu_j} / \nu_j = n_1^{\nu_1} / \nu_1 \) (from reaction stoichiometry), (A-5) becomes

\[
(n_j^{\nu_j} / (\nu_1 D_j)) = \left( \frac{v}{RT} \right) \sum (P_j / D_j) \quad (A-6)
\]

Defining \( P/D = \sum P_j / D_j \), one gets

\[
(n_1^{\nu_1} / \nu_1) \sum (\nu_j / D_j) = \left( \frac{v}{RT} \right) (P/D)
\]

\[
n_1^{\nu_1} = \left( \frac{v}{RT} \right) (P/D) (\nu_1 / \left( \sum (\nu_j / D_j) \right)) \quad (A-7)
\]

Let \( \gamma = (D/\nu_1) \sum (\nu_j / D_j) \), one has

\[
n_1^{\nu_1} = \left( \frac{v}{RT} \right) (P/\gamma) \quad (A-8)
\]

Substituting (A-8) into (A-3) with \( j=1 \), one obtains

\[
dP_1/dr = (vP_1 / D_1) - (RT / D_1) \left( \frac{v}{RT} \right) (P/\gamma)
\]

\[
= (vP_1 / D_1) - (v / D_1) (P/\gamma)
\]

\[
= (v / D_1) (P_1 - P/\gamma) \quad (A-9)
\]

Rearranging Equation (A-9), one has

\[
(1 / (P_1 - P/\gamma)) d(P_1) = \left( \frac{v}{D_1} \right) dr
\]

\[
= \left( \frac{v}{D_1} \right) (a/r)^2 dr \quad (A-10)
\]
Integrating (A-10) from bulk (at \( r=a+\delta \)) to surface (at \( r=a \)), one obtains

\[
\int_{l_{b}}^{l_{a}} \frac{1}{(P_{1}-P/\gamma)} \, dP = \int_{(a+\delta)}^{a} \left( \frac{v_{a}}{D_{1}} \right) \left( \frac{a}{r} \right)^{2} \, dr
\]

\[
\ln\left( \frac{P_{1a}-P/\gamma}{P_{1b}-P/\gamma} \right) = v_{a} a^{2} \left( \frac{1}{(a+\delta)}-1/a \right)
\]

\[
v_{a} = \frac{D_{1}}{a^{2}} \left( \frac{1}{(a+\delta)}-1/a \right) \ln\left( \frac{P_{1a}-P/\gamma}{P_{1b}-P/\gamma} \right)
\]

(A-11)

For reaction \( 2C+O_{2}+3.76N_{2} \rightarrow 2CO+3.76N_{2} \), one has from stoichiometry relation

\[
\gamma = \frac{D}{v_{1}} \sum \frac{v_{j}}{D_{j}}
\]

\[
= \frac{D}{(-1)} \left( \frac{-1}{D_{O_{2}}+(-3.76)/D_{N_{2}}+2/D_{CO}+3.76/D_{N_{2}}} \right)
\]

\[
= \frac{D}{(-1)} \left( 1/D \right); \text{ since } D = D_{O_{2}} = D_{CO} = D_{N_{2}}
\]

\[
= -1 \quad \text{(A-12)}
\]

Therefore, Equation (A-11) may be simplified as

\[
v_{a} = \frac{D_{1}}{a^{2}} \left( \frac{1}{(a+\delta)}-1/a \right) \ln\left( \frac{P_{1a}-P}{P_{1b}+P} \right)
\]

(A-13)

This equation can thus be plugged into equation (A-8),

\[
n_{ja}'' = \frac{(v_{a}/(RT))(P/\gamma)}{(-P/(RT))v_{a}}
\]

\[
= \frac{(-P/(RT))(D_{j}/(a^{2}(1/(a+\delta)) - 1/a))}{\ln((y_{j}+1)/(y_{jb}+1))}
\]

(A-14)
where \( j \) indicates oxidant, \( O_2 \) in this case. \( y_j \) is the molar fraction of \( j \) and is related to mass fraction \( C_{oj} \) as

\[
C_{oj} = \frac{M_{o2} y_j}{(M_{o2} y_j + M_{N2} (1-y_j))} \quad \text{(A-15)}
\]

where \( M_{o2}, \) and \( M_{N2} \) are molecular weight of \( O_2 \) and \( N_2 \), respectively.
Appendix B:  
Kinetics of Pore Reaction

Pore reaction, in general, is classified into three reaction regimes according to the pore size and reaction temperature. They are kinetically limited, continuum diffusion limited and knudsen diffusion limited regimes.

The rate expression of kinetically limited reaction is described in Simons' study (27)

\[
m_{pj} = k_j S_t \tag{B-1}
\]

where

\[
k_j = \left( \frac{1}{k_{dj} + \frac{1}{(k_{aj} C_{oj})}} \right)^{-1}
\]

\[
= \frac{k_{dj}}{1 + \epsilon_j}
\]

\[S_t = \text{specific pore surface.}\]

\[
\epsilon_j = \frac{k_{dj}}{(k_{aj} C_{oj})}
\]

The diffusion limited reactions were derived as

\[
m_{pj} = \pi r_p^{3/2} \left( 4k_{dj} \rho g D_j C_{oj} \right)^{1/2} \left( 1 + (2\epsilon_j)^{1/2} \right) \tag{B-2}
\]

where

\[
k_{aj} = \text{adsorption reaction constant.}\]

\[
k_{dj} = \text{desorption reaction constant.}\]

\[
\rho_g = \text{gas phase density.}\]

\[
C_{oj} = \text{mole concentration at particle surface}\]

Equation (B-2) is valid for both continuum limited and Knudsen diffusion limited regimes. The diffusion coefficient \(D_j\) is, however, different in each regime.
\( D_{cj} = \lambda_j v_j / 3 \) for continuum regime and \( D_{kj} = 2r_pv_j / 3 \) for Knudsen regime). This expression has been corrected due to an error discovered in Simons' derivations.

Before integrating these expressions for the overall rate, transition among these three regimes has to be determined. The transition between kinetically limited and continuum diffusion limited regimes was determined at the \( r_p \) where the rates calculated by equation (B-1) and (B-2) are equal. Upon equating Equations (B-1) and (B-2), one has

\[
r_{cj} = (\theta^{1/3} r_{min}(1+\epsilon_j)/K_0(1-\theta))^{1/3}
\]

\[
(\rho g D_{cj} C_{oj} / k_{dj})^{1/3} / (1+(2\epsilon_j)^{1/2})^{2/3}
\]

For the transition between kinetically limited and Knudsen diffusion limited regimes, a similar expression may be obtained by replacing \( D_{cj} \) in Equation (B-2) with \( D_{kj} \) and equating that to Equation (B-1), which gives

\[
r_{ckj} = (\theta^{1/3} r_{min}(1+\epsilon_j)/K_0(1-\theta))^{1/3}
\]

\[
(2\rho g v_j C_{oj} / (3k_{dj}))^{1/2} / (1+(2\epsilon_j)^{1/2})^{1/2}
\]

The transition between the two diffusion limited regimes was set at the pore radius where \( D_{cj} \) is equal to \( D_{kj} \). This is obtained from equating two different expression of diffusivities. Therefore,

\[
r_{dj} = 3D_j / 2v_j
\]
where $V_j$ = thermal speed of the molecule $j$.

$D_j$ = diffusivity of molecule $j$

The overall rates for three regimes may thus be integrated over $r_p$. For the kinetically limited case, one integrates from $r_{\text{min}}$ to $r_{ckj}$, that is

$$M_{pkj} = \int_{r_{\text{min}}}^{r_{ckj}} \left( \frac{k_{dj}}{(1+\epsilon_j)} \right) (S_{t}) (4\pi a^2) g(r_p) (dr_p)$$

$$= \left( \frac{k_{dj}}{(1+\epsilon_j)} \right) (4\pi a^2) \int_{r_{\text{min}}}^{r_{ckj}} \left( 2K_0 r_p^3 (1-\theta) \right)$$

$$/\theta^{1/3} r_{\text{min}} (\theta/(2\pi \beta r_p^3) (dr_p)$$

$$=4\pi a^2 \left( \frac{k_{dj}}{(1+\epsilon_j)} \right) (K_0 (1-\theta)^{2/3}/\beta r_{\text{min}})$$

(B-6)

For the Knudsen diffusion limited regime, one has

$$M_{pkj} = \int_{r_{ckj}}^{r_{dj}} \left( \frac{2\pi V_j C_{oj} k_{dj}/3}{(2\epsilon_j)^{1/2}} \right) (2\pi r_p^2 g(r_p) d(r_p)) 4\pi a^2$$

$$=4\pi a^2 \left( \frac{2\pi V_j C_{oj} k_{dj}/3}{(2\epsilon_j)^{1/2}} \right)^{1/2} (1+$$

$$(2\epsilon_j)^{1/2} \int_{r_{ckj}}^{r_{dj}} 2 r_p^2 (\theta/2\pi \beta r_p^3) d(r_p)$$

$$=4\pi a^2 \left( \frac{2\pi V_j C_{oj} k_{dj}/3}{(2\epsilon_j)^{1/2}} \right)^{1/2} (1+$$

$$(2\epsilon_j)^{1/2} \int_{r_{ckj}}^{r_{dj}} (\theta/\beta) r_p^{-1} d(r_p)$$

$$=4\pi a^2 \left( \frac{2\pi V_j C_{oj} k_{dj}/3}{(2\epsilon_j)^{1/2}} \right)^{1/2} (1+$$

$$(2\epsilon_j)^{1/2} \left( \theta/\beta \right) \ln(r_{dj}/r_{ckj})$$

(B-7)
Finally, for the continuum diffusion limited regime, one integrates from \( r_{dj} \) to \( r_{\text{max}} \). thus

\[
M_{\text{pjc}} = \int_{r_{dj}}^{r_{\text{max}}} 4\pi a^2 \left( \frac{\rho_g D_j C_{0j} k_d j}{1} \right) \left( 1 + \left(2\varepsilon_j \right)^{1/2} \right) \frac{2}{3} g(r_p) (dr_p)
\]

\[
= 4\pi a^2 \left( \frac{\rho_g D_j C_{0j} k_d j}{1} \right) \left( 1 + \left(2\varepsilon_j \right)^{1/2} \right) \left( \frac{\theta}{2\pi \rho} \right) \left( r_p ^{-3/2} \right) (dr_p)
\]

\[
= 4\pi a^2 \left( \frac{\rho_g D_j C_{0j} k_d j}{1} \right) \left( 1 + \left(2\varepsilon_j \right)^{1/2} \right) \left( -\frac{\theta}{\beta} \right) \left( r_{\text{max}} ^{-1/2} - r_{dj} ^{-1/2} \right)
\]

(B-8)
Appendix C:

Rate of Temperature Change of Char Particle

It has been shown that Biot modulus is less than 0.2 for the three cases studied. Under these conditions, one may neglect the temperature gradients within the char particle. The rate of change of particle temperature can thus be described by the general expression,

\[
\text{Heat accumulation} = \text{Heat in} - \text{Heat out}
\]

where Heat in includes heat generated by reaction.

Mathematically, one has (64)

\[
d\left(\rho V C_s T_s\right)/dt = -4\pi a^2 (e + q_r)
\]

where \( V \) = volume of the char particle.
\( \rho \) = density of the char.
\( C_s \) = thermal capacity of char.
\( q_r \) = heat losses by radiation,
\[ q_r = \sigma \varepsilon (T_s^4 - T_b^4) . \]
\( e \) = energy flux
\[ e = (H_{CO} - 1/2H_{O2})(zM_t/(4\pi a^2 M_c)) \]
\[ + (-k_g (dT/dr|_a)) \]

where \( H \) = enthalpy on mole basis.
\( k_g \) = thermal conductivity of gas phase.
Expanding the left hand side of equation (C-1), one has

\[
\frac{d(\rho \VC S \TS)}{dt} = \frac{d((4/3) \pi a^3 \rho \CS \TS)}{dt}
\]

\[
= (4/3) \pi \CS (a^3 \rho (d\TS/dt)) + \CS \TS \frac{d((4/3) \pi a^3 \rho)}{dt} \tag{C-3}
\]

Since \(d((4/3) \pi a^3 \rho)/dt = -z\ MT\), one gets

\[
\frac{d(\rho \VC S \TS)}{dt} = (4/3) \pi \CS (a^3 \rho (d\TS/dt)) - \CS \TS (zM_t) \tag{C-4}
\]

Substituting e and the above equation into (C-1),

\[
(4/3) \pi a^3 \rho \CS (d\TS/dt) - \CS \TS M_c (zM_t/M_c)
\]

\[
= -4 \pi a^2 ((H_{co} - 1/2H_{o2}) (zM_t/(4 a^2 M_c)) +
\]

\[
(-k_g (dT/dr)\big|_a + q_r) \tag{C-5}
\]

Rearranging,

\[
(4/3) \pi a^3 \rho \CS (d\TS/dt) = M_c \CS (zM_t/M_c) - (zM_t/M_c) (H_{co} - 1/2H_{o2}) +
\]

\[
4 \pi a^2 (k_g (dT/dr)\big|_a) - 4 \pi a^2 q_r
\]

\[
=(zM_t/M_c) (H_{c+1}/2H_{o2} - H_{co}) +
\]

\[
4 \pi a^2 k_g (dT/dr)\big|_a - 4 \pi a^2 q_r
\]

\[
= (zM_t/M_c) (-\Delta H_r) + 4 \pi a^2
\]

\[
k_g ((T_b - T_s)/\delta) - 4 \pi a^2 q_r \tag{C-6}
\]

Noting that \((dT/dr)\big|_a\) has been replaced by \((T_b - T_s)/\delta\) (linear temperature profile assumed); where \(\delta\) is the thermal boundary layer thickness. The \(\delta\) is
approximately equal to \(a/(1 + \text{Re}^{1/2} \text{Pr}^{1/3})\), which is equal to particle radius \(a\) since \(\text{Re}\) is essentially zero in a stagnant gas surroundings.

Now that \(\Delta H = H_{\text{CO}} - H_{\text{C}} - 1/2 H_{\text{O}_2}\), Equation (C-6), once divided by \((4/3) \pi a^3 \rho C_s\), becomes

\[
\frac{dT_s}{dt} = \frac{3zM_t}{(4 \pi a^3 C_s M_C)} (-\Delta H_r) +
\]

\[
(3kg/a \rho C_s) \left(\frac{(T_b - T_s)}{\delta}\right) - 3q_r/(a \rho C_s)
\]

\[
= (3kg/a \rho C_s) \left(\frac{(T_b - T_s)}{\delta}\right) - \frac{(3zM_t \Delta H_r)}{(4 \pi a^3 C_s M_C)} - 3q_r/(a \rho C_s)
\]

\(\text{(C-7)}\)
Appendix D:
Rate of Change in Radius \( (da/dt) \) and Rate of Change in Porosity \( (d\theta/dt) \) in Terms of Carbon Removal Rate

The combustion of a porous char particle occurs both internally and externally. External combustion undoubtedly decreases the particle radius. Internal combustion may, however, increase porosity and decrease particle radius. In general, diffusion limited combustion (both Knudsen and continuum diffusion) occurs either at surface or near the pore opening, which results in a decrease in radius. The kinetically limited reaction may affect both radius and porosity depending upon how far the oxidant diffuses before reacting with carbon. To clarify this, it is postulated that pores with diameters larger than or equal to oxidant penetration length (see Appendix E) increases porosity while those smaller decreases particle radius.

To find the \( r_p \) which separates \( M_{pjsl} \) and \( M_{pjs2} \), Equation (E-3) is solved for \( r_p \) by replacing \( L \) with (which is a criteria set in Appendix E). This gives

\[
r_{pjs} = \frac{4k_{d,j}x^2M_{air}}{(.21\rho)g_{D,j}M_j + (k_{d,j} / (.21k_{aj}))}
\]  

(D-1)

With this, Equation (B-6) may be divided into two terms, i.e., \( M_{pjsl} \) and \( M_{pjs2} \). These are \( P_{jsl} \) and \( P_{js} \).
Based on these expressions, $\frac{da}{dt}$ and $\frac{d\theta}{dt}$ are derived as follows:

$$\frac{dm}{dt} = zM_t = z(M_{pjs} + M_{pjk} + M_{pjc} + M_{psj}) \quad (D-4)$$

Since $m = \rho V$, one can also write

$$\frac{dm}{dt} = d(\rho V)/dt$$

$$= V(d\rho/dt) + \rho(dV/dt)$$

$$= V(d(\rho_s(1-\theta))/dt) + \rho(4\pi a^2)(da/dt)$$
The first term on the right hand side of equation (D-5) shows the decrease in mass due to change in porosity. This is obviously caused by the kinetically limited reaction in pores with a diameter larger than or equal to the penetration length (see Appendix E), i.e., \( z_{M_{pjs1}} \). Thus, one obtains

\[
-(4/3)\pi a^3 \rho_s (-d\theta/dt) = z_{M_{pjs1}} \quad (D-6)
\]

The second term describes the decrease of mass due to the change in particle radius, which is contributed from the depletion rates of carbon through external reaction \( z_{M_{sj}} \), diffusion-limited reactions \( z_{M_{pjk}} \) and \( z_{M_{pjc}} \), and the other fraction from from kinetically limited reaction \( z_{M_{pjs2}} \). Therefore

\[
-4\pi a^2 \rho (da/dt) = z(M_{sj} + M_{pjk} + M_{pjc} + M_{pjs2}) \quad (D-7)
\]

Rearranging (D-6) and (D-7), one gets

\[
d\theta/dt = 3z(M_{pjs})/(4\pi a^3 \rho_s) \quad (D-8)
\]

\[
da/dt = -z(M_{sj} + M_{pjk} + M_{pjc} + M_{pjs2})/(4\pi a^2 \rho) \quad (D-9)
\]
Appendix E:
Pore Penetration Length

In the kinetically limited pore reaction, the removal of solid carbon leads to either a decrease in radius or an increase in porosity. A criteria at which the mean free path is set equal to the penetration length has been chosen to separate these two contributions. The penetration length of oxidant into a single pore is derived as follows:

The pore is visualized as a cylinder with a diameter $r_p$, an effective length $l_p$, and an inclination of 45 degrees to the normal of char surface (see Figure below)

Let $L$ be the penetration length. At steady state, the diffusion rate is equal to surface reaction rate $\left(\frac{k_d j}{(1+\epsilon_j)}\right)$; therefore,

$$
\rho g D_j (1/2^{1/2}) \pi r_p^2 \left( \frac{dc}{dt} \right) \bigg|_{x=0} = \left( \frac{k_d j}{(1+\epsilon_j)} \right) (2\pi r_p L) (2^{1/2}) \quad (E-1)
$$
Since \((\text{dc/dx})\) at \(x=0\) equals to \(c_s/L\), one has

\[
\rho_gD_j(1/2^{1/2}) \pi r_p^2 (c_s/L) = \\
\left( \frac{k_{d_j}}{(1+\epsilon_j)} \right) (2 \pi r_p L)^{1/2} \\
\] (E-2)

Rearranging the above equation, one obtain immediately

\[
L = \left( \frac{1}{4} \right) \left( \frac{1+\epsilon_j}{k_{d_j}} \right) \left( \rho_g D_j c_s r_p \right)^{1/2} \\
\] (E-3)

where \(\rho_g\) = gas density.

\(D_j\) = diffusion coefficient.
Appendix F:
Flow Information Diagram

Independent variable: \( t \)

Dependent variables: \( T_s, a, \theta, Y_i, C_{oj}, M_{sj}, \)
\( M_{pjs1}, M_{pjs2}, M_{pjk}, M_{pjc}, \)
\( k_{dj}, k_{aj}, k_1, k_2, k_1', e_j, M_t, \)
\( r_{max}, r_{min}, r_{min0}, \beta, r_{dj}, \)
\( v_j, \lambda_j, d_m, \rho, r_{ck}, r_{ckj}, \)
\( \rho_g, N, \delta, T_{avg}, r_{pjs}, D_j, \)
Appendix G:
Modification of NOTS Program

The NOTS program was originally designed to evaluate rocket propellants and has been adopted for computing chemical equilibria in flames. In the original program, gases were assumed to be ideal. Condensed phases were considered to be immiscible. The program itself was written for the IBM 7094 electronic data processing machine. Thermodynamic data of potential combustion species are first generated by PEPAUX (35). The main program then reads input data, calls for thermodynamic data formerly created, performs equilibrium calculations and prints out the results. The program used in this study is the third revised version. The first one was edited by Ulrich et al. (65) to use in the computation system in Cabot Cooperation. The second one was made by Desrosiers (66) to circumvent the limitation of ideal, immiscible condensed phases, and to run on Dec-10 system at the University of New Hampshire. This, however, was not successfully fulfilled. The flaws have been debugged and corrected. The corrected version has been tested by checking machine calculated equilibrium constants and comparing them with equilibrium constants listed in the JANAF thermochemical tables. Results are satisfactory.
Program updated requires activity coefficients for all the condensed species considered. To input these, option switches #9 and #10 (35, 66) were designed so that \(10* (#9) + #10\) stands for the number of condensed species. To isolate a species as a pure phase when needed, option switch #18 has to be set to 1, and the number of solid phase has to be specified in the input file. In this study, carbon has been taken as a pure phase because of its distinct nature.

A typical input and output from running this updated version are included in Tables G-1 and G-2. In these, option switch #5 has been set to 1, with switch #16 specifying a 5 multiple of the number of runs, to create a set of binary data containing compositions of all gas species and equilibrium temperature.
Table G-1. Input to Equilibrium Surface Composition Computation
Table G-2. Output from Equilibrium Surface Composition Computation
Appendix H:
Simulation Program List

The 34 equations simulating char burning and ash vapor transport (see Table III-1 and Appendix F) have been solved simultaneously using a digital analog simulator, namely, the Continuous System Modelling Program (CSMP). The simulator itself interprets a set of differential equations, which are coded in Fortran programming language, through Fortran compiler. Execution of CSMP program is well-documented in the Dec-10 system application library at the University of New Hampshire.

Program codes for this simulation are the same for all three cases except those parameters describing coal properties and combustion conditions. These properties such as char porosity, specific surface area and ash analysis information were lumped in the PARAMETER section. The surface concentration-temperature relationship, which is also different for each combustor, was programmed in the FUNCTION section. They are subject to change for each combustor in question.

Table H-1 included a typical run (simulating the CF boiler). For the pf boiler and DT furnace, input data as shown in Tables H-2 and H-3 are to replace that of the CF boiler in Table H-1 before program should be executed.
TABLE 4:
A PROGRAM LIST FOR CHAR
COMBUSTION AND VAPOR TRANSPORT SIMULATION

<table>
<thead>
<tr>
<th>LABEL</th>
<th>CHAR BURNING SIMULATION</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>*************************************************************************</td>
</tr>
<tr>
<td></td>
<td>* THIS PROGRAM SIMULATES THE BURNING OF A POROUS COAL</td>
</tr>
<tr>
<td></td>
<td>* CHAR PARTICLE, COMPUTING METALLIC ( OR METAL OXIDE)</td>
</tr>
<tr>
<td></td>
<td>* VAPOR TRANSPORTED FROM BURNING PARTICLE SURFACE TO</td>
</tr>
<tr>
<td></td>
<td>* THE BULK GAS PHASE.</td>
</tr>
<tr>
<td></td>
<td>*************************************************************************</td>
</tr>
<tr>
<td></td>
<td>INTEGER IFLAG'S</td>
</tr>
<tr>
<td></td>
<td>FIXED IT, IFLAG1, IFLAG2, IFLAG3, IFLAG4, IFLAG5</td>
</tr>
<tr>
<td></td>
<td>*************************************************************************</td>
</tr>
<tr>
<td></td>
<td>MACRO ( SIMILAR TO SUBROUTINE) ROUTINE TO CALCULATE</td>
</tr>
<tr>
<td></td>
<td>SEPARATE VAPOR SPECIES TRANSPORTED.</td>
</tr>
<tr>
<td></td>
<td>*************************************************************************</td>
</tr>
<tr>
<td></td>
<td>MACRO Y1,Y2,Y3,Y4=TSP(ARG1,ARG2,ARG3,ARG4,ARG5)</td>
</tr>
<tr>
<td></td>
<td>IF(ARG5 .EQ. 1.0) GO TO 71</td>
</tr>
<tr>
<td></td>
<td>Y0=FTAB(ARG4,ARG3)</td>
</tr>
<tr>
<td></td>
<td>GO TO 72</td>
</tr>
<tr>
<td></td>
<td>71 CONTINUE</td>
</tr>
<tr>
<td></td>
<td>Y0=ARG4</td>
</tr>
<tr>
<td></td>
<td>72 CONTINUE</td>
</tr>
<tr>
<td></td>
<td>PROCEDURE Y1=BLOCK1(ARG2)</td>
</tr>
<tr>
<td></td>
<td>IF(ARG2 .GT. 1600.) GO TO 76</td>
</tr>
<tr>
<td></td>
<td>Y1=0.0</td>
</tr>
<tr>
<td></td>
<td>GO TO 77</td>
</tr>
<tr>
<td></td>
<td>76 CONTINUE</td>
</tr>
<tr>
<td></td>
<td>Y10=FTAB(ARG1,ARG2)</td>
</tr>
<tr>
<td></td>
<td>Y1=10**Y10</td>
</tr>
<tr>
<td></td>
<td>77 CONTINUE</td>
</tr>
<tr>
<td></td>
<td>ENDPRO</td>
</tr>
<tr>
<td></td>
<td>Y2=MFACTR<em>DFACTR</em>ARG3<em>Y0</em>(Y1-0.0)*FCTKN</td>
</tr>
<tr>
<td></td>
<td>Y3=INTGRL(0.0,Y2)</td>
</tr>
<tr>
<td></td>
<td>Y4=Y3/ARG3</td>
</tr>
<tr>
<td></td>
<td>ENDMAC</td>
</tr>
</tbody>
</table>

************************************************************************* |
| INITIALIZATION                                                         |
| ************************************************************************* |
| INPUT OR CALCULATE INITIAL VALUES AND PARAMETERS.                      |
| ************************************************************************* |
| DESIGNATIONS:                                                          |
| D : MOLECULAR COLLISION DIAMETER                                       |
| FFIXC : FRACTION OF CARBON IN TOTAL CHAR                                |
TEMPS0 : INITTEMPERATURE OF COAL CHAR, BEING SET TO EQUAL TO GAS PHASE TEMPERATURE.

RHOS0 : A FUNCTION OF % H IN DRY BASIS USED IN EVALUATING CHAR TRUE DENSITY.

RHOS : CHAR TRUE DENSITY.

SPAREA : INTERNAL SURFACE AREA IN TERMS OF WT. OF CHAR.

RMINO : INITIAL MINIMUM PORE RADIUS.

RMAXO : INITIAL MAXIMUM PORE RADIUS.

VOLBLK : BULK PHASE VOLUME.

TOTCHA : TOTAL INPUT OF CHAR IN EQUILIBRIUM COMPUTATION.

WTCHAR : WEIGHT OF A CHAR PARTICLE.

CNCHAR : CONCetration OF CHAR PARTICLES IN BOILER (NO./CC).

INITIAL

D = (3.0*B/(2.*PI*L))**(1.0/3.0)

FFIXC = PFIXC/(PASH+PFIXC)

TEMPS0 = TBLK

SET UP INITIAL VALUE FOR COJ INTEGRATION, FIRST GUESS WAS TAKEN BY MULTIPLYING OXIDANT AT BULK PHASE BY A RANDOM NUMBER (BETWEEN 0 AND 1) PROGRAM WILL CALL RERUN IF FIRST CHOICE IS NOT SATISFIED.

PROCEDURE COJTMP=BLOCKC(IFLAG1,COJABS)

IF (IFLAG1 .EQ. 1) GO TO 17

COJTMP = COJABS*RAN(1)

GO TO 16

CONTINUE

COJTMP = COJABS*RAN(1)

CALL FLGCLR(IFLAG1)

CONTINUE

ENDPRO

RHOS0 = 1.0/(.4397+.1223*PHDAF-.01715*PHDAF**2+.001077*PHDAF**3)

RHOS = 100.*RHOS0/(PASH*RHOS0+3.*(100.-PASH))

SPAREA = S0*FFIXC

RMINO = IMPL(1.0E-8,ERROR1,FRMINO)

RMAXO = (2.*THETA0**(1./3.)*A0/(3.*K0))

FRMINO = 2.*M*THETA0/RHOS/SPAREA ALOG(RMAXO/RMINO)

VOLBLK = VENT*R*BLK/P

TOTCHA = 0.15*COALFD*(PFIXC+PASH)/100.

WTCHAR = 4.*PI*(A0**3.)*RHOS*(1.-THETA0)/3.

CNCHAR = TOTCHA/WTCHAR/VOLBLK

CONSTANTS AND PARAMETERS

DESIGNATIONS:

B : OXIDANT MOLECULAR VOLUME

L : AVOGADRO'S NUMBER

CJBLK : BULK OXIDANT FRACTION

P : BOILER PRESSURE

RE : REYNOLDS NUMBER
K0 : EMPIRICAL VALUE, APPROXIMATELY 5.0 FROM SIMONS'S STUDY
M : DEFINED VALUE, TAKEN AS 2.0 FROM SIMON'S STUDY
R : GAS CONSTANT
EPSLN : EMISSIVITY
SIGMA : STEPHAN-BOLTZMAN CONSTANT
P0 : REFERENCE PRESSURE
TEMP0 : REFERENCE TEMPERATURE
M????? : MOLECULAR WEIGHT OF ?????
D????? : DIFFUSIVITIES OF ?????
TBLK : GAS TEMPERATURE
PASH : ASH PERCENTAGE IN CHAR
PFIXC : FIXED CARBON PERCENTAGE IN CHAR
PHDAF : % HYDROGEN IN DAF BASIS
THETA0 : INITIAL CHAR POROSITY
SP0 : INITIAL INTERNAL SURFACE AREA
AO : INITIAL PARTICLE RADIUS
VENT : TOTAL MOLES OF GASES AT BULK
COALFD : COAL INPUT IN THERMAL EQUILIBRIUM PROGRAM

CONSTANT B=31.8, L=6.022E3, PI=3.14, ERROR1=0.001,...
IFLAG2=0, CJBKL=0.22, P=1.013E6, RE=0.0,...
IFLAG3=0, Z=0.75, K0=5.0, M=2.0, MN2=28., MJ=32,...
IFLAG4=0, R=8.314E7, ERROR2=0.001,...
IFLAG1=0, EPSLN=0.98, SIGMA=5.68E-5,...
P0=1.013E6, TBLK0=1500., NSH=2.0, MC=12.0, MAIR=28.9,...
DAL=3.037, DALO=2.751, DALSF=2.032, DMG=3.058, DSIO=1.888,...
DNA=2.633, DNOH=2.81, DSI=2.748, DSI0=2.598, DSI1=1.950,...
MAL=26.98, MALH=27.98, MALO=42.98, MALS=58.98,...
MALOH=43.98, MALI20=69.96, MCA=40.08, MCAO=56.08,...
MFE=55.85, MFEO=71.85, MK=39.09, MKOH=56.09, MMG=24.3,...
MMGO=40.3, MMG=56.3, MNA=22.0, MNAOH=39.0, MSI=28.09,...
MSIH=29.09, MSI0=44.09, MSI2=60.09, MSI1=60.15,...
MAL203=101.96, MFE203=159.70, MK2=55.09, MNA20=60.00

PARAMETER TBLK=1991.,PASH=6.85,PFIXC=56.3,PHDAF=5.86,THETA0=0.60,...
SP0=4.3E6,A0=.0050,VENT=241.294,COALFD=500.

FUNCTION Ktherm=(1500.,9.46E3),(1600.,1.00E4),(1700.,1.05E4),...
(1800.,1.11E4),(1900.,1.17E4),(2000.,1.24E4),...
(2100.,1.31E4),(2200.,1.39E4),(2300.,1.49E4),...
(2400.,1.61E4),(2500.,1.75E4)

FUNCTION DOXIDE=(20.,3.35),(30.,2.80),(40.,2.45),(50.,2.30),...
(60.,2.10),(70.,1.95),(80.,1.85),(90.,1.80),...
(100.,1.70),(110.,1.65),(120.,1.60),...
(140.,1.50),(160.,1.50)

TABULATING THERMAL CONDUCTIVITY DATA, BULK PHASE IS TAKEN
AS AIR PROPERTIES. DATA TAKEN FROM HOLMAN'S HEAT TRANSFER.

DIFFUSION COEFFICIENT VERSUS MOLECULAR WEIGHT AS CORRELATED
OVER 70 SPECIES USING CHAPMAN AND ENSKOGS' PREDICTION MODEL.
HEAT OF REACTION (C + 1/2 O2 = CO), DATA TAKEN FROM JANAF THERMOCHEMICAL TABLES.

FUNCTION THRXN=(1500.,-27.537), (1600.,-27.700), (1700.,-27.865), ...
(1800.,-28.032), (1900.,-28.201), (2000.,-28.372), ...
(2100.,-28.543), (2200.,-28.719), (2300.,-28.894), ...
(2400.,-29.074), (2500.,-29.254), (2600.,-29.438), ...
(2700.,-29.623)

SURFACE VAPOR FRACTIONS AS DETERMINED FROM EQUILIBRIUM COMPUTATION BY REDUCING OXIDANT CONTENT TILL SOLID CARBON APPEARS. DATA RANGING FROM 1500 TO 2400 DEGREE KELVIN.

FUNCTION TAL=(1500.,-11.9491), (1550.,-10.8241), (1600.,-9.7952), ...
(1650.,-8.8346), (1700.,-7.9344), (1750.,-7.0856), ...
(1800.,-6.2866), (1850.,-5.5346), (1900.,-4.8276), ...
(1950.,-4.1760), (2000.,-3.6349), (2100.,-2.9512), ...
(2200.,-3.2536), (2300.,-3.2434), (2400.,-3.2392)

FUNCTION TALH=(1500.,-12.2519), (1550.,-11.4845), (1600.,-10.6285), ...
(1650.,-9.6365), (1700.,-8.8008), (1750.,-8.0128), ...
(1800.,-7.2715), (1850.,-6.5740), (1900.,-5.9186), ...
(1950.,-5.3163), (2000.,-4.8220), (2100.,-4.5656), ...
(2200.,-4.6077), (2300.,-4.6711), (2400.,-4.7354)

FUNCTION TALO=(1500.,-15.3231), (1550.,-14.7375), (1600.,-13.8389), ...
(1650.,-13.0014), (1700.,-12.2161), (1750.,-11.4761), ...
(1800.,-10.7790), (1850.,-10.1232), (1900.,-9.5078), ...
(1950.,-8.9421), (2000.,-8.4825), (2100.,-8.2966), ...
(2200.,-8.3904), (2300.,-8.5047), (2400.,-8.6144)

FUNCTION TALS=(1500.,-10.6069), (1550.,-9.7280), (1600.,-8.9219), ...
(1650.,-8.1907), (1700.,-7.5304), (1750.,-6.9282), ...
(1800.,-6.3780), (1850.,-5.8730), (1900.,-5.4086), ...
(1950.,-4.9943), (2000.,-4.6839), (2100.,-4.7552), ...
(2200.,-5.1145), (2300.,-5.4606), (2400.,-5.7833)

FUNCTION TALOH=(1500.,-18.0165), (1550.,-17.0913), (1600.,-16.2492), ...
(1650.,-15.4645), (1700.,-14.7286), (1750.,-14.0351), ...
(1800.,-13.3818), (1850.,-12.7671), (1900.,-12.1906), ...
(1950.,-11.6617), (2000.,-11.2370), (2100.,-11.1095), ...
(2200.,-11.2678), (2300.,-11.4357), (2400.,-11.5950)

FUNCTION TAL2O=(1500.,-15.3230), (1550.,-13.8316), (1600.,-12.4845), ...
(1650.,-11.2319), (1700.,-10.0596), (1750.,-8.9550), ...
(1800.,-7.9161), (1850.,-6.9406), (1900.,-6.0283), ...
(1950.,-5.1999), (2000.,-4.5686), (2100.,-4.7193), ...
(2200.,-5.4056), (2300.,-6.0795), (2400.,-6.7076)

FUNCTION TCA=(1500.,-11.8554), (1550.,-10.0119), (1600.,-10.2678), ...
(1650.,-9.5787), (1700.,-8.9325), (1750.,-8.3210), ...
(1800.,-7.7430), (1850.,-7.1979), (1900.,-6.6801), ...
FUNCTION TCAO = (1950., -6.1761), (2000., -5.6475), (2100., -4.6894), ...
(2200., -3.9854), (2300., -3.7466), (2400., -3.7470)...

FUNCTION TFE = (1950., -8.8028), (1550., -8.1930), (1600., -7.6901), ...
(1800., -7.2296), (1700., -6.8003), (1750., -6.4014), ...
(1950., -6.0337), (1850., -5.6979), (1900., -5.3884), ...
(2100., -5.0892), (2000., -4.7635), (2100., -4.1936), ...

FUNCTION TFE O = (1500., -14.7995), (1550., -14.2516), (1600., -13.8064), ...
(1650., -13.4099), (1700., -13.0225), (1750., -12.6721), ...
(1800., -12.3494), (1850., -12.0560), (1900., -11.7873), ...
(2000., -11.5257), (2050., -11.2359), (2100., -10.7327), ...

FUNCTION TK = (1500., -4.4332), (1550., -4.4332), (1600., -4.4332), ...
(1650., -4.4332), (1700., -4.4332), (1750., -4.4332), ...
(1800., -4.4332), (1850., -4.4332), (1900., -4.4332), ...
(2000., -4.4332), (2050., -4.4332), (2100., -4.4332), ...

FUNCTION TMG = (1500., -7.7576), (1550., -6.6994), (1600., -6.3379), ...
(1650., -5.7364), (1700., -5.2057), (1750., -4.7872), ...
(1800., -4.5285), (1850., -4.4086), (1900., -4.3621), ...
(1950., -4.3449), (2000., -4.3384), (2100., -4.3355), ...
(2200., -4.3352), (2300., -4.3354), (2400., -4.3354)

FUNCTION TMA G O = (1500., -14.6352), (1550., -13.8955), (1600., -13.2508), ...
(1650., -12.6659), (1700., -12.1497), (1750., -11.7455), ...
(1800., -11.4994), (1850., -11.3911), (1900., -11.3561), ...
(1950., -11.3487), (2000., -11.3516), (2100., -11.3662), ...
(2200., -11.3813), (2300., -11.3946), (2400., -11.4066)

FUNCTION TMG S = (1500., -9.1241), (1550., -8.4868), (1600., -7.9251), ...
(1650., -7.4374), (1700., -7.0379), (1750., -6.7636), ...
(1800., -6.6569), (1850., -6.6926), (1900., -6.8019), ...
(1950., -6.9398), (2000., -7.0860), (2100., -7.3630), ...
(2200., -7.6180), (2300., -7.8544), (2400., -8.0715)

FUNCTION TNA = (1500., -4.3222), (1550., -4.2935), (1600., -4.2826), ...
(1650., -4.2778), (1700., -4.2758), (1750., -4.2747), ...
(1800., -4.2743), (1850., -4.2740), (1900., -4.2738), ...
(1950., -4.2739), (2000., -4.2740), (2100., -4.2741), ...
(2200., -4.2743), (2300., -4.2747), (2400., -4.2751)

FUNCTION TNA O H = (1500., -7.0528), (1550., -7.2831), (1600., -7.5149), ...
(1650., -7.7288), (1700., -7.9512), (1750., -8.1529), ...
(1800., -8.3433), (1850., -8.5234), (1900., -8.6947), ...
(2200., -9.5572), (2300., -9.7951), (2400., -10.0140)

* FUNCTION TSI = (1500., -12.7466), (1550., -12.1303), (1600., -11.6247), ...
(1650., -11.1400), (1700., -10.6617), (1750., -10.1907), ...
(1800., -9.7302), (1850., -9.2831), (1900., -8.8508), ...
(1950., -8.4338), (2000., -8.0324), (2100., -7.7910), ...
(2200., -6.6168), (2300., -5.9997), (2400., -5.4366)

* FUNCTION TSIH = (1500., -16.2489), (1550., -15.6070), (1600., -15.0776), ...
(1650., -14.5705), (1700., -14.0714), (1750., -13.5808), ...
(1800., -13.1020), (1850., -12.6375), (1900., -12.1890), ...
(1950., -11.7568), (2000., -11.3411), (2100., -10.5734), ...

* FUNCTION TSIO = (1500., -6.1480), (1550., -6.0267), (1600., -5.9848), ...
(1650., -5.9364), (1700., -5.8680), (1750., -5.7839), ...
(1800., -5.6880), (1850., -5.5855), (1900., -5.4804), ...
(1950., -5.3728), (2000., -5.2653), (2100., -5.0701), ...
(2200., -4.8922), (2300., -4.7274), (2400., -4.5779)

* FUNCTION TSIO2 = (1500., -12.2143), (1550., -12.2008), (1600., -12.2593), ...
(1650., -12.3054), (1700., -12.3246), (1750., -12.3235), ...
(1800., -12.3046), (1850., -12.2746), (1900., -12.2383), ...
(1950., -12.1946), (2000., -12.1478), (2100., -12.0645), ...
(2200., -11.9873), (2300., -11.9126), (2400., -11.8446)

* FUNCTION TSIS = (1500., -3.1334), (1550., -3.0559), (1600., -3.0421), ...
(1650., -3.0393), (1700., -3.0388), (1750., -3.0387), ...
(1800., -3.0389), (1850., -3.0392), (1900., -3.0395), ...
(1950., -3.0400), (2000., -3.0408), (2100., -3.0424), ...
(2200., -3.0448), (2300., -3.0484), (2400., -3.0539)

* *********************************************************
* SIMULATION EQUATIONS DESCRIBING THE SYSTEM
* *********************************************************
* TAVG : FILM TEMPERATURE, ONE HALF OF BULK TEMP. AND SURFACE TEMPERATURE.
* DJBLK0 : DIFFUSIVITY OF OXIDANT AT THE BULK PHASE AT TEMPERATURE 1500 DEGREE KELVIN AND ONE ATMOSPHERE.
* DFACTR : CORRELATION FACTOR OF DIFFUSIVITY FROM TEMPERATURE AND PRESSURE AT WHICH DJBLK0 IS DEFINED TO ANY TEMPERATURE AND PRESSURE IN QUESTION.
* RHOBK : DENSITY OF AIR AT BULK CONDITIONS.
* VJ : THERMAL MEAN VELOCITY.
* RHOG : DENSITY OF GASES IN THERMAL EQUILIBRIUM WITH COAL CHAR, USED IN PORE DIFFUSION.
* N : MOLECULAR DENSITY (NO. OF MOLES PER CC)
* LAMDAJ : MEAN FREE PATH OF OXIDANT
* KN : KNUSDEN NUMBER (LAMDAJ/RADIUS)
* FCTKN : CORRECTION FACTOR INTRODUCED TO INCLUDE KNUSDEN DIFFUSION COUPLED IN ORDINARY DIFFUSION WHEN THE PARTICLE DIAMETER IS SMALL.
* DCJ : KNUSDEN DIFFUSION COEFFICIENT.
* RDJ : CRITICAL PORE RADIUS SEPARATING KNUSDEN AND CONTINUOUS DIFFUSION CONTROLLED REGIMES.
* RHO : CHAR DENSITY (INSTANTANEOUS DENSITY)
* RMAX : MAXIMUM PORE RADIUS *
* RMIN : MINIMUM PORE RADIUS *
* BETA : DEFINED AS ALOG(RMAX/RMIN) *
* RMINTM : DEFINED AS TEMPORARY MINIMUM PORE RADIUS *

***********************************************************************

DYNAMIC

TAVG=(TEMPS+TBLK)/2.0
DJBLK0=FTAB(DOXIDE,MJ)
DFACR=(P0/P)*(TAVG/TBLK0)**1.75
DJBLK=DJBLK0*DFACR
RHOBK=P*MAIR/(R*TAVG)
VJ=((8.*R*TEMPS)/(PI*MJ))**.5
RHOL=P*MAIR/(R*TEMPS)
N=L*P/R/TEMPS
LAMDAJ=1.0/(2.*0.5*PI*N*D**2.0)
KN=LAMDAJ/A
FCTKN=(1.*KN)/(1.0+1.71*KN+1.333*KN*KN)
DCJ=(1./3.)*LAMDAJ*VJ
RDJ=(3.*DCJ)/(2.*VJ)
RHO=RHOS*(1.-THETA)
RMAX=(2.*A*THETA**(1./3.))/(3.*K0)
RMIN=RMINO*(THETA/THETAO)**(1./3.)

***********************************************************************

* MANIPULATING THE LIMITING CASE THETA=0.0 *

***********************************************************************

PROCEDURE BETA=BLOCKF(RMIN, RMAX, THETA)
IF(THETA .EQ. 0.0) GO TO 66
BETA=(ALOG(RMAX)-ALOG(RMIN))
GO TO 67

66 CONTINUE
BETA=1.0
67 CONTINUE
ENDPRO

***********************************************************************

** SET MINIMUM PORE DIAMEQUAL TO RMIN AT INITIAL POROSITY **

***********************************************************************

PROCEDURE RMINTM, IFLAG4=BLOCKD(RMIN0, RMIN)
IF(RMIN .LT. RMIN0) GO TO 26
RMINTM=RMIN
GO TO 27

26 CONTINUE
RMINTM=RMIN0
IFLAG4=1
27 CONTINUE
ENDPRO

***********************************************************************

* CALCULATE RATE CONSTANTS *
* DESIGNATIONS:
K1F : FORWARD RATE CONSTANT OF RXN ( C + 1/2 O2 = CO2 )
K1R : BACKWARD RATE CONSTANT OF RXN ( C + 1/2 O2 = CO2 )
K2F : FORWARD RATE CONSTANT OF RXN ( CO + 1/2 O2 = CO2 )
KDJ : RATE EXPRESSION WHEN RXN IS CONTROLLED BY DESORPTION
KAJ : RATE EXPRESSION WHEN RXN IS CONTROLLED BY ADSORPTION
KBLK : RATE EXPRESSION USED IN TERMS OF SOLID CARBON CONSUMED
KIR : BACKWARD RATE CONSTANT OF RXN ( C + 1/2 O2 = CO2 )
R2 : PORE RADIUS AT WHICH PENETRATION LENGTH IS SET EQUAL TO MEAN FREE LENGTH.

FiND OXYGEN CONCENTRATION AT PARTICLE SURFACE
DESIGNATIONS:
COJ : OXIDENT MASS FRACTION AT PARTICLE SURFACE
COJMOL : OXIDANT MOLAR FRACTION AT PARTICLE SURFACE
EJ : DEFINED AS KDJ/(KAJ*COJMOL), RATE EXPRESSION
RCJ : CRITICAL PORE RADIUS SEPARATING KINETICALLY LIMITED REGIMES FROM KNUSSDEN DIFFUSION CONTROLLED REGIME.

* K1F=900.*EXP(-19000./TEMPS)
* K2F=90.*EXP(-19000./TEMPS)
* K1R=200.*K2F*K1F*EXP(-3500./TEMPS)
PROCEDURE KAO=Q(K1F,TEMPS)
IF(TEMPS .GT. 2000) GO TO 90
KAO=K1F
90 CONTINUE
KAO=(1./200.)*EXP(3500./TEMPS)
92 CONTINUE
ENDPRO

KAJ=KAO/Z
KDJ=K2F/Z
KBLK=KDJ/(1.+(KDJ/(.21*KAJ))
R2=4.*KBLK*LAMDAJ**2.*MAIR/RHOG/DCJ/MJ/.21

FIND OXYGEN CONCENTRATION AT PARTICLE SURFACE
DESIGNATIONS:
COJ : OXIDENT MASS FRACTION AT PARTICLE SURFACE
COJMOL : OXIDANT MOLAR FRACTION AT PARTICLE SURFACE
EJ : DEFINED AS KDJ/(KAJ*COJMOL), RATE EXPRESSION
RCJ : CRITICAL PORE RADIUS SEPARATING KINETICALLY LIMITED REGIMES FROM KNUSSDEN DIFFUSION CONTROLLED REGIME.

* K1F=900.*EXP(-19000./TEMPS)
* K2F=90.*EXP(-19000./TEMPS)
* K1R=200.*K2F*K1F*EXP(-3500./TEMPS)
PROCEDURE KAO=Q(K1F,TEMPS)
IF(TEMPS .GT. 2000) GO TO 90
KAO=K1F
90 CONTINUE
KAO=(1./200.)*EXP(3500./TEMPS)
92 CONTINUE
ENDPRO

KAJ=KAO/Z
KDJ=K2F/Z
KBLK=KDJ/(1.+(KDJ/(.21*KAJ))
R2=4.*KBLK*LAMDAJ**2.*MAIR/RHOG/DCJ/MJ/.21

*
** THETA : INSTANTANEOUS POROSITY
** DADT : RATE CHANGE IN PARTICLE RADIUS
** A : INSTANTANEOUS PARTICLE RADIUS
** TEMPSF : PARTICLE TEMPERATURE IN DEGREE FARHENHEIT
** CFASH : HEAT CAPACITY OF ASH
** CPFIX1 : INTERMEDIATE EXPRESSION FOR HEAT CAPACITY OF FIXED C
** CPFIX2 : INTERMEDIATE EXPRESSION FOR HEAT CAPACITY OF FIXED C
** CPSFPS : HEAT CAPACITY OF CHAR PARTICLE IN FPS SYSTEM
** CPS : HEAT CAPACITY OF CHAR PARTICLE IN CGS SYSTEM
** HRXN1 : HEAT OF RXN (C + 1/2 O2 = CO ) IN KCAL/MOLE
** HRXN : HEAT OF REACTION IN JOULE/MOLE
** K : THERMAL CONDUCTIVITY.
** QCOND : HEAT TRANSPORTED BY CONDUCTION FROM PARTICLE TO GAS PHASE.
** QRXN : HEAT EXCHANGE BY REACTION
** QRAD : HEAT TRANSPORTED BY RADIATION
** DTMPT : RATE OF CHANGE OF PARTICLE TEMPERATURE
** TEMPS : INSTANTANEOUS PARTICLE TEMPERATURE
**

```plaintext
* COJ=IMPL(COJ/TEMP,ERROR2,FCOJ)
COJMO=(COJ/MJ)/(COJ/MJ)+(1.-COJ)/MN2)
EJ=KDJ/(KAJ*COJMO)
RCKJA=THETA**(1./3.)*RMINTM*(1.+EJ)/(K0*(1.-THETA))
RCKJB=(2.*RHG*VJ*COJ/3./KDJ)**.5/(1.+2.*EJ)**.5
RCKJ=RCKJA*RCKJB
RCJA=(RHG*DCJ*COJ/KDJ)**(1./3.)/(1.+2.*EJ)**.5)**(2./3.)
RCJ=RCJA*RCKJA*(2./3.)
AREA=4.*PI*A**2.0
MSJ=(AREA*(1.-THETA)*KDJ)/(1.+EJ)
```

** CONTROLLING VARIOUS REGIME OF PORE REACTION
**

```plaintext
PROCEDURE TRANS3,TRANS4=BLOCKA(RMAX,RCJ,RDJ,RCKJ,RMINTM)
IF(RCJ .LT. RMAX) GO TO 56
TRANS4=RMAX
TRANS3=RMAX
GO TO 37
56 IF(RCJ .LT. RDJ) GO TO 46
TRANS4=RCJ
TRANS3=RCJ
GO TO 37
46 CONTINUE
IF(RMINTM .GE. RCKJ) GO TO 1
TRANS3=RCKJ
GO TO 2
1 TRANS3=RMINTM
GO TO 2
2 CONTINUE
IF(RDJ .GE. RMAX) GO TO 36
TRANS4=RDJ
GO TO 37
36 CONTINUE
TRANS4=RMAX
37 CONTINUE
```
ENdpro

*  

\[
S_0 = k_{DJ} \cdot \text{AREA} \cdot k_0 \cdot (1 - \Theta) \cdot \Theta^{(2/3)} / (\beta \cdot (1 + E)) \\
MP_F = \text{AREA} \cdot \Theta / \beta \\
MP_F = (2 \cdot \rho \cdot V \cdot C_{OJ} \cdot k_{DJ} / 3)^{0.5} / (1 + (2 \cdot E)^{0.5}) \\
E_0 = MP_F \cdot MP_F \\
MP_J = \text{AREA} \cdot (1 - \Theta) / (\beta \cdot (l. + E)) \\
E_0 = MP_J \cdot MP_J \\
I_0 = MP_J \cdot MP_J \\
\]

PROCEDURE S1, S2, MPJ1, MPJE = P(TMINTM, TRANS3, TRANS4, RMAX, R2, S0, I0, E0)

IF (R2 .GT. TRANS3) GO TO 80
S1 = S0 * (R2 - TMINTM) / TMINTM
S2 = S0 * (TRANS3 - R2) / TMINTM
GO TO 82

80 CONTINUE
S1 = S0 * (TRANS3 - TMINTM) / TMINTM
S2 = 0.0
GO TO 82

82 CONTINUE
MPJE = E0 * (ALOG(TRANS4) - ALOG(TRANS3)) / (1 + (2 * E)^{0.5})
MPJ1 = I0 * (RMAX^{0.5} - TRANS4^{0.5})

ENDPRO

*  

MPJ = S1 + S2 + MPJE + MPJ1
DELTA = A / (1 + (RE**0.5 ^ 2))
C_{OJ} = (MPJ + MSJ) * R * TAVG * (1 / (A + DELTA) - 1) / (4 * PI * DJBLK * PMJ)
C_{OJ} = (21 + 1) * EXP(C_{OJ}A) - 1
FC_{OJ} = M2 * C_{OJ}B / (M2 * C_{OJ}B + M2 * (1 - C_{OJ}B))

DT_HAD = (3 * Z * (S2)) / (4 * PI * RHO * A**3) * FFIXC
\Theta = INTEGRAL(\Theta_0, DTHAD)
DAD = (1 - Z) * (MSJ + S1 + MPJE + MPJ1) / ((AREA * RHO) * FFIXC)
A = INTEGRAL(A0, DAD)
TEMPS = TEMPS + 1.8 - 459.67
CP = 180 + (7.78E-5) * TEMPS
CPF1 = 145 + (4.7E-4) * TEMPS - (2.6E-7) * TEMPS**2
CPF2 = CPF1 + (5.2E-11) * TEMPS**3
CPF = CPF1 * CPF2
CP = 252 * (1.8E7) * 1.8 * CPSFFPS / 453.6
HRXN = PTAB(THRXX, TEMPS)
HRXN = 4.18E10 * HRXN1
K = PTAB(KTHERM, TAVG)
QCOND = (3 * K / (RHO * CPS * A**3)) * (TBLK - TEMPS) * (1 + RE**0.5 / 2)
QRXN = (3 * Z * HRXN / (A * RHO * CPS * MC)) * ((MSJ + MPJ) / AREA)
RAD = (3 / (A * RHO * CPS)) * (SIGMA * EPSLN * (TEMPS**4 - TBLK**4))
DTMP = QCOND - QRXN - RAD
TEMPS = INTEGRAL(TEMPS0, DTMPDT)

*  

**************************************************************************
*  

CHECK 0.0 <= COJ <= CJBLK
*  

**************************************************************************
*  

PROCEDURE IFLAG1, IFLAG2, IFLAG3 = BLOCKB(COJ, CJBLK, A)
IF (COJ .LT. 0.0) GO TO 60
GO TO 5
IF (COJ .GT. CJBLK) GO TO 50
GO TO 5
IF (A .LT. 0.0) GO TO 40
GO TO 5
CONTINUE
IFLAG1=1
GO TO 5
CONTINUE
IFLAG2=1
GO TO 5
CONTINUE
IFLAG3=1
CONTINUE

ENDPRO

*******************************************************************************

* CALCULATING BURNING RATE AND % BURNOUT
* RATE : CARBON CONSUMPTION RATE
* DFBDT : RATE OF BURNOUT FRACTION
* FB : BURNOUT FRACTION
*******************************************************************************

NOSORT
RATE=(DTHADT/RHO)-(3.*DADT/A)
DFBDT=2*(MSJ-MPJ)/(4.*PI*(A0**3.)*RHOS*(1.-THETA0)*FFIXC/3.)
FB=INTGRL(0.0,DFBDT)

*******************************************************************************

PREDICTING TRANSPORTED METAL OXIDES FROM DIFFUSION MODEL

*MFACTR : FACTOR USED IN MASS TRANSFER EXPRESSION*
*D?????? : RATE OF MASS TRANSFERRED (DM/DT)*
*M?????? : MASS OF VAPOR TRANSPORTED AS A FUNCTION OF TIME*
*N?????? : MOLE OF VAPOR TRANSPORTED AS A FUNCTION OF TIME*
*TOSASH : TOTAL AMOUNT OF ASH OF CHAR PARTICLE*
*PC?????? : PERCENTAGE OF ASH VAPORIZED TO TOTAL ASH IN SITU*

*******************************************************************************

MFACTR=(1.-0.0)*AREA*NSH*P/(R*TAVG*2.0*A)

YAL,DALDT1,MAL01,NAL01=TSP(TAL,TEMPS,MAL,DAL,1.0)
YALH,DALDT2,MAL02,NAL02=TSP(TALH,TEMPS,MALH,DOXIDE,0.0)
YALO,DALDT3,MAL03,NAL03=TSP(TALO,TEMPS,MALO,DALO,1.0)
YALS,DALDT4,MAL04,NAL04=TSP(TALS,TEMPS,MALS,DALS,1.0)
YALOH,DALDT5,MAL05,NAL05=TSP(TALOH,TEMPS,MALOH,DOXIDE,0.0)
YAL20,DALDT6,MAL06,NAL06=TSP(TAL20,TEMPS,MAL20,DOXIDE,0.0)
MALSUM=MAL01+MAL02+MAL03+MAL04+MAL05+MAL06
NALSUM=NAL01+NAL02+NAL03+NAL04+NAL05+NAL06+2.*NAL06

YCA,DCADT1,MCA01,NCA01=TSP(TCA,TEMPS,MCA,DOXIDE,0.0)
YCAO,DCADT2,MCA02,NCA02=TSP(TCAO,TEMPS,MCAO,DOXIDE,0.0)
MCASUM=MCA01+MCA02
NCASUM=NCA01+NCA02

YFE,DFE DT1,MFE01,NFE01=TSP(TFE,TEMPS,MFE,DOXIDE,0.0)
YFE0,DFE DT2,MFE02,NFE02=TSP(TFEO,TEMPS,MFE0,DOXIDE,0.0)
MFE SUM=MFE01+MFE02
NFESUM=NFE01+NFE02

★ YK,DKDT1,MK01,NK01=TSP(TK,TEMPS,MK,DOXIDE,0.0)
YKOH,DKDT2,MK02,NK02=TSP(TKOH,TEMPS,MKOH,DOXIDE,0.0)
MKSUM=MK01+MK02
NKSUM=NK01+NK02

★ YMG,DMGDT1,MMG01,NMG01=TSP(TMG,TEMPS,MMG,DMG,1.0)
YMGO,DMGDT2,MMG02,NMG02=TSP(TMGO,TEMPS,MMGO,DOXIDE,0.0)
YMGS,DMGDT3,MMG03,NMG03=TSP(TMGS,TEMPS,MMGS,DOXIDE,0.0)
NMGSUM=MMG01+MMG02+MMG03

★ YNA,DNADT1,MNA01,NNAO1=TSP(TNA,TEMPS,MNA,DNA,1.0)
YNAOH,DNADT2,MNA02,NNAO2=TSP(TNAOH,TEMPS,MNAOH,DNAOH,1.0)
MNASUM=MNA01+MNA02
NNASUM=NNAO1+NNAO2

★ YSI,DSIDT1,MSI01,NSI01=TSP(TSI,TEMPS,MSI,DSI,1.0)
YSIH,DSIDT2,MSI02,NSI02=TSP(TSIH,TEMPS,MSIH,DOXIDE,0.0)
YSIO,DSIDT3,MSI03,NSI03=TSP(TSIO,TEMPS,MSIO,DSIO,1.0)
YSIO2,DSIDT4,MSI04,NSI04=TSP(TSIO2,TEMPS,MSIO2,DSIO2,1.0)
YSIS,DSIDT5,MSI05,NSI05=TSP(TSIS,TEMPS,MSIS,DSIS,1.0)
NSISUM=MSI01+MSI02+MSI03+MSI04+MSI05
NSISUM=MSI01+MSI02+MSI03+MSI04+MSI05
NSISUM=MSI01+MSI02+MSI03+MSI04+MSI05
NSISUM=MSI01+MSI02+MSI03+MSI04+MSI05

PCAL=100.* (0.5*NALSUM*MAL203/TOTASH)
PCCA=100.* (NCASUM*MCAO/TOTASH)
PCFE=100.* (0.5*NFESUM*MFE203/TOTASH)
PCK =100.* (0.5*NKSUM*MK2O/TOTASH)
PCMG=100.* (NMGSUM*MMGO/TOTASH)
PCNA=100.* (0.5*NNASUM*MN2O2/TOTASH)
PCSI=100.* (NSISUM*MSI02/TOTASH)

******************************************************************************

* TERMINAL SECTION CONTROLLING RERUN LOOP, IF CONDITIONS SATISFIED, PRINT RESULTS OR PROMPT MESSAGE
******************************************************************************

TERMINAL

IF(IFLAG1 .EQ. 1) GO TO 15
GO TO 20
15 CONTINUE
WRITE(6,100)
COJABS=ABS(COJ)
CALL RERUN
20 CONTINUE
WRITE(6,11)
WRITE(6,13)
WRITE(6,110)
WRITE(6,12) PCAL,PCCA,PCFE,PCK,PCMG,PCNA,PCSI
WRITE(6,102)
WRITE(6,103)
CALL OUT(TBLK,CNCHAR,MAL01,MAL02,MAL03,MAL04,MAL05,MAL06)
WRITE(6,104)
CALL OUT(TBLK,CNCHAR,MCA01,MCA02,0.0,0.0,0.0,0.0,0.0)
CALL OUT(TBLK,CNCHAR,MFE01,MFE02,0.0,0.0,0.0,0.0,0.0)
WRITE(6,106)
CALL OUT(TBLK,CNCHAR,MK01,MK02,0.0,0.0,0.0,0.0)
WRITE(6,107)
CALL OUT(TBLK,CNCHAR,MMG01,MMG02,MMG03,0.0,0.0,0.0,0.0)
WRITE(6,108)
CALL OUT(TBLK,CNCHAR,MNA01,MNA02,0.0,0.0,0.0,0.0,0.0)
WRITE(6,109)
CALL OUT(TBLK,CNCHAR,MS101,MS102,MS103,MS104,MS105,0.0)

******************************************************************************

* FORMAT FOR OUTPUT DATA
******************************************************************************

11 FORMAT(1X,'------- SIMULATION COMPLETED -------')
100 FORMAT(1X,'------ CONC. OF ASH VAPORIZED (NG/STD. CC)------')
102 FORMAT(1X,' AL ALH ALO ALS ALOH AL20')
104 FORMAT(CA CAO')
105 FORMAT(PEPEO')
106 FORMAT(K KOH')
107 FORMAT(MGMGOMGO'MGS')
108 FORMAT(NA NAOH')
109 FORMAT(SI SIH SIO SIO2 SIS')
110 FORMAT(AL2O3 CAO FE2O3 K2O MGO NA2O SIO2')
12 FORMAT(7F7.2)
13 FORMAT(1X,'-------% ASH VAPORIZED TO ASH IN SITU------')
30 CONTINUE

******************************************************************************

* CONTROLLING COMMANDS
******************************************************************************

* TIMER DELT=1.0E-5, FINITM=0.50
FINISH FB=.990
END

TIMER PRDEL=0.002, OUTDEL=0.02
PRINT NALSUM, NCASUM, NFESUM, NKSUM, NMGSUM, NNASUM, NSISUM, NTOTAL
END
STOP

******************************************************************************

* SELF-SUPPORTED SUBROUTINES
******************************************************************************

* SUBROUTINE FLGCLR(I)
* THIS SUBROUTINE CLEARS FLAGS
* I=0
* RETURN
* END

FUNCTION FTAB(TABLE,XARG)
FUNCTION SUBPROGRAM TO READ TABULATED DATA

NLGEN : NONLINERFUNCTION GENERATOR SUPPLIED IN CSMP

REAL NLGEN
FTAB=NLGEN(TABLE,XARG)
RETURN
END

SUBROUTINE OUT(TBLK,A0,A1,A2,A3,A4,A5,A6)

SUBROUTINE TO CALCULATE FINAL TRANSPORTED VAPOR OXIDE IN
THE UNIT OF NANOGRAM PER CUBIC CENTIMETER AND PRINT FINAL
RESULTS.

DIMENSION A(6)
A(1)=A1
A(2)=A2
A(3)=A3
A(4)=A4
A(5)=A5
A(6)=A6
INDEX=0
DO 10 I=1,6
IX=I
IF(A(IX) .EQ. 0.0) GO TO 10
INDEX=INDEX+1
A(I)=1.0E09*A(I)*A0*(TBLK/273.)
10 CONTINUE
WRITE(6,100) (A(I),I=1,INDEX)
100 FORMAT(6(2XF6.2),/) RETURN
END

ENDJOB
TABLE H-2
INPUT COAL DATA AND SURFACE VAPOR COMPOSITION
(DT FURNACE)

PARAMETER TBLK=1719, PASH=7.85, PFIXD=42.5, PHDAF=6.28, THETA0=0.68, ...
SP0=4.7E6, A0=.0035, VENT=185.512, COALEF=500.

SURFACE VAPOR FRACTIONS AS DETERMINED FROM EQUILIBRIUM
COMPUTATION BY REDUCING OXIDANT CONTENT TILL SOLID CARBON
APPEARS. DATA RANGING FROM 1500 TO 2400 DEGREE KELVIN.

FUNCTION TAL=(1500.,-12.1109), (1550.,-11.0057), (1600.,-9.9604), ...
(1650.,-8.9832), (1700.,-8.0700), (1750.,-7.2117), ...
(1800.,-6.3965), (1850.,-5.6280), (1900.,-4.9082), ...
(1950.,-4.2400), (2000.,-3.6523), (2100.,-3.2081), ...
(2200.,-3.1752), (2300.,-3.1666), (2400.,-3.1632)

FUNCTION TALH=(1500.,-12.6210), (1550.,-11.5935), (1600.,-10.6210), ...
(1650.,-9.7123), (1700.,-8.8635), (1750.,-8.0666), ...
(1800.,-7.3090), (1850.,-6.5952), (1900.,-5.9271), ...
(1950.,-5.3081), (2000.,-4.7673), (2100.,-4.4104), ...
(2200.,-4.4573), (2300.,-4.5220), (2400.,-4.5867)

FUNCTION TALO=(1500.,-15.9040), (1550.,-14.9383), (1600.,-13.0239), ...
(1650.,-12.1687), (1700.,-11.3705), (1750.,-10.6200), ...
(1800.,-10.0072), (1850.,-9.2935), (1900.,-8.6603), ...
(1950.,-9.0249), (2000.,-8.5187), (2100.,-8.2260), ...
(2200.,-8.3301), (2300.,-8.4461), (2400.,-8.5566)

FUNCTION TALS=(1500.,-10.8970), (1550.,-10.0611), (1600.,-9.4087), ...
(1650.,-8.9293), (1700.,-8.4433), (1750.,-8.0182), ...
(1800.,-7.5704), (1850.,-7.0904), (1900.,-6.6060), ...
(1950.,-6.1474), (2000.,-5.7551), (2100.,-5.6660), ...
(2200.,-5.9456), (2300.,-6.2208), (2400.,-6.4690)

FUNCTION TALOH=(1500.,-18.1246), (1550.,-17.2194), (1600.,-16.3614), ...
(1650.,-15.5591), (1700.,-14.8104), (1750.,-14.1066), ...
(1800.,-13.4376), (1850.,-12.8062), (1900.,-12.2169), ...
(1950.,-11.6723), (2000.,-11.2010), (2100.,-10.9730), ...
(2200.,-11.1354), (2300.,-11.3047), (2400.,-11.4645)

FUNCTION TAL20=(1500.,-15.6656), (1550.,-14.2138), (1600.,-12.8346), ...
(1650.,-11.5477), (1700.,-10.3494), (1750.,-9.2250), ...
(1800.,-8.1542), (1850.,-7.1455), (1900.,-6.2074), ...
(1950.,-5.3468), (2000.,-4.6223), (2100.,-4.5716), ...
(2200.,-5.2669), (2300.,-5.9441), (2400.,-6.5737)

FUNCTION TCA=(1500.,-9.9640), (1550.,-9.1579), (1600.,-8.3813), ...
(1650.,-7.5366), (1700.,-6.9844), (1750.,-6.3519), ...
(1800.,-5.7432), (1850.,-5.1676), (1900.,-4.6354), ...
(1950.,-4.1401), (2000.,-3.6607), (2100.,-2.9636), ...
\[(2200.,-2.9484), (2300.,-2.9487), (2400.,-2.9492)\]
(2200.,-11.1204), (2300.,-11.1277), (2400.,-11.1467)

* FUNCTION TSIS=(1500.,-4.2715), (1550.,-3.6428), (1600.,-3.2913), ...
(1650.,-3.1367), (1700.,-3.0697), (1750.,-3.0399), ...
(1800.,-3.0273), (1850.,-3.0241), (1900.,-3.0248), ...
(1950.,-3.0275), (2000.,-3.0314), (2100.,-3.0408), ...
(2200.,-3.0513), (2300.,-3.0643), (2400.,-3.0811)
TABLE H-3
INPUT COAL DATA AND SURFACE VAPOR COMPOSITION

(PF BOILER)

* PARAMETER TBLK=1565, PASH=17.50, PFIXC=50.4, PHDAP=4.42, THETA0=0.73, ...
   SP0=5.0E6, AO=.0031, VENT=192.670, COALFD=500.

* SURFACE VAPOR FRACTIONS AS DETERMINED FROM EQUILIBRIUM
* COMPUTATION BY REDUCING OXIDANT CONTENT TILL SOLID CARBON
* APPEARS. DATA RANGING FROM 1500 TO 2400 DEGREE KELVIN.

* FUNCTION TAL=(1500.,-11.7859), (1550.,-10.6795), (1600., -9.6499), ...
   (1650., -8.6833), (1700., -7.7599), (1750., -6.8729), ...
   (1800., -6.0459), (1850., -5.2773), (1900., -4.5597), ...
   (1950., -3.9397), (2000., -3.2941), (2100., -2.7241), ...
   (2200., -2.6349), (2300., -2.6149), (2400., -2.6093)

* FUNCTION TALH=(1500., -12.3656), (1550., -11.3370), (1600., -10.3805), ...
   (1650., -9.4826), (1700., -8.6240), (1750., -7.7982), ...
   (1800., -7.0291), (1850., -6.3152), (1900., -5.6494), ...
   (1950., -5.0326), (2000., -4.4799), (2100., -3.9976), ...
   (2200., -3.9883), (2300., -3.9042), (2400., -4.1050)

* FUNCTION TALO=(1500., -15.5789), (1550., -14.6110), (1600., -13.7121), ...
   (1650., -12.8682), (1700., -12.0603), (1750., -11.2815), ...
   (1800., -10.5561), (1850., -9.8841), (1900., -9.2580), ...
   (1950., -8.6774), (2000., -8.1602), (2100., -7.7419), ...
   (2200., -7.7902), (2300., -7.8946), (2400., -8.0026)

* FUNCTION TALS=(1500., -10.9231), (1550., -10.5585), (1600., -10.3618), ...
   (1650., -10.2039), (1700., -9.9820), (1750., -9.5719), ...
   (1800., -9.0060), (1850., -8.4118), (1900., -7.8397), ...
   (1950., -7.3049), (2000., -6.8297), (2100., -6.4874), ...
   (2200., -6.6010), (2300., -6.7564), (2400., -6.8913)

* FUNCTION TALOH=(1500., -17.8692), (1550., -16.9618), (1600., -16.1195), ...
   (1650., -15.3287), (1700., -14.5706), (1750., -13.8386), ...
   (1800., -13.1572), (1850., -12.5265), (1900., -11.9394), ...
   (1950., -11.3956), (2000., -10.9134), (2100., -10.5600), ...
   (2200., -10.6669), (2300., -10.8252), (2400., -10.9826)

* FUNCTION TAL2O=(1500., -15.0156), (1550., -13.5604), (1600., -12.2124), ...
   (1650., -10.9473), (1700., -9.7294), (1750., -8.5476), ...
   (1800., -7.4524), (1850., -6.4444), (1900., -5.5107), ...
   (1950., -4.6528), (2000., -3.9055), (2100., -3.6025), ...
   (2200., -4.1867), (2300., -4.6412), (2400., -5.4658)

* FUNCTION TCA=(1500., -11.6690), (1550., -10.8613), (1600., -10.1175), ...
   (1650., -9.4162), (1700., -8.7253), (1750., -8.0362), ...
   (1800., -7.4021), (1850., -6.8265), (1900., -6.2948), ...
   (1950., -5.7927), (2000., -5.2783), (2100., -4.2328), ...
<table>
<thead>
<tr>
<th>Function</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCAO</td>
<td>(2200 , -3.4740), (2300 , -2.9874), (2400 , -2.9759)</td>
</tr>
<tr>
<td>TFE</td>
<td>(1500 , -9.1885), (1550 , -8.5279), (1600 , -8.1236), (1650 , -7.6414), (1700 , -7.2383)</td>
</tr>
<tr>
<td>TFO</td>
<td>(1500 , -15.2041), (1550 , -14.6045), (1600 , -14.1821), (1650 , -13.4792), (1700 , -12.7780)</td>
</tr>
<tr>
<td>TK</td>
<td>(1500 , -4.5146), (1550 , -4.5148), (1600 , -4.5150), (1650 , -4.5157), (1700 , -4.5161)</td>
</tr>
<tr>
<td>TKOH</td>
<td>(1500 , -7.9481), (1550 , -8.1815), (1600 , -8.4012), (1650 , -8.6078), (1700 , -8.8026)</td>
</tr>
<tr>
<td>TMG</td>
<td>(1500 , -7.5032), (1550 , -6.7802), (1600 , -6.1161), (1650 , -5.4915), (1700 , -4.8806)</td>
</tr>
<tr>
<td>TMGO</td>
<td>(1500 , -14.4000), (1550 , -13.6943), (1600 , -13.0474), (1650 , -12.4390), (1700 , -11.8434)</td>
</tr>
<tr>
<td>TNA</td>
<td>(1500 , -4.3316), (1550 , -4.1954), (1600 , -4.1280), (1650 , -4.0960), (1700 , -4.0807)</td>
</tr>
<tr>
<td>TNAO</td>
<td>(1500 , -7.0781), (1550 , -7.2000), (1600 , -7.3759), (1650 , -7.5725), (1700 , -7.7726)</td>
</tr>
</tbody>
</table>

(* *)
Appendix I:
Diffusivity Estimation

Multicomponent diffusion coefficients for metallic vapors in question are required to compute vapor transport. In this study, metallic vapor compositions are relatively low in total combustion gases (mostly N₂ and CO₂). Therefore, binary diffusion coefficients were used. The bulk phase is considered as N₂.

To evaluate binary diffusion coefficients for systems at high temperatures, the model developed by Chapman and Enskog is generally employed. According to this model, diffusivity $D_{ab}$ is expressed as (52)

$$D_{ab} = \frac{1.858 \times 10^{-3} T^{3/2}}{((1/M_a + 1/M_b)^{1/2} / (P \sigma_{ab} \Omega_d))} \quad (I-1)$$

where

- $D_{ab}$ = diffusion coefficient, cm²/s
- $T$ = temperature, K.
- $P$ = pressure, atm.
- $\sigma$ = characteristic length, Å.
- $\Omega_d$ = diffusion collision integral, dimensionless.

$\Omega_d$ is usually tabulated as a function of $kT/\epsilon_{ab}$. The analytical approximation by Neufeld et al. (67) was used for the convenience of machine computation, i.e.,

$$\Omega_d = A/T^b + C/\text{Exp}(DT^*) + E/\text{Exp}(FT^*) + G/\text{Exp}(HT^*) \quad (I-2)$$
where \( T^* = \frac{kT}{\epsilon_{ab}} \), \( A = 1.06036 \), \( B = 0.15610 \)
\( C = 0.19300 \), \( D = 0.47635 \), \( E = 1.03587 \)
\( F = 1.52996 \), \( G = 1.76474 \), \( H = 3.89411 \)

\( \sigma_{ab} \) was calculated as \( (\sigma_a + \sigma_b)/2 \), and \( \epsilon_{ab} \)
as \( (\epsilon_a \cdot \epsilon_b)^{1/2} \). \( \sigma_a \), \( \sigma_b \), \( \epsilon_a \) and \( \epsilon_b \) are
parameters defined in Lennard-Jones 12-6 potential. A
correlation of diffusivity versus molecular weight has been
prepared based on more than 70 species with known \( \epsilon \) and \( \sigma \).
Results are plotted in Figure (I-1).
Figure 1-1. Diffusivity versus Molecular Weight
Appendix J:

Bulk Gas Properties from Equilibrium Calculation

This Appendix includes outputs from gas phase equilibrium calculations. Tables J-1, J-2 and J-3 were results for the CF, PF and DT combustors, respectively. Note the fact that solid carbon does not appear as an equilibrium component as does in surface equilibrium calculation, where the oxidant level is much lower.
The table below presents data on the equilibrium composition of the gas phase in a cyclone-fired boiler. The data includes mole fractions, temperature, and pressure conditions. The table also shows the mole numbers of various compounds and their associated energy values. The notation used in the table is consistent with the conventions used in chemical engineering and thermodynamics to describe these systems.
Table J-2. Adiabatic Flame Temperature and Equilibrium Composition of the gas phase (Pulverized-Fuel Boiler)
Table J-3. Adiabatic Flame Temperature and Equilibrium Composition of the gas phase (Drop Tube Furnace)/Cyclone Fired Boiler
Appendix K:
Notes on Aly's Thesis

Aly (33) integrated numerically the rate of mass transfer for metallic vapors (equation K-1 as follows) from zero time to burnout time.

\[ m = \frac{D_i (MW_i)_{\text{m}}}{RT_m (d/2)} \left( 4 \pi d^2 \left( 1 - F_a \right) / 4 \right) \]

\[ (P_s - P_g i) \]

(K-1)

She obtained a $0.84 \times 10^{-7}$ g of ash vapor and ratioed this to 69.90 g (residual ash formed from burning 1000 g of coal, see reference (33) cited). This calculation gave $1.2 \times 10^{-7}$ % ash vaporization. As a matter of fact, equation (K-1) was, originally derived by Desrosiers (68), based on a single particle. Instead of being ratioed 69.90 g, the $0.84 \times 10^{-7}$ g should have been divided by the total ash in a coal particle (ash fraction*$(4/3) \pi r^3$). For a 6.4 micron particle and density from Aly's study, the corrected percentage follows:

\[ \% \text{ ash vaporized} = \left(\frac{0.84 \times 10^{-7}}{0.175 \times (4/3) \pi (3.1 \times 10^{-3})^3 \times 1.45}\right) \times 100 \]

= 265% (overestimated)

This impossible result indicates the possibility of error from either Aly's surface concentration calculation (by assuming ash liquid phase as a pure phase—see Appendix G) or the improper choice of a char burning model. In any event, Aly's original conclusion has to be justified.
Appendix L:

The Influence of Coal Particle Size Distribution on
The Prediction of Total Vapor Transport

In predicting the total amount of ash vapor, a uniform weight-mean particle size has been used. This was justified by the fact that coal particle distribution has little effect on the total vapor transport.

To illustrate this, vaporization calculations were done for three different distributions (using Rasin-Rammler correlation (69)), i.e., a uniform weight-mean size, a five-sized group, and a ten-sized group (see Tables L-1 and L-2 for each weight fraction).

Results, for the drop tube furnace, are almost the same for the distributions (see Table L-3). Deviations do exist in the pf boiler calculation (see Table L-4). This, however, might have been caused by the weird coal particle distribution as noted from the distorted size distribution (Figure L-1). A normal pulverized coal particle usually follows a bell-shaped distribution. Such is the case for the DT furnace (see Figure L-2). Figure L-1 shows the opposite trend which is abnormal from mechanical pulverization.
Table L-1
Coal Size Distribution (DT Furnace)

Rosin Rammler Distribution Formular;

\[ R = 100 \exp \left(-\left(\frac{X}{77.4}\right)^{5.2}\right) \]

Where \( R \) = Wt. Percent of Material of Particle Size
Greater Than X
\( X \) = Particle Diameter

Size Distribution Based on the above Correlation

(1) Uniform Size : Weight Mean Size \( X = 71.2 \) Micron

(2) 5-sized Groups

<table>
<thead>
<tr>
<th>Diameter(µm)</th>
<th>Fraction Distributed</th>
<th>Wt.(g) Based on 500g</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.026</td>
<td>11.3</td>
</tr>
<tr>
<td>88</td>
<td>0.405</td>
<td>203.0</td>
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<tr>
<td>62</td>
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<td>25</td>
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(3) 10-sized Groups

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<th>Fraction Distributed</th>
<th>Wt.(g) Based on 500g</th>
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</thead>
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<td>11.3</td>
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<td>44.6</td>
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<td>85</td>
<td>0.193</td>
<td>96.5</td>
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<tr>
<td>75</td>
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<td>124.0</td>
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<tr>
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<td>0.062</td>
<td>33.1</td>
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<td>0.025</td>
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<td>3.1</td>
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<tr>
<td>10</td>
<td>0.001</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Table L-2
Coal Size Distribution (PF Boiler)

Rosin Rammler Distribution Formula;
\[ \ln(\ln(100/R)) = 0.974 \ln(X) - 4.02 \]
Where \( R \) = Wt. Percent of Material of Particle Size Greater Than \( X \)
\( X \) = Particle Diameter

Size Distributions Based on the above Correlation

(1) Uniform Size : Weight Mean Size \( X = 62 \) Micron

(2) 5-sized Groups

<table>
<thead>
<tr>
<th>Diameter(( \mu m ))</th>
<th>Fraction Distributed</th>
<th>Wt.(g) Based on 500g</th>
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</thead>
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(3) 10-sized Groups

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Table L-3

Comparison of Metallic Vapors Transported to Bulk Phase Using Different Size Distributions (DT Furnace)

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<th>Al</th>
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<th>Al2O</th>
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<td>0.00</td>
<td>2.17</td>
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<td>0.00</td>
<td>0.14</td>
<td>0.00</td>
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</tr>
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<td>ca</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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Table L-4

Comparison of Metallic Vapors Transported to Bulk Phase Using Different Size Distributions (PF Boiler)

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<th>Al₂O</th>
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<th>SiH</th>
<th>SiO</th>
<th>SiS</th>
<th>SiO₂</th>
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<td>0.00</td>
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Figure L-1. Coal Particle Size Distribution: Weight Distribution vs. Particle Diameter
Figure L-2. Coal Particle Size Distribution: Weight Distribution vs. Particle Diameter
Appendix M:
Notes on Ulrich's Growth Model

Modifications made on Ulrich's growth model (70) are discussed as follows:

First, the coefficient of the exponential term of Equation (III-40) has been corrected to 0.4 as it should be (34,70).

Secondly, to control the transition from single particles to aggregates, total surface area is kept the same if fusion is negligible (i.e., \( \Delta R_p/R_p \ll 0.001 \) as calculated from Equation (III-39). The primary particle size of aggregate building blocks is taken as the surface-mean size of particles formed before the transition occurs. Originally, the arithmatic mean size was used. This lead to an increase in calculated surface area instead of a decrease as particles grow further, which in not proper.
Appendix N:
Influence of Activity Coefficient on Equilibrium Metallic Vapor Composition

In this study, activity coefficients were obtained based on major species of coal ash (Al₂O₃, SiO₂, CaO and FeO). These values could diverge from the actual ones. To see the dependence of equilibrium surface composition on activity coefficient, a 50% error was assumed to exist in estimated activity coefficient of Al₂O₃. Comparison of equilibrium composition at two different sets of activity coefficients was made at different temperatures as shown in Table N-1. A 30% difference were observed for temperatures below 2000 K. At higher temperatures, surface composition is basically independent of activity coefficient.
Table N-1

Equilibrium Surface Compositions of Al Compounds at Different Activity Coefficient

<table>
<thead>
<tr>
<th>Temp(K)</th>
<th>CF Boiler (\gamma = 0.63)</th>
<th>CF Boiler (\gamma = 0.32)</th>
<th>DT Boiler (\gamma = 0.61)</th>
<th>DT Boiler (\gamma = 0.31)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>2.65E-11</td>
<td>1.89E-11</td>
<td>1.37E-11</td>
<td>9.76E-12</td>
</tr>
<tr>
<td>1550</td>
<td>2.05E-10</td>
<td>1.46E-10</td>
<td>9.93E-11</td>
<td>7.08E-11</td>
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<tr>
<td>1600</td>
<td>1.39E-09</td>
<td>9.89E-10</td>
<td>5.24E-10</td>
<td>3.73E-10</td>
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<tr>
<td>1650</td>
<td>8.15E-09</td>
<td>5.80E-09</td>
<td>2.52E-09</td>
<td>1.79E-09</td>
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<tr>
<td>1700</td>
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<td>5.97E-04</td>
<td>5.97E-04</td>
<td>7.13E-04</td>
<td>7.13E-04</td>
</tr>
</tbody>
</table>

\(\gamma\) = activity coefficient of Al species.